

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**THE SYNTHESIS AND CHARACTERIZATION OF PERIPHERY
FUNCTIONAL MULTIARM STAR POLYMERS**



Ph.D. THESIS

Neşe ÇAKIR YİĞİT

Department of Polymer Science and Technology

Polymer Science and Technology Programme

FEBRUARY 2017

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**THE SYNTHESIS AND CHARACTERIZATION OF PERIPHERY
FUNCTIONAL MULTIARM STAR POLYMERS**

Ph.D. THESIS

Neşe ÇAKIR YİĞİT
(515102012)

Department of Polymer Science and Technology

Polymer Science and Technology Programme

Thesis Advisor: Prof. Dr. Gürkan HIZAL

FEBRUARY 2017

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

**ÇEVRE FONKSİYONLU ÇOK KOLLU YILDIZ POLİMERLERİN SENTEZİ
VE KARAKTERİZASYONU**

DOKTORA TEZİ

**Neşe ÇAKIR YİĞİT
(515102012)**

Polimer Bilim ve Teknolojisi Anabilim Dalı

Polimer Bilim ve Teknolojisi Programı

Tez Danışmanı: Prof. Dr. Gürkan HIZAL

ŞUBAT 2017

Neşe Çakır Yiğit, a Ph.D. student of ITU Graduate School of Science Engineering and Technology student ID 515102012, successfully defended the thesis entitled “THE SYNTHESIS AND CHARACTERIZATION OF PERIPHERY FUNCTIONAL MULTIARM STAR POLYMERS”, which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor : **Prof. Dr. Gürkan HIZAL**
İstanbul Technical University

Jury Members : **Prof. Dr. Ümit TUNCA**
İstanbul Technical University

Prof. Dr. Candan ERBİL
İstanbul Technical University

Prof. Dr. Nergis ARSU
Yıldız Technical University

Assoc. Prof. Dr. Ersin ACAR
Boğaziçi University

Date of Submission : 29 December 2016

Date of Defense : 06 February 2017





To my beloved family,



FOREWORD

First, I would like to give my most sincere thanks to my advisor, Prof. Dr. Gürkan Hızal for accepting me to his research group. During all these years, I have greatly benefited from his inspiring comments and scientific support. Without his knowledge and expertise, I would have never been able to accomplish the work of my graduate research. Besides, I am honored to have Prof. Dr. Ümit Tunca and Prof. Dr. Nergis Arsu in the committee. Their thoughtful questions and comments were valued greatly. I would like to also extend my sincere gratitude to Assoc. Prof. Dr. Hakan Durmaz for his support and understanding, which guided me during my thesis study. In addition, I appreciate him spending his time to assist me with the papers written.

I would like to thank to Assoc. Prof. Dr. Aydan Dag, for training me with synthesis skills and her great help through my study.

Also, many thanks to Dr. Duygu Sevinç Esen (Yıldız Technical University) for assistance with photo-DSC measurements.

I wish to thank to my present and past labmates for all their help and guidance, especially Res. Assist. Ufuk Saim Günay, Dr. Çiğdem Bilir and Pınar Sinem Omurtag Özgen for their support and understanding during my PhD study. It was really a great pleasure for me to know all of them.

I wish to express my warm thanks to my friends, Neşe Cerit, Esra Erbil, Hatice Şahin Sever, Tuğçe İnan, and Berna Öztürk for all their help and moral support. All have been great friends with throughout the years.

I would like to thank to all my institution colleagues of Polymer Engineering Department of Yalova University, who afforded me a friendly and very supportive environment.

I also need to thank to Dr. C. Remzi Becer for giving chance to study in his group in Queen Mary University. It has been a unique experience for me to live and study in London, from which I have eventually learned a lot about science field. Moreover, his enthusiasm and working style left me a deep impression, and will surely exert a significant impact on my future career.

I would like to thank my family: my parents, Gülsüm and Rami Çakır, and to my brother Recep, for supporting me spiritually throughout my education and my life in general. Words cannot express how grateful I am to you for all of the sacrifices that you've made on my behalf.

A special thanks to my second mother and second father, Hafize and İsmail Tendürek, for opening their homes and their hearts to me, seeing as their own daughter. I am very grateful to them for where I am today.

My final appreciation goes to my lovely husband, Gökhan Yiğit, whose encouragement, help, patience and importantly loving moral support during all stages of my life is so appreciated.

Thanks to all of you!

February 2017

Neşe ÇAKIR YİĞİT
(Chemist, Msc.)

TABLE OF CONTENTS

	<u>Page</u>
FOREWORD	ix
TABLE OF CONTENTS	xi
ABBREVIATIONS	xv
SYMBOLS	xvii
LIST OF TABLES	xix
LIST OF FIGURES	xxi
SUMMARY	xxv
ÖZET	xxix
1. INTRODUCTION	1
2. THEORETICAL PART	7
2.1 Living Polymerizations	7
2.2 Controlled/Living Radical Polymerization (C/LRP)	7
2.2.1 Atom transfer radical polymerization (ATRP)	9
2.2.1.1 Basic components of ATRP	10
2.2.1.2 Other types of ATRP systems	13
2.2.2 Nitroxide-mediated radical polymerization (NMP)	13
2.2.3 Reversible addition-fragmentation chain transfer polymerization (RAFT)	16
2.3 Click Chemistry	18
2.3.1 Copper(I) Catalyzed Azide-Alkyne Cycloaddition (CuAAC)	18
2.3.2 Diels-Alder Reaction	19
2.3.3 Thiol-ene reaction	21
2.3.4 <i>Para</i> -fluoro addition reaction	23
2.4 Orthogonal Multiple Click Reactions	25
2.5 Star Polymers	28
2.5.1 “Core-first” approach	30
2.5.2 “Arm-first” approach	32
2.5.3 “Coupling-onto” approach	38
2.6 Functionalized Polymers	41
2.6.1 End-functional polymers	41
2.6.2 Pendant functional polymers	43
2.7 Polymeric Photoinitiators	45
2.7.1 Type I polymeric photoinitiators	46
2.7.2 Type II polymeric photoinitiators	47
2.8 Supramolecular Polymers	48
3. EXPERIMENTAL PART	53
3.1 Materials	53
3.2 Instrumentation	53
3.3 Synthesis Methods	55

3.3.1 Synthesis of (pentafluorophenyl)methyl 2-bromo-2-methylpropanoate (1)	55
3.3.2 Synthesis of α -fluoro- ω -bromide end-functional PS (α -fluoro-PS)	56
3.3.3 Preparation of (fluoro-PS) _n -polyDVB multiarm star polymer	56
3.3.4 Synthesis of (PEG) _m -(PS) _n -polyDVB multiarm star block copolymer with (fluoro-PS) _n -polyDVB multiarm star polymer and PEG chains	57
3.3.5 Preparation of <i>N</i> -acetyl-L-cysteine methyl-ester functionalized multiarm star polymer ((cysteine-PS) _n -polyDVB) via thiol- <i>para</i> -fluoro click reaction	57
3.3.6 Synthesis of allyl 2-bromo-2-methylpropanoate (2)	57
3.3.7 Model reaction between α -fluoro-PS and <i>N</i> -acetyl-L-cysteine methyl ester	58
3.3.8 Synthesis of α -allyl- ω -bromide end-functional PS (α -allyl-PS)	58
3.3.9 Model reaction between α -allyl-PS and 1-propanethiol	59
3.3.10 One-pot preparation of α -fluoro and α -allyl-end-functionalized PS mixture (α -fluoro-PS + α -allyl-PS)	59
3.3.11 Preparation of (fluoro-PS) _m -polyDVB-(allyl-PS) _m multiarm star polymer bearing pentafluoro and allyl functionalities at the periphery	59
3.3.12 Thiol- <i>para</i> -fluoro click reaction with 1-propanethiol and (fluoro-PS) _m -polyDVB-(allyl-PS) _m multiarm star polymer	60
3.3.13 Radical thiol-ene click reaction between <i>N</i> -acetyl-L-cysteine methyl-ester and (propyl-PS) _m -polyDVB-(allyl-PS) _m multiarm star polymer	60
3.3.14 Synthesis of 2-oxo-1,2-diphenylethyl 2-bromo-2-methylpropanoate (3)	61
3.3.15 Preparation of benzoin end-functional PS (Benzoin-PS)	61
3.3.16 Synthesis of multiarm (Benzoin-PS) _m -polyDVB star polymer	62
3.3.17 Synthesis of 2-hydroxy-1,2-bis(4-(methylsulfanyl-phenyl)-ethanone (MTB))	62
3.3.18 Synthesis of 1,2-bis(4-(methylthio)phenyl)-2-oxoethyl 2-bromo-2-methylpropanoate (4)	63
3.3.19 Preparation of MTB end-functional PS (MTB-PS)	63
3.3.20 Synthesis of multiarm (MTB-PS) _p -polyDVB star polymer	63
3.3.21 Photopolymerization of MMA	64
3.3.22 Photo-DSC procedure	64
3.3.23 Synthesis of 1-adamantane methyl-2-bromo isobutyrate (5)	64
3.3.24 Synthesis of mono-6-deoxy-6-(<i>p</i> -tolylsulfonyl)- β -cyclodextrin (β -CD-OTs)	65
3.3.25 Synthesis of mono-6-deoxy-6-azido- β -cyclodextrin (β -CD-N ₃)	65
3.3.26 Synthesis of alkyne end-functionalized PEG (Alkyne-PEG)	66
3.3.27 CuAAC click reaction of Alkyne-PEG with β -CD-N ₃ (β -CD-PEG)	66
3.3.28 Synthesis of adamantyl end-functionalized PS (ada-PS)	67
3.3.29 Preparation of (ada-PS) _n -polyDVB multiarm star polymer	67
3.3.30 Preparation of supramolecular (CD-PEG) _p -(ada-PS) _n -polyDVB multiarm star bock copolymer via ile CD/adamantane “host-guest” interaction	68
4. RESULTS AND DISCUSSION	69
4.1 Post-Functionalization of Multiarm Star polymers via Nucleophilic Substitution of the <i>para</i> -Fluoro Substituent of Pentafluorophenyl Groups at the Periphery	69
4.2 Synthesis of Hetero-Functionalized Multiarm Star Polymers via Sequential Thiol- <i>para</i> -Fluoro and Thiol-Ene Double Click Reactions	82

4.3 Synthesis of Multiarm Star Polymer as Novel Polymeric Photoinitiator for Free Radical Polymerization	96
4.4 Synthesis of Multiarm Star Block Copolymer Based on "Host-Guest" Inclusion Complexation	110
5. CONCLUSION.....	125
REFERENCES.....	127
CURRICULUM VITAE.....	149





ABBREVIATIONS

Ada	: Adamantane
ATRP	: Atom Transfer Radical Polymerization
β-CD	: β -cyclodextrin
CDCl₃	: Deuterated chloroform
CH₂Cl₂	: Dichloromethane
C/LRP	: Controlled/living radical polymerization
CuAAC	: Copper catalyzed azide-alkyne cycloaddition
DLS	: Dynamic Light Scattering
DMAP	: 4-dimethylaminopyridine
DMF	: <i>N,N</i> -Dimethylformamide
DMPA	: Dimethoxyphenyl acetophenone
DMSO-d₆	: Deuterated dimethyl sulfoxide
DP	: Degree of polymerization
DVB	: Divinyl benzene
EtOAc	: Ethyl acetate
Et₃N	: Triethylamine
FPT	: Freeze-pump-thaw
FRP	: Free radical polymerization
FT-IR	: Fourier Transform Infrared Spectrophotometer
GC	: Gas Chromatography
GPC	: Gel Permeation Chromatography
¹H NMR	: Proton Nuclear Magnetic Resonance Spectroscopy
MeOH	: Methanol
MI	: Macroinitiator
MMA	: Methyl Methacrylate
MWD	: Molecular Weight Distribution
NaH	: Sodium hydride
NMP	: Nitroxide Mediated Polymerization
PDI	: Polydispersity Index
PEG	: Poly(ethylene glycol)
Photo-DSC	: Photo Differential Scanning Calorimeter
PMDETA	: <i>N, N, N', N'', N'''</i> -Pentamethyldiethylenetriamine
PMMA	: Poly(methyl methacrylate)
PS	: Poly(styrene)
PTFE	: Poly(tetrafluoro ethylene)
RAFT	: Reversible Addition Fragmentation Chain Transfer
RP	: Radical polymerization
St	: Styrene
TD-GPC	: Triple Detector-Gel Permeation Chromatography
TEMPO	: 2,2,6,6-Tetramethylpiperidine- <i>N</i> -oxyl
THF	: Tetrahydrofuran
UV	: Ultraviolet



SYMBOLS

A	: Absorbance
C	: Concentration
°C	: Celsius
dn/dc	: Refractive index increment
ε	: Molar extinction coefficient
f	: Number of arms
g'	: Contraction factor
K	: Mark-Houwink-Sakurada constant
k_{act}	: Activation rate constant
k_{deact}	: Deactivation rate constant
K_{eq}	: Equilibrium constant
K_p	: Propagation rate constant
λ	: Wavelength
[η]	: Intrinsic viscosity
M	: Molarity
[M]₀/[I]₀	: Monomer concentration to initiator concentration ratio
M_w/M_n	: Polydispersity index
M_n	: The number average molecular weight
M_w	: The weight average molecular weight
nm	: Nanometer
ppm	: Parts per million
R·	: Radical
R_h	: Hydrodynamic radius
R_p	: Rate of polymerization
X•	: Stable radical



LIST OF TABLES

	<u>Page</u>
Table 4.1 : GPC and TD-GPC characterization of fluoro-end functionalized PS polymer, multiarm star polymer, and post-functionalized multiarm star (co)polymers.....	81
Table 4.2 : The characterization of multiarm star polymer, heterofunctionalized multiarm star polymer, and result of linear polymer used in the synthesis of multiarm star polymer.....	87
Table 4.3 : The conditions and results of linear polymers used in the model reactions.....	89
Table 4.4 : The reaction conditions and results of linear polymers used in the synthesis of benzoin and MTB functional multiarm star polymers.....	102
Table 4.5 : TD-GPC characterization of benzoin and MTB functional multiarm star polymers	106
Table 4.6 : Photopolymerization of MMA (4.68 mol.L^{-1}) with all photoinitiators at the same O.D.....	108
Table 4.7 : The conditions and results of linear polymers used in the synthesis of multiarm star and multiarm star block copolymer.....	118
Table 4.8 : TD-GPC characterization of Ada functional multiarm star polymer before and after “host-guest” interaction	124



LIST OF FIGURES

	<u>Page</u>
Figure 1.1 : Synthetic pathway for the functionlization of pentafluorophenyl bearing multiarm star polymer via nucleophilic <i>para</i> -fluoro addition reactions	3
Figure 1.2 : Synthetic pathway for the synthesis of hetero-functionalized multiarm star polymer via sequential double click reactions, involving thiol- <i>para</i> -fluoro and radical thiol-ene chemistry	4
Figure 1.3 : Synthetic pathway for the synthesis of photo active group bearing multiarm star polymers and their usage as polymeric photoinitiators for free radical polymerization of MMA	5
Figure 1.4 : Synthetic pathway for the synthesis of multiarm star block copolymers via “host-guest” interaction	5
Figure 2.1 : Schematic representation of star polymer structures	29
Figure 2.2 : Schematic representation of the sythesis of star and star block copolymers by “core-first” approach.....	30
Figure 2.3 : Schematic representation of the “arm-first” approach for star polymer synthesis	33
Figure 2.4 : Proposed mechanism for the formation of multiarm star polymers by “arm-first” approach	35
Figure 2.5 : Synthesis of miktoarm star polymers by “in-out” strategy.	36
Figure 2.6 : Synthesis of miktoarm star copolymers by concurrently incorporation of the two linear macroinitiators.....	36
Figure 2.7 : Schematic representation of the sythesis of star polymers by “coupling-onto” approach.....	38
Figure 2.8 : Common strategies for incorporating functionality into polymer chains	41
Figure 2.9 : General strategy toward the preparation of supramolecular comb-shaped polymers in water	50
Figure 2.10 : Schematic representation of the inclusion complexes formed via “host-guest” interactions between β -CD-core star polymer and adamantyl-containing PEGs	50
Figure 2.11 : Modification of three-armed stars with cholesterol and the subsequent formation of an inclusion complexation with β -CD.....	51
Figure 2.12 : Synthetic route to supramolecular ABC miktoarm star terpolymer	51
Figure 4.1 : ^1H NMR spectrum of (pentafluorophenyl)methyl 2-bromo-2-methylpropanoate (1) in CDCl_3	70
Figure 4.2 : ^{19}F NMR spectrum of (pentafluorophenyl)methyl 2-bromo-2-methylpropanoate (1) in CDCl_3	70
Figure 4.3 : ^1H NMR spectrum of α -fluoro-PS in CDCl_3	71
Figure 4.4 : ^{19}F NMR spectrum of α -fluoro-PS in CDCl_3	72

Figure 4.5 : Evolution of GPC traces of (fluoro-PS) _n -polyDVB multiarm star polymer using RI detector in THF at 30 °C ([DVB] ₀ /15 = [fluoro-PS] ₀ = [CuBr] ₀ = [PMDETA] ₀ = 0.020 M in anisole at 110 °C).....	73
Figure 4.6 : ¹ H NMR spectrum of (fluoro-PS) _n -polyDVB multiarm star polymer in CDCl ₃	73
Figure 4.7 : ¹⁹ F NMR spectrum of (fluoro-PS) _n -polyDVB multiarm star polymer in CDCl ₃	74
Figure 4.8 : ¹ H NMR spectrum of (PEG) _m -(PS) _n -polyDVB multiarm star block copolymer in CDCl ₃	77
Figure 4.9 : ¹⁹ F NMR spectrum of (PEG) _m -(PS) _n -polyDVB multiarm star block copolymer in CDCl ₃	77
Figure 4.10 : GPC traces of (PEG) _m -(PS) _n -polyDVB, (fluoro-PS) _n -polyDVB multiarm star polymer and linear PEG ₅₅₀ -OH precursors using RI detector in THF at 30 °C	79
Figure 4.11 : ¹ H NMR spectrum of (cysteine-PS) _n -polyDVB multiarm star polymer in CDCl ₃	80
Figure 4.12 : ¹⁹ F NMR spectrum of (cysteine-PS) _n -polyDVB multiarm star polymer in CDCl ₃	80
Figure 4.13 : GPC traces of (cysteine-PS) _n -polyDVB and (fluoro-PS) _n -polyDVB multiarm star polymer using RI detector in THF at 30 °C	80
Figure 4.14 : ¹ H NMR spectrum of allyl 2-bromo-2-methylpropanoate (2) in CDCl ₃	83
Figure 4.15 : ¹ H NMR spectrum of mixture of linear α-fluoro-PS and α-allyl-PS in CDCl ₃	84
Figure 4.16 : ¹⁹ F NMR spectrum of mixture of linear α-fluoro-PS and α-allyl-PS in CDCl ₃	84
Figure 4.17 : a) Dependence of DVB conversion and ln([M] ₀ /[M]) on reaction time and b) evolution of GPC traces during synthesis of (fluoro-PS) _m -polyDVB-(allyl-PS) _m star polymer using RI detector in THF at 30 °C. Experimental conditions: ([DVB] ₀ /15 = [fluoro-PS] ₀ = [CuBr] ₀ = [PMDETA] ₀ = 0.023 M in anisole at 110 °C. Linear PS standards were used for calibration of the THF GPC	86
Figure 4.18 : ¹ H NMR spectrum (a) and ¹⁹ F NMR spectrum (b) of (fluoro-PS) _m -polyDVB-(allyl-PS) _m multiarm star polymer in CDCl ₃	88
Figure 4.19 : ¹⁹ F NMR spectra (a) of model α-fluoro-PS before (top) and after (bottom) the reaction with <i>N</i> -acetyl-L-cysteine methyl ester. GPC traces (b) of model α-fluoro-PS before (green) and after (black) the reaction with <i>N</i> -acetyl-L-cysteine methyl ester	90
Figure 4.20 : ¹ H NMR spectra of α-fluoro-PS before (top) and after (bottom) the model reaction in CDCl ₃	91
Figure 4.21 : ¹ H NMR spectra (a) of model α-allyl-PS before (top) and after (bottom) the reaction with 1-propanethiol. GPC traces (b) of model α-allyl-PS before (red) and after (black) the reaction with 1-propanethiol	92
Figure 4.22 : ¹⁹ F NMR spectra for the online measurement of the thiol- <i>para</i> -fluoro “click” reaction between (fluoro-PS) _m -polyDVB-(allyl-PS) _m multiarm star polymer and 1-propanethiol in CDCl ₃ . Purple round represents the all multiarm star polymer except one perfluoro functionality	93

Figure 4.23 : ^1H NMR spectrum of (propyl-PS) _m -polyDVB-(allyl-PS) _m multiarm star polymer after thiol- <i>para</i> -fluoro “click” reaction of (fluoro-PS) _m -polyDVB-(allyl-PS) _m multiarm star polymer and 1-propanethiol in CDCl ₃	94
Figure 4.24 : ^1H NMR spectrum of hetero-functionalized (propyl-PS) _m -polyDVB-(cysteine-PS) _m multiarm star polymer in CDCl ₃	95
Figure 4.25 : ^{19}F NMR spectrum of hetero-functionalized (propyl-PS) _m -polyDVB-(cysteine-PS) _m multiarm star polymer in CDCl ₃	95
Figure 4.26 : Overlay TD-GPC traces of α -fluoro-PS + α -allyl-PS (pink), (fluoro-PS) _m -polyDVB-(allyl-PS) _m multiarm star polymer (black), (propyl-PS) _m -polyDVB-(allyl-PS) _m multiarm star polymer (green) and hetero-functionalized (propyl-PS) _m -polyDVB-(cysteine-PS) _m multiarm star polymer (blue).....	96
Figure 4.27 : ^1H NMR spectrum of 2-oxo-1,2-diphenylethyl 2-bromo-2-methylpropanoate (3) in CDCl ₃	98
Figure 4.28 : ^1H NMR spectrum of 2-Hydroxy-1,2-bis(4-(methylsulfanyl-phenyl)-ethanone (MTB) in CDCl ₃	99
Figure 4.29 : ^1H NMR spectrum of 1,2-bis(4-(methylthio)phenyl)-2-oxoethyl 2-bromo-2-methylpropanoate (4) in CDCl ₃	99
Figure 4.30 : ^1H NMR spectrum of benzoin end-functionalized PS (benzoin-PS) in CDCl ₃	101
Figure 4.31 : ^1H NMR spectrum of MTB end-functionalized PS (MTB-PS) in CDCl ₃	101
Figure 4.32 : GPC traces of a) benzoin-PS and (benzoin-PS) _m -polyDVB, b) MTB-PS and (MTB-PS) _p -polyDVB in THF at 30 °C	104
Figure 4.33 : ^1H NMR spectrum of multiarm (benzoin-PS) _m -polyDVB star polymer in CDCl ₃	104
Figure 4.34 : ^1H NMR spectrum of multiarm (MTB-PS) _p -polyDVB star polymer in CDCl ₃	105
Figure 4.35 : Photolysis of a) multiarm (MTB-PS) _p -polyDVB star polymer (2.17x10 ⁻⁶ M) and b) (Benzoin-PS) _m -polyDVB star polymer (1.13x10 ⁻⁶ M) in CH ₂ Cl ₂	107
Figure 4.36 : Photo-DSC conversion graphs for polymerization of HDDA using (Benzoin-PS) _m -polyDVB star polymer (0.5% w/w and 1% w/w) and (MTB-PS) _p -polyDVB star polymer (0.5% w/w and 1% w/w) at a) 20 mW/cm ² light intensity and b) 40 mW/cm ² light intensity.....	109
Figure 4.37 : Photo-DSC reaction rates graphs for polymerization of HDDA using (Benzoin-PS) _m -polyDVB star polymer (0.5% w/w and 1% w/w) and (MTB-PS) _p -polyDVB star polymer (0.5% w/w and 1% w/w) at a) 20 mW/cm ² light intensity and b) 40 mW/cm ² light intensity.....	109
Figure 4.38 : Photo-DSC heat flow graphs for polymerization of HDDA using (Benzoin-PS) _m -polyDVB star polymer (0.5% w/w and 1% w/w) and (MTB-PS) _p -polyDVB star polymer (0.5% w/w and 1% w/w) at a) 20 mW/cm ² light intensity and b) 40 mW/cm ² light intensity.....	110
Figure 4.39 : ^1H NMR spectrum of 1-adamantane methyl-2-bromo isobutyrate (5) in CDCl ₃	111
Figure 4.40 : ^1H NMR spectrum of β -CD-OTs in DMSO- <i>d</i> ₆ at room temperature	112
Figure 4.41 : ESI-MS spectrum of β -CD-OTs in methanol.....	112

Figure 4.42 : ^1H NMR spectrum of $\beta\text{-CD-N}_3$ in $\text{DMSO-}d_6$ at room temperature...	113
Figure 4.43 : ESI-MS spectrum of $\beta\text{-CD-N}_3$ in methanol.....	113
Figure 4.44 : ^1H NMR spectrum of alkyne-PEG in CDCl_3	114
Figure 4.45 : ^1H NMR spectrum of $\beta\text{-CD-PEG}$ in $\text{DMSO-}d_6$ at room temperature	115
Figure 4.46 : FT-IR spectra of $\beta\text{-CD-OTs}$ (pink) (a), $\beta\text{-CD-N}_3$ (red) (b), Alkyne-PEG (blue) (c) and obtained compound $\beta\text{-CD-PEG}$ (black) (d).....	116
Figure 4.47 : Evolution of GPC traces of $\beta\text{-CD-PEG}$, Alkyne-PEG and $\beta\text{-CD-N}_3$ using RI detector in DMF at 60 °C	116
Figure 4.48 : ^1H NMR spectrum of adamantane end-functional PS (ada-PS) in CDCl_3	117
Figure 4.49 : Evolution of GPC traces of $(\text{ada-PS})_n\text{-polyDVB}$ multiarm star polymer using RI detector in THF at 30 °C. ($[\text{DVB}]_0/15 = [\text{Ada-PS}]_0 = [\text{CuBr}]_0 = [\text{PMDETA}]_0 = 0.020 \text{ M}$ in anisole at 110 °C).....	119
Figure 4.50 : ^1H NMR spectrum of multiarm $(\text{ada-PS})_n\text{-polyDVB}$ star polymer in CDCl_3	119
Figure 4.51 : Preparation of supramolecular $(\text{CD-PEG})_p\text{-(ada-PS)}_n\text{-polyDVB}$ multiarm star block copolymer with gradually decreased DMF amount in mixture	120
Figure 4.52 : ^1H NMR spectrum of supramolecular $(\text{CD-PEG})_p\text{-(ada-PS)}_n\text{-polyDVB}$ multiarm star block copolymer in CDCl_3	121
Figure 4.53 : ROESY NMR spectrum of the supramolecular $(\text{CD-PEG})_p\text{-(ada-PS)}_n\text{-polyDVB}$ multiarm star block copolymer in CDCl_3 at 25°C (magnified in the right side).....	122
Figure 4.54 : Comparison of the number average particle size distribution of $(\text{Ada-PS})_n\text{-polyDVB}$ multiarm star polymer obtained from DLS measurements at room temperature	123

THE SYNTHESIS AND CHARACTERIZATION OF PERIPHERY FUNCTIONAL MULTIARM STAR POLYMERS

SUMMARY

Several recent advances, which well-known to design of molecular-level control in organic chemistry, allow preparation of well-defined macromolecules with controlled compositions and architectures. Despite the importance of exact control of chemical structures and functionalities at the macromolecular level, it should be noted that synthetic techniques in organic chemistry are not an easy processes to transfer the polymer synthesis. Rather, the characteristic properties of macromolecules (e.g., number of functional groups, molecular weight distribution, and purification techniques) compared to small molecules, structural fidelity and high degree of functional group compatibility is very important in the elucidation of polymer synthesis. Although free radical polymerization has been widely used in macromolecule synthesis, it has no effect on the polymer compositions and functionalities as do ionic polymerizations. In recent years, enormous progress has been developed in various controlled radical polymerization methods. Controlled/living radical polymerization (C/LRP) methods including atom transfer radical polymerization (ATRP), nitroxide mediated radical polymerization (NMP), and reversible addition-fragmentation chain transfer polymerization (RAFT) are the most common polymerizations that enable the preparation of synthetic polymers with controlled molecular weight, relatively low dispersities, different composition (block, graft, star and alternating gradient copolymers), and various functionalities.

Click chemistry is a chemical reaction that proceeds with complete specificity, high yield, and energetically favored reactions. First, they were used in synthetic organic chemistry, then it has become extremely popular in polymer and materials science as universal tools. Click reactions, especially, Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) reaction, Diels-Alder reaction, and thiol-ene reaction, have recently shown to be quite succesful tools for advanced macromolecular design. Additionally, it is well-known in organic chemistry that the labile *para*-fluoro groups of pentafluorophenyl (C₆F₅) ring can undergo nucleophilic addition reactions with primary amino and thiol groups. Most of these reactions are extremely efficient and give high yields under the employed conditions. Although in essence it is a nucleophilic substitution reaction, the versatility and efficiency of the amine or thiol substitution to the *para* position of C₆F₅ has been developed by scientists to comply with the click chemistry requirements. Since their development, all of these strategies have been quickly integrated into synthetic polymer chemistry. Also, one type of click reaction is not enough for the preparation of complex macromolecular structures; therefore multiple click reaction has been more preferred. Therefore, different click reactions have been applied in an orthogonal way to introduce multiple functional groups at different sites along a polymer backbone.

Functional groups in polymer chains can be introduced by end or pendant functionality. The most common ways to obtain end functionalized polymers, functional initiators and the post-polymerization transformation of end groups can be used. In addition, direct polymerization of functional monomers gives pendant functionalized polymers. ATRP is widely used in the synthesis of functional polymers. Various functional monomers can be polymerized in a controlled fashion, yielding well-defined polymers with pendant functional groups. The produced polymer can further be used to obtain block copolymers because of its “livingness” nature. Additionally, to obtain end functionalized polymers, alkyl halides containing functional groups were used to initiate polymerization. The resulting end functionalized polymer can be converted to other functional groups using either nucleophilic substitution reactions, electrophilic or radical addition reactions for synthesizing block copolymers.

This process is also widely used to prepare of star polymers included “core-first”, “arm-first”, and “coupling-onto” approaches. All approaches are also successful for the preparation of end-functional stars. In the “core-first” and “coupling-onto” approaches, polymerization starts from a core and end functionality can be introduced by either directly displacing the end-functional halogens or through radical addition of functional alkenes. The “arm-first” approach is also suited for the end-functional stars and employs functional initiators and the subsequent coupling of end-functional arms with difunctional vinyl monomers. Obtained multiarm star polymers include high-chain end functionality at the periphery, for this reason, end functionality is called as periphery functionality in star polymers.

In this thesis, periphery functional multiarm star polymers were investigated. Novel periphery functional multiarm star polymers were successfully synthesized, combining “arm-first” approach with ATRP and click chemistry.

In the first study, nucleophilic *para*-fluoro addition reaction was investigated as a click concept for the synthesis of periphery post-functionalized multiarm star polymers and multiarm star block copolymers. For this purpose, pentafluorophenyl functionalized PS (α -fluoro-PS) is prepared by ATRP of Styrene (St) and used as macroinitiator in a crosslinking reaction with divinyl benzene (DVB) yielding (fluoro-PS)_n-polyDVB multiarm star polymer. The obtained multiarm star polymer with pentafluorophenyl moiety at the periphery is then used for nucleophilic substitution reactions for postfunctionalization. (PEG)_m-(PS)_n-polyDVB multiarm star block copolymer was achieved *via* nucleophilic addition of linear PEG₅₅₀-OH precursor with (fluoro-PS)_n-polyDVB multiarm star polymer in the presence of sodium hydride (NaH) in tetrahydrofuran (THF). (Cysteine-PS)_n-polyDVB post-functionalized multiarm star polymer was obtained *via* nucleophilic addition of *N*-acetyl-L-cysteine methyl ester with (fluoro-PS)_n-polyDVB multiarm star polymer in the presence of triethylamine (Et₃N) in dimethylformamide (DMF). Both procedures were successfully accomplished and easily reacted with labile *para*-fluoro groups by alcohols and thiols. In the second study, the successful postfunctionalization of multiarm star polymer with pentafluorophenyl and allyl moieties at the periphery is demonstrated employing modular thiol-*para*-fluoro and photoinduced radical thiol-ene double click reactions, respectively. α -Fluoro and α -allyl functionalized PS (α -fluoro-PS and α -allyl-PS) are in situ prepared by ATRP of St and their mixture is used as macroinitiator in a crosslinking reaction with DVB yielding (fluoro-PS)_m-polyDVB-(allyl-PS)_m multiarm star polymer. The obtained multiarm star polymer is then reacted with 1-propanethiol through thiol-*para*-fluoro click reaction to give (propyl-PS)_m-polyDVB-(allyl-PS)_m multiarm star polymer, which is subsequently reacted with *N*-acetyl-L-

cysteine methyl ester *via* radical thiol-ene click reaction in order to give well-defined heterofunctionalized (propyl-PS)_m-polyDVB-(cysteine-PS)_m multiarm star polymer. In the third study, we investigated novel multiarm star polymers as polymeric photoinitiators. The main motivation for investigating polymeric photoinitiating systems is that they are usually expected to display a higher efficiency with respect to the low molecular counterparts, due to a “polymer effect!”. In this context, we focused on benzoin and derivative, MTB, due to their already well-known tendency on photochemistry. Firstly, we prepared benzoin and MTB functional PS (Benzoin-PS and MTB-PS) were prepared by ATRP of St and used as macroinitiators in a cross-linking reaction with DVB to yield multiarm star homopolymers with benzoin and MTB periphery. Obtained multiarm (Benzoin-PS)_m-polyDVB and (MTB-PS)_p-polyDVB star polymers were used as polymeric photoinitiators and photokinetics of 1,6-hexanediol diacrylate (HDDA) were studied by Photo-DSC, respectively. These polymeric photoinitiators were used in free radical photopolymerization of methyl methacrylate (MMA) in air atmosphere.

In the last study, we concerned with supramolecular chemistry on multiarm star polymers. Supramolecular interactions such as hydrogen bonding, ligand-metal coordination or “host-guest” inclusion complexation has significant impact on polymer science and especially on the formation of complex macromolecular architectures. In this spirit, we turned our attention to study multiarm star block copolymer using “host-guest” interactions. Firstly, multiarm star polymer with adamantane (Ada) functionality as reactive periphery groups was prepared by a cross-linking reaction of DVB using adamantane end functionalized PS (Ada-PS) as a macroinitiator. Further, obtained multiarm star polymer, (Ada-PS)_n-polyDVB, was reacted with β-cyclodextrin (β-CD) end functionalized PEG (β-CD-PEG) resulting in the multiarm star block copolymer, (CD-PEG)_p-(Ada-PS)_n-polyDVB, *via* “host-guest” inclusion complexation.



ÇEVRE FONKSİYONLU ÇOK KOLLU YILDIZ POLİMERLERİN SENTEZİ VE KARAKTERİZASYONU

ÖZET

Organik kimyada moleküler seviyede kontrolü sağlamak için kullanılan yöntemler, son zamanlardaki gelişmeler ile kontrollü kompozisyon ve yapılarda iyi tanımlanmış makromoleküllerin sentezinde de kullanılmaktadır. Makromoleküler düzeyde kimyasal yapı ve fonksiyonların doğru bir şekilde kontrolü önemli olmasına rağmen, organik kimyadaki bu sentetik teknikleri polimer sentezine aktarmanın kolay bir süreç olmadığı unutulmamalıdır. Daha doğrusu, makromoleküllerin karakteristik özellikleri (ör. fonksiyonel grup sayısı, molekül ağırlığı dağılımı, ve saflaştırma teknikleri) küçük moleküllerle kıyaslandığında, yapısal doğruluk ve yüksek derecede fonksiyonel grup uyumluluğunun tespiti polimer sentez yöntemlerinin aydınlatılmasında oldukça önemlidir. Serbest radikalik polimerleşme makromolekül sentezinde oldukça yaygın kullanılmasına rağmen, iyonik polimerleşmede de olduğu gibi polimer yapı ve fonksiyonu üzerinde etkisi yoktur. Son yıllarda kontrollü radikal polimerleşme metodları üzerinde muazzam bir ilerleme olmuştur. Atom transfer radikal polimerleşmesi (ATRP), nitroksit ortamlı radikal polimerleşmesi (NMP), ve tersinir eklenme-ayırılma zincir transfer polimerleşmesi (RAFT) gibi polimerleşme çeşitleri en sık kullanılan kontrollü/“yaşayan” radikal polimerizasyon (C/LRP) methodlarından olup, farklı kompozisyonlarda (blok, aşı, yıldız ve alternatif dönüşümlü kopolimerler), düşük dağılımlı, kontrollü molekül ağırlığına sahip ve çeşitli fonksiyoniteler içeren sentetik polimerlerin hazırlanmasını sağlar.

Click kimyası özel olarak ilerleyen, yüksek verimli, enerji olarak tercih edilen kimyasal reaksiyonlardır, bunlar ilk başta sentetik kimyada kullanılmış daha sonra polimer ve malzeme biliminde oldukça popüler olarak kullanılan evrensel araçlar haline gelmiştir. Click reaksiyonları, özellikle Cu (I)-katalizli azit-alkin siklokatılma (CuAAC) reaksiyonu, Diels-Alder reaksiyonu ve tiyol-en reaksiyonu, son zamanlarda gelişmiş makromoleküler tasarım için son derece güçlü araçlar olduğu gösterilmiştir. Ayrıca, pentaflorofenol grupların kararsız *para*-floro gruplarının birincil amin ve tiyol grupları ile nükleofilik katılma reaksiyonları verdiği organik kimyada oldukça iyi bilinmektedir. Bu reaksiyonların çoğu kullanılan koşullar altında oldukça etkili ve yüksek verimle gerçekleşirler. Özünde nükleofilik katılma reaksiyonu olmasına rağmen, C₆F₅ halkasının *para* pozisyonunun amin ve tiyollerle çok yönlü ve verimli olduğu bilim adamları tarafından geliştirilip click kimyası gerekliliğine uyduğu kanıtlanmıştır. Bunların gelişmesinden itibaren, bütün bu stratejiler hızlı bir şekilde sentetik polimer kimyası alanına entegre edilmiştir. Ayrıca, tek tip click reaksiyonu kompleks makromoleküler yapıların eldesinde çok yeterli olmadığından birden fazla click reaksiyonu daha çok tercih edilmiştir. Bu nedenle, farklı click reaksiyonları polimer ana zinciri boyunca farklı yerlerde birden fazla fonksiyonel grup eklemek için ortogonal yolla uygulanmaktadır.

Polimer zincirlerindeki fonksiyonel gruplar uç gruplarda veya polimer zincirine asılı olarak değişebilir. Uç grup fonksiyonlu polimerler elde etmek için en sık kullanılan yollar fonksiyonel başlatıcıların kullanımı ve her bir uç grupların polimerleşme sonrası dönüşümüdür. Polimer zincirine asılı fonksiyonlar elde etmek için de fonksiyonel monomerlerin direkt polimerizasyonu kullanılabilir. ATRP fonksiyonel polimerlerin sentezinde yaygın olarak kullanılır. Çeşitli fonksiyonel monomerler kontrollü bir şekilde polimerleşerek asılı fonksiyon içeren iyi tanımlanmış polimerler elde edilir. Oluşan polimer yaşayan polimer olduğundan daha sonra blok kopolimer yapımında da kullanılır. Ayrıca, fonksiyonel başlatıcılar kullanılarak da uç grup fonksiyonlu polimerler kullanılır. Elde edilen polimerin uç grubu nükleofilik katılma reaksiyonu, elektrofilik veya radikal katılma reaksiyonlarıyla farklı fonksiyonel gruplara çevrilerek blok kopolimer yapımında kullanılır. Bu yöntem “core-first”, “arm-first”, ve “coupling-onto” yaklaşımları ile elde edilen yıldız polimerlerin hazırlanmasında da sıklıkla kullanılmaktadır. Bütün yaklaşımlar uç grup fonksiyonlu yıldız polimerlerin hazırlanmasında başarılıdır. “Core-first” ve “coupling-onto” yaklaşımlarında, polimerleşme çekirdekten başlar ve uç fonksiyonite ya uç fonksiyonel halojenlerin direkt yer değiştirmesiyle yada fonksiyonel alkenlerin radikal katılımıyla elde edilir. “Arm-first” yaklaşımı da uç fonksiyonel yıldız polimerler için uygundur ve fonksiyonel başlatıcı ve daha sonra uç fonksiyonlu kolların iki fonksiyonlu vinil monomerleriyle birleşiminden oluşur. Elde edilen çok kollu yıldız polimerler çevresinde yüksek zincirli uç grup fonksiyonallitesi içerir, bu yüzden de, uç fonksiyonallite daha çok çevre fonksiyonallitesi olarak adlandırılır.

Bu tezde, çevre fonksiyonlu çok kollu yıldız polimerler araştırılmıştır. Yeni çevre fonksiyonlu çok kollu yıldız polimerler “arm-first” yaklaşımıyla ATRP ve click kimyası ile birleştirilerek başarılı bir şekilde sentezlenmiştir.

İlk çalışmada, çevre fonksiyonlu çok kollu yıldız polimerlerin ve çok kollu yıldız blok kopolimerlerin sentezinde nükleofilik *para*-floro katılma reaksiyonu click konsepti içinde araştırılmıştır. Bu amaçla pentaflorofenil fonksiyonlu PS (α -floro-PS) stirenin ATRP ile hazırlanmış ve DVB’nin çapraz bağlanma reaksiyonunda (floro-PS)_n-poliDVB çok kollu yıldız polimerler vererek makrobaşlatıcı olarak kullanılmıştır. Elde edilen çevresinde pentaflorofenil grupları olan çok kollu yıldız polimerler daha sonra postfonksiyonlandırma nükleofilik katılma reaksiyonunda kullanılmıştır. (PEG)_m-(PS)_n-poliDVB çok kollu yıldız blok kopolimer lineer PEG₅₅₀-OH polimeri ile (floro-PS)_n-poliDVB çok kollu yıldız polimerin THF içinde NaH ortamında nükleofilik katılmasıyla elde edilmiştir. (Sistein-PS)_n-poliDVB postfonksiyonlu çok kollu yıldız polimer *N*-asetil-l-sistein metil ester ile (floro-PS)_n-poliDVB çok kollu yıldız polimerin DMF içinde trietilamin ortamında nükleofilik katılmasıyla elde edilmiştir. Her iki yöntem de başarılı bir şekilde tamamlanmıştır ve kararsız *para*-floro grupları alkol ve tiyollerle kolayca yer değiştirmiştir.

İkinci çalışmada, çevresinde pentaflorofenil ve alkil grubu içeren çok kollu yıldız polimerin sırasıyla, modüler tiyol-*para*-floro ve fotokimyasal radikal tiyol-en ikili click reaksiyonu ile postfonksiyonlanması gösterilmiştir. α -Floro ve α -allil fonksiyonlu PS (α -floro-PS and α -allil-PS) stirenin ATRP reaksiyonu ile tek aşamada hazırlanmıştır ve karışımları DVB’nin çapraz bağlanmasında (floro-PS)_m-poliDVB-(allil-PS)_m çok kollu yıldız polimerini vermek için makrobaşlatıcı olarak kullanılmıştır. Elde edilen çok kollu yıldız polimer tiyol-*para*-floro click reaksiyonu sayesinde daha sonra (propil-PS)_m-poliDVB-(allil-PS)_m çok kollu yıldız polimerini vermek için 1-propantiyol ile reaksiyona girmiştir, bu da daha sonra iyi tanımlanmış heterofonksiyonlu (propil-PS)_m-poliDVB-(sistein-PS)_m çok kollu yıldız polimerini

elde etmek için *N*-asetil-l-sistein metil ester ile radikal tiyol-en click reaksiyonu ile reaksiyona sokulmuştur.

Üçüncü çalışmada, yeni çok kollu yıldız polimerleri polimerik fotobaşlatıcı olarak inceledik. Polimerik fotobaşlatıcı sistemlerini araştırmamızdaki ana motivasyonumuz, “polimer etkisi” ‘nden dolayı düşük moleküllü emsallerine göre genellikle daha yüksek bir verim göstereceğinin düşünülmesidir. Bu içerikte, fotokimya da zaten yatkınlıkları bilinen benzoin ve türevi olan MTB üzerinde odaklandık. İlk önce, benzoin ve MTB fonksiyonlu PS (Benzoin-PS ve MTB-PS) ayrı ayrı ATRP ile hazırlandı ve DVB’nin çapraz bağlanma reaksiyonunda benzoin ve MTB çevre fonksiyonlu çok kollu yıldız homopolimerler vermesi için makrobaşlatıcı olarak kullandık. Elde edilen (Benzoin-PS)_m-poliDVB ve (MTB-PS)_p-poliDVB yıldız polimerler polimerik fotobaşlatıcı olarak kullanıldı ve sırasıyla 1,6-hekzandiol diakrilat (HDDA) ile fotokinetikleri foto-DSC ile çalışıldı. Bu polimerik fotobaşlatıcılar hava atmosferinde metil metakrilatın (MMA) serbest radikalik fotopolimerleşmesinde kullanıldı.

Son çalışmada, çok kollu yıldız polimerlerde supramoleküler kimya ile ilgilendik. Hidrojen bağları, ligand metal koordinasyonu veya “host-guest” iç kompleksleşme gibi supramoleküler etkileşimler polimer bilim ve özellikle karmaşık makromoleküler yapıların oluşumunda önemli bir etkiye sahiptir. Bu ruh içerisinde, dikkatimizi “host-guest” etkileşimlerini kullanarak çok kollu yıldız blok kopolimer çalışmasına verdik. Öncelikle, aktif çevre grupları olarak adamantan (Ada) fonksiyonu içeren çok kollu yıldız polimer, adamantan uç gruplu PS (Ada-PS) polimerinin makrobaşlatıcı olarak kullanıldığı DVB’nin çapraz bağlanma reaksiyonu ile hazırlandı. Ayrıca, elde edilen yıldız polimer, (Ada-PS)_n-poliDVB, β-siklodekstrin uç fonksiyonlu PEG (β-CD-PEG) ile reaksiyona girerek, “host-guest” iç kompleksleşmesiyle çok kollu yıldız blok kopolimerini, (CD-PEG)_p-(Ada-PS)_n-poliDVB vermiştir.



1. INTRODUCTION

Multiarm star polymers containing linear polymeric chains emanating as “arms” from a central branching point, or core, represent one of the simplest branched topologies with spherical shape, high functionality, low viscosity, and dense structure and provide properties and functions as compared to their linear analogs with similar molecular weight [1-4]. Until recently, the living ionic polymerization procedures mostly anionic polymerization were the only system for the preparation of the multiarm star polymers [5-7]. Without a doubt, the introduction of controlled/living radical polymerization (C/LRP) routes has enabled the synthesis of multiarm star polymers with a cross-linked core from a wide range of monomers under less stringent reaction conditions with good control over dispersity [8, 9]. The “core-first”, “arm-first” and “coupling-onto” approaches are well-known methods to prepare multiarm star polymers by using C/LRP routes. The “core-first” approach includes a core, possessing a large amount of initiating sites that have an ability to initiate the radical polymerization and thus to enable the growth of arms from the core. For the “arm-first” approach, cross-linking agent (difunctional monomer), and linear arm (macroinitiator) with suitable end groups react with each other to generate a polymer involving an enormous number of pendant vinyl groups that keep reacting with the radical formed at the end of chain to produce multiarm star polymer. The third approach involves the synthesis of preformed arms followed by reaction with a multifunctional coupling agent [6].

The coupling reactions can readily be accomplished by the click reactions which have already been used for the preparation of macromolecular structures with various topologies, e.g., block, graft, star, star-block, H-shaped polymers, dendrimers, and miktoarm stars [10-15]. The Cu(I)-catalyzed azide/alkyne cycloaddition (CuAAC) and Diels–Alder reactions as foremost members of the click reactions family have been received growing interest for the preparation of nonlinear macromolecular structures with different composition and topology. Besides the classical and popular CuAAC and Diels–Alder click reactions, a variety of other click-type reactions have recently been employed to prepare polymeric materials [16]. Thiol-based couplings are

excellent examples of click reactions and have recently emerged as a powerful tool for chemists and proved an impressive versatility and certain inherent benefits in various fields of application [17, 18]. Among them, the radical thiol-ene/yne [19] reactions, thiol-epoxy [20], thio-bromo [21], and *para*-fluorine/thiolnucleophilic substitution reactions [22, 23] have particularly attracted great interest and readily been applied to polymer synthesis. The radical thiol-ene reactions involve the free radical addition of thiol to alkene via thermal or photochemical process resulting in thioether product with high degree of antiMarkovnikov selectivity [24-27]. Thiol-ene click reactions have shown good potential in both polymer science and molecular synthesis including ease of implementation, high yield and conversion, and rapid reaction rates. Moreover, it is well known that the labile *para*-fluorine substituents of pentafluorophenyl groups can undergo nucleophilic substitution reactions particularly with thiol based nucleophiles even at room temperature [28, 29]. Although it is mainly a nucleophilic substitution reaction, the versatility and efficiency of thiol substitution of the *para*-fluoro group has been demonstrated to follow with most of the click chemistry requirements in literature [30-33].

Orthogonal multiple click reactions provide a chemical reaction platform for synthesis of well-defined complex macromolecular structures and advanced materials [34]. The most common methods for the synthesis of various functional polymers include the use of functional initiators and the postpolymerization functionalization for the end group functionality and the direct polymerization of functional monomers for the pendant functionality [35]. The end group functionalized polymers have been used to prepare a variety of complex macromolecular structures. For instance, photo active group containing polymers could be used as polymeric photoinitiators due to their advantages in comparison with their corresponding low molecular weight photoinitiators [36-38].

With respect to an increasing need for more defined polymer structures, there is a high demand in C/LRP and click chemistry combination based on from the covalent connections. Meanwhile, some noncovalent interactions, such as “host–guest” interactions between β -cyclodextrin (β -CD) and adamantane (Ada) are strong enough to keep the structures in aqueous solution just like the covalent bonds. In general, these types of noncovalent interactions provide easy and facile approaches for the construction of supramolecular architectures [39].

In this thesis, we investigated nucleophilic *para*-fluoro addition reaction as a click concept for the synthesis of periphery functional multiarm star polymers using both individually and the combination with thiol-ene click reactions, respectively. In addition, different types of photo active group bearing periphery functional multiarm star polymers were used as polymeric photoinitiators for vinyl polymerization for the first time. Moreover, here, the effect of supramolecular interactions between β -CD and Ada were investigated on periphery functional multiarm star polymers to obtain multiarm star block copolymers.

For these purposes, in the first study, α -fluoro functionalized PS (α -fluoro-PS) is prepared by ATRP of St and used as macroinitiator in a crosslinking reaction with DVB yielding (fluoro-PS)_n-polyDVB multiarm star polymer. The obtained multiarm star polymer with pentafluorophenyl moiety at the periphery is then used for nucleophilic substitution reactions for postfunctionalization and derivatization as outlined in Figure 1.1.

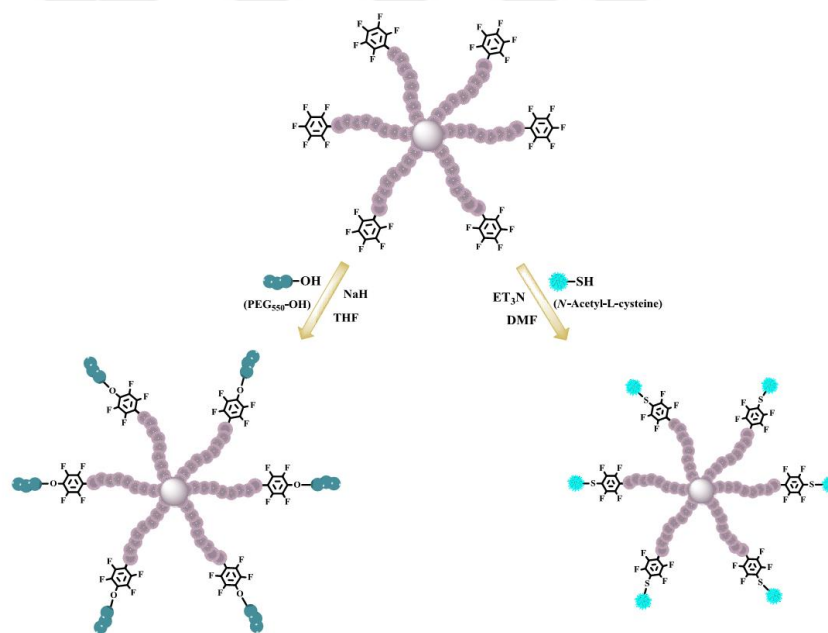


Figure 1.1 : Synthetic pathway for the functionalization of pentafluorophenyl bearing multiarm star polymer via nucleophilic *para*-fluoro addition reactions.

In the second work, previously studied synthetic approaches were enlarged and combined with thiol-ene click reaction. Here, α -fluoro and α -allyl functionalized PS (α -fluoro-PS and α -allyl-PS) are in situ prepared by ATRP of St and their mixture is used as macroinitiator in a crosslinking reaction with DVB yielding (fluoro-PS)_m-

polyDVB-(allyl-PS)_m multiarm star polymer. It is followed by orthogonal thiol-*para*-fluoro and thiol-ene double click reactions with 1-propanethiol and *N*-acetyl-l-cysteine methyl ester, respectively, resulting in formation of the target heterofunctionalized (propyl-PS)_m-polyDVB-(cysteine-PS)_m multiarm star polymer (Figure 1.2).

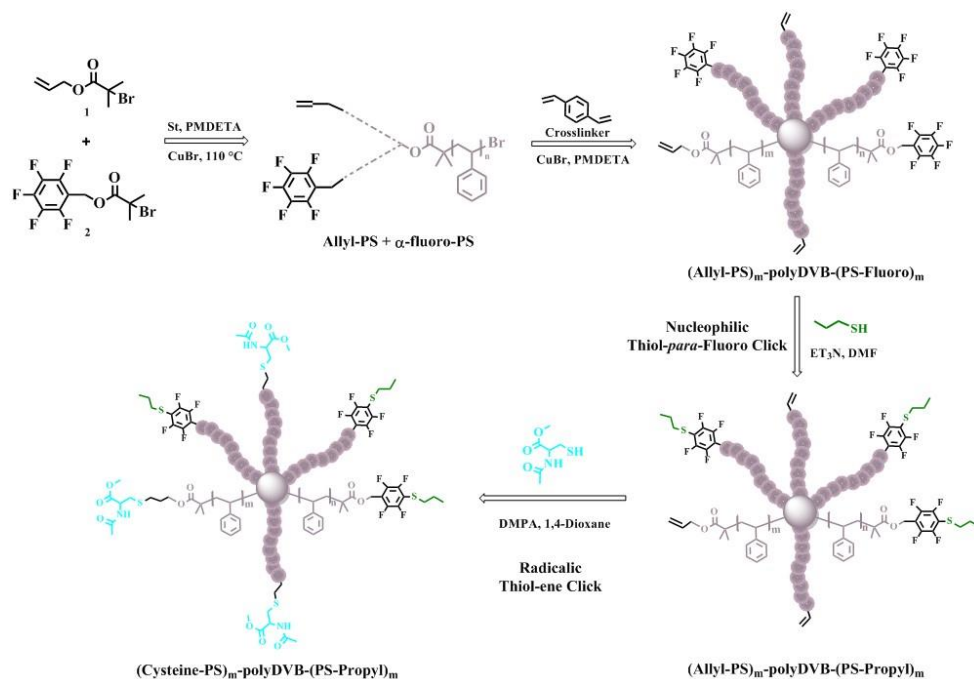


Figure 1.2 : Synthetic pathway for the synthesis of hetero-functionalized multiarm star polymer via sequential double click reactions, involving thiol-*para*-fluoro and radical thiol-ene chemistry.

Thirdly, as a new approach, multiarm star polymer was studied and used as novel polymeric photoinitiator for free radical polymerization. For this aim, benzoin and MTB functional PS (Benzoin-PS and MTB-PS) were prepared by ATRP of St and used as macroinitiators in a cross-linking reaction with DVB to yield multiarm star homopolymers with benzoin and MTB periphery, respectively. Obtained multiarm (Benzoin-PS)_m-polyDVB and (MTB-PS)_p-polyDVB star polymers were used as polymeric photoinitiators. Photokinetics of 1,6-hexanediol diacrylate (HDDA) with multiarm (Benzoin-PS)_m-polyDVB and (MTB-PS)_p-polyDVB star polymers were studied by Photo-DSC. These polymeric photoinitiators were used in free radical photopolymerization of methyl methacrylate (MMA) in air atmosphere (Figure 1.3).

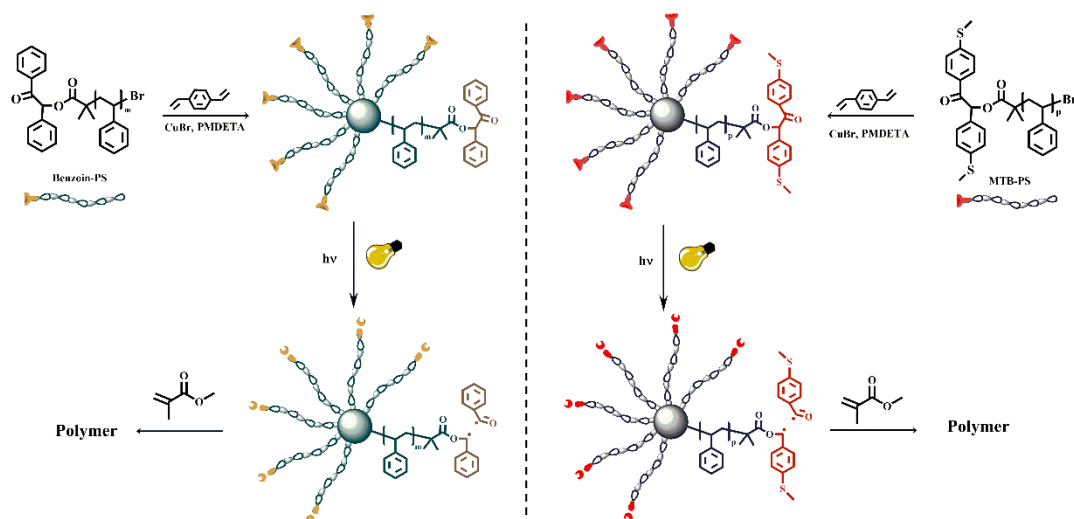


Figure 1.3 : Synthetic pathway for the synthesis of photo active group bearing multiarm star polymers and their usage as polymeric photoinitiators for free radical polymerization of MMA.

Finally, multiarm star block copolymer was synthesized with a new approach: host-guest inclusion complexation. Firstly, multiarm star polymer with adamantane (Ada) functionality as reactive periphery groups was prepared by a cross-linking reaction of DVB using Ada end functionalized PS (Ada-PS) as a macroinitiator. Thus, obtained multiarm star polymer was reacted with β -cyclodextrin end functionalized PEG (β -CD-PEG) resulting in the multiarm star block copolymers via host-guest inclusion complexation (Figure 1.4).

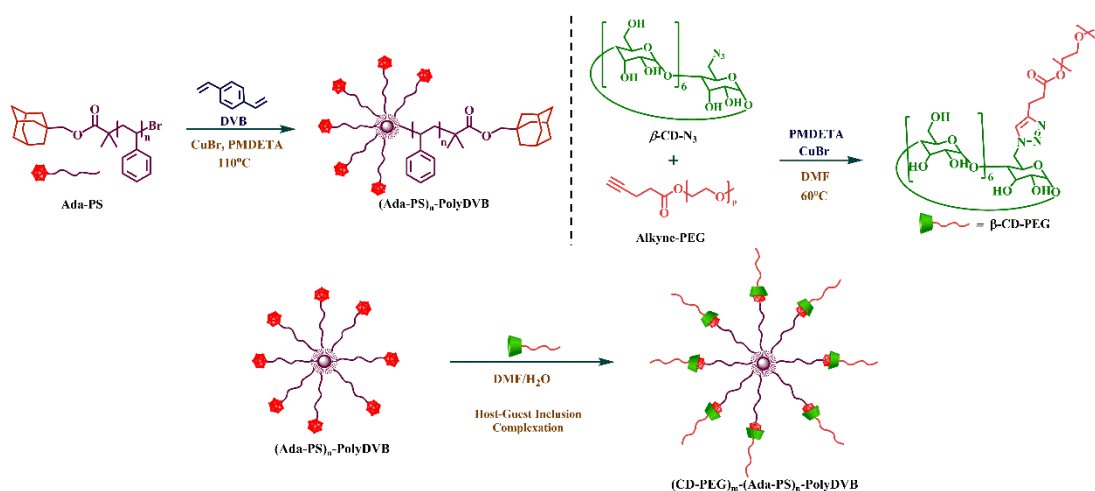


Figure 1.4 : Synthetic pathway for the synthesis of multiarm star block copolymer via “host-guest” interaction.



2. THEORETICAL PART

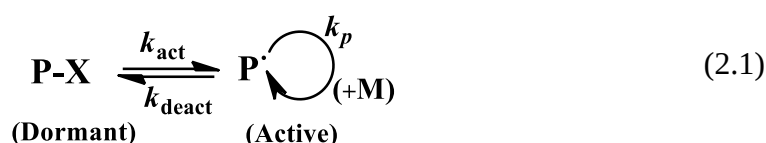
2.1 Living Polymerizations

The term “living polymerization” was initially discovered by Michael Szwarc in 1956 in the anionic polymerization of styrene with sodium naphthalenide initiating system in THF. The term living polymerization was initially used to describe a chain polymerization without chain transfer and chain termination reactions [40]. Living polymerization is one of the most effective methods for well-defined functional polymers with fully controllable molecular characteristics. The synthesis of such polymers by living polymerization demands fast initiation and relatively slow propagation in order that the narrow molecular weight distributions (MWDs) be obtained [41-43]. The living ionic polymerizations have met several requirements in order to obtain well-defined polymers with controlled chain end functionalities. These polymerizations have to be carried out with nearly complete exclusion of moisture and often at low temperatures. Moreover, only a limited number of monomers can be used, and the presence of functionalities in the monomers can cause undesirable side reactions. On the other hand, radical polymerizations (RP) have offered many advantages over ionic polymerizations since, is tolerant to impurities, very versatile with respect to compatibility with broad range of functional monomers, and relatively easy to implement in an industrial plant. In this regard, living radical polymerization has been among the most challenging frontiers in precision polymer synthesis and polymer chemistry.

2.2 Controlled/Living Radical Polymerization (C/LRP)

Free radical polymerization (FRP) is one of the most widely applied techniques for the commercial production of a variety of polymeric materials since it provides high versatility, compatibility with a wide variety of reaction conditions and tolerance to many functionalities and impurities. However, free radical polymerization strongly limits the chain control in molecular weight and chain end structure as well as it is

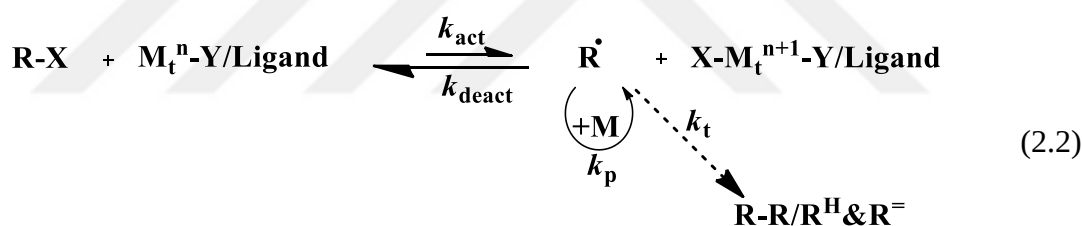
As a consequence of the inability to control molecular weight distribution and end functional groups, new techniques have been developed achieving better control over polymer structure and possessing the characteristics of a living process. Thus, the concept of controlled/“living” radical polymerization (C/LRP) has been introduced to control and precision of living polymerization to prepare new complex architectures with well-defined structures such as control molecular weights, narrow molecular weight distributions ($M_w/M_n < 1.1$), high degrees of functionality and compositional variation under relatively facile conditions. Transfer and termination reactions are allowed in a controlled polymerization if their contribution is sufficiently reduced by the correct choice of the reaction conditions such that polymer structure is not affected [41, 44, 45].

$$\begin{array}{ccc}
\mathbf{P-X} & \xrightleftharpoons[k_{\text{deact}}]{k_{\text{act}}} & \mathbf{P} \cdot \begin{array}{c} \circlearrowright^{k_p} \\ (+M) \end{array} \\
\text{(Dormant)} & & \text{(Active)}
\end{array} \quad (2.1)$$


2.2.1 Atom transfer radical polymerization (ATRP)

The name atom transfer radical polymerization comes from the atom transfer step, which is the key elementary reaction accountable for the uniform growth of the polymeric chains. ATRP, which is the most efficient method to obtain polymers with high control over compositions, architectures, and functionalities, uses a wide variety of monomers, catalysts, solvents, and reaction temperature.

The synthetic outline of the ATRP is shown in Scheme 2.2. ATRP is based on the reversible homolytic cleavage of carbon-halogen bond by redox reaction due to repetitive nature of activation and deactivation steps. The radicals, or the active species ($R\bullet$), are generated through a reversible redox process catalyzed by a transition metal complex (activator, $M_r^n - Y/\text{ligand}$, where Y may be another ligand or a counterion) which undergoes a one-electron oxidation with abstraction of a (pseudo)halogen atom, X, from a dormant species, $R-X$. Radicals react reversibly with the oxidized metal complexes, $X-M_r^{n+1}/\text{ligand}$, the deactivator, to reform the dormant species and the activator.



This process occurs with a rate constant of activation, k_{act} , and deactivation k_{deact} , and polymer chains grow by the addition of the free radicals to monomers like a conventional radical polymerization, with the rate constant of propagation, k_p . These processes are rapid, and dynamic equilibrium favors the dormant species. All chains can begin growth at the same time, and the concentration of the free radicals is quite low, so no more than a few percent of the polymer chains undergo termination by radical coupling and disproportionation in a well-controlled ATRP. This leads to control over the topology (stars, combs, branched), the composition (block, gradient, alternating, statistical), and the end functionality [62-64].

The equilibrium constant ($K_{\text{eq}} = k_{\text{act}}/k_{\text{deact}}$) plays an important role in ATRP because it determines the concentration of radicals and, therefore, the rates of polymerization (R_p), defined by equation 2.1, has been shown to be the first order with respect to the

monomer [M] and initiator [R-X], by ensuring the growth of all polymer chains, resulting in well-defined polymers with narrow molecular weight distributions. K_{eq} must be low to maintain a low stable concentration of radicals; thus, the termination reaction is suppressed.

$$R_p = k_p \cdot K_{eq} \frac{[R-X][M_t^n]}{[M_t^{n+1}]} \cdot [M] \quad (2.1)$$

$$\frac{M_w}{M_n} = 1 + \left(\frac{k_p [R-X]}{k_{deact} [M_t^{n+1}]} \right) \left(\frac{2}{p} - 1 \right) = 1 + \frac{2}{k_{act} [M_t^n] t} \quad (2.2)$$

Equation 2.2, which shows how the polydispersity index in ATRP (in the absence of chain termination and transfer) relates to the concentrations of initiator (R-X) and deactivator (M_t^{n+1}), the rate constants of propagation (k_p), deactivation (k_{deact}), and monomer conversion (p). Lower polydispersities are obtained at higher conversion, higher k_{deact} relative to k_p , a higher concentration of deactivator, and higher monomer to initiator ratio, $[M]_0/[I]_0$ [47, 65, 66].

ATRP is one of the most powerful techniques of controlled radical polymerization due to its facile experimental setup, the use of currently available and inexpensive catalysts (usually copper complexes with any suitable ligands), a wide variety of monomers, and simple initiators (alkyl halides). A detailed discussion of the basic components of ATRP is elucidated extensively in the following sections.

2.2.1.1 Basic components of ATRP

Monomers

Most vinyl monomers are capable to polymerize via ATRP, e.g. styrene (St) derivatives [67], (meth)acrylates [68], acrylamides [69, 70], vinylpyridines [71, 72], and acrylonitrile [73] which contain substituents that are capable of stabilizing the propagating radicals. Furthermore, ATRP shows tolerance towards many functional groups in monomers, however, a few monomers can not be polymerized with currently available ATRP catalysts. Some groups react rapidly with the catalyst system (such as acids; (meth)acrylic acid) giving metal carboxylates which are ineffective catalysts for ATRP. Some other monomers may be difficult to polymerize since they exhibit side reactions. For example, 4-vinyl pyridine (4-VP) monomer, which can undergo quaternization by the (alkyl halide) initiator [74]. The most common monomers in the

order of their decreasing ATRP reactivity are methacrylates, acrylonitrile, styrenes, acrylates, (meth)acrylamides [75].

Initiators

The primary role of the initiator is to determine the number of dormant chains and to provide the end groups of the polymer chains. Generally, initiators used in ATRP are alkyl halides (RX) (or pseudohalides,) with α -phenyl, vinyl, carbonyl, cyano groups and halogens at α -carbon to stabilize the generated free radicals. For the successful polymerization, initiation should be quantitative and faster than propagation. To obtain well-defined polymers with narrow molecular weight distributions, the halide group, X, should transfer rapidly between the growing chain and the transition metal complex. Thus, when X is either bromine or chlorine, the molecular weight control is best. Iodine works well for acrylate polymerizations; however, in styrene polymerizations, the heterolytic elimination of hydrogen iodide is too fast at high temperatures. Fluorine is not used because the carbon–fluorine bond strength is too strong for the fast activation–deactivation cycle with atom transfer. As for other X groups, some pseudohalogens, specifically thiocyanates, have been used successfully in the polymerization of acrylates and styrenes [76].

The initiator can not only be a small molecule, but also a polyfunctional small molecule, or a macromolecule, which would produce end-functional polymers, star polymers, and graft copolymers, respectively.

Catalysts

Catalyst is the key component of ATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. There are several requirements for an efficient transition metal catalyst [47]. Mainly, an efficient catalyst should be able to expand its coordination sphere and oxidation number upon halogen abstraction from an initiator (alkyl halide) or dormant polymer chains. The metal center should have suitable affinity toward a halogen. Additionally, the catalyst should not participate in any side reactions which would lower its activity or change the radical nature of the ATRP process.

Various transition metals, such as Re [77], Ru [78], Rh [79], Fe [80-82], Ni [83], Pd [84] and Cu [47, 48] have been successfully used as catalysts for ATRP. Among them, Cu seems to be the most efficient metal as determined by the successful application of its

complexes as catalysts in the ATRP of a broad range of monomers in diverse media. Matyjaszewski and co-workers [85] describes Cu systems with kinetic and spectroscopic studies to determine the precise structure and reactivities of the Cu(I) and Cu(II) species. Then, Sawamoto and co-workers shows that the Ru-based complexes can compete with the Cu-based systems on many fronts. A specific Fe-based catalyst has also been reported to polymerize vinyl acetate via an ATRP mechanism [86].

Ligands

Ligand plays a critical role in ATRP to solubilize the transition metal salt in the organic media and to justify the redox potential and halogenophilicity of the metal center forming a complex with an appropriate reactivity and dynamics for the atom transfer. The ligand should complex strongly with the transition metal, and should also allow expansion of the coordination sphere, and should allow selective atom transfer without promoting other reactions. The type of a ligand including electronic, steric and solubility characters, greatly affects the reactivity of the catalyst complex and control over the polymerization [48, 87].

The most common copper complexes with various multidentate N-containing ligands for ATRP systems are substituted bipyridines [88, 89], alkyl pyridylmethanimines and multidentate aliphatic tertiary amines such as *N,N,N',N'',N'''* pentamethyl diethylenetriamine (PMDETA) [90], tris[2-(dimethylamino) ethyl]amine (Me₆-TREN) [91]. While nitrogen ligands are typically used for copper-based ATRP, phosphorus-based ligands are used for most other transition metals in ATRP.

Solvents

ATRP can be performed in bulk, in solution and in heterogeneous systems (e.g. emulsion and suspension). Generally used solvents are nonpolar, such as toluene, xylene, benzene but some polar aprotic solvents, such as anisole, p-dimethoxybenzene, diphenyl ether, *N,N*-dimethylformamide, ethylene carbonate, acetonitrile, and polar protic solvents such as alcohols and water have been successfully used in ATRP. The solvent can have a large influence on the polymerization reaction, both on the polymerization rate and the final properties of the prepared polymer. The influence of solvents on the polymerization rate is attributed to a change in the structure of the catalyst and/or a change in the solubility of the catalyst complex. A solvent is

sometimes necessary, especially when the polymer is insoluble in its monomer (e.g., polyacrylonitrile). Several factors affect the solvent choice. Chain transfer to solvent should be minimal. In addition, specific interactions between solvent and the catalytic system should be considered. Catalyst poisoning by the solvent (e.g., carboxylic acids or phosphine in copper-based ATRP) [92] and solvent-assisted side reactions, such as elimination of HX from polystyryl halides, which is more pronounced in a polar solvent [93], should be minimized.

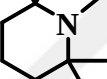
2.2.1.2 Other types of ATRP systems

ATRP is especially sensitive to oxygen, since oxygen can inhibit polymerization not only by the formation of unreactive peroxy radicals but also by the irreversible oxidation of transition metal catalysts. To overcome this problem using air stable catalysts in their higher oxidation states was successfully developed and used as a tool in preparing well-defined polymers [94]. Additionally, reducing the concentrations of catalyst would be beneficial from both industrial and environmental standpoints. Several modified ATRP techniques have been developed that require significantly reduced the amount of catalyst used in ATRP systems [95, 96]. These techniques include initiators for continuous activator regeneration (ICAR) ATRP [97], activator regenerated by electron transfer (ARGET) ATRP [98], activators generated by electron transfer (AGET) ATRP [99, 100] and single electron transfer living radical polymerization (SET-LRP) [101, 102]. In these systems, oxidatively stable Cu(II) complexes were reduced to the Cu(I) complexes at the beginning of the reaction with radicals formed by decomposition of radical initiators or various reducing agents, such as tin(II) 2-ethylhexanoate [98, 100], ascorbic acid [103], phenol [104] or thiophenol and derivatives [105] or sugars [106]. SET-LRP is distinct in that it uses metallic copper as the catalyst.

2.2.2 Nitroxide-mediated radical polymerization (NMP)

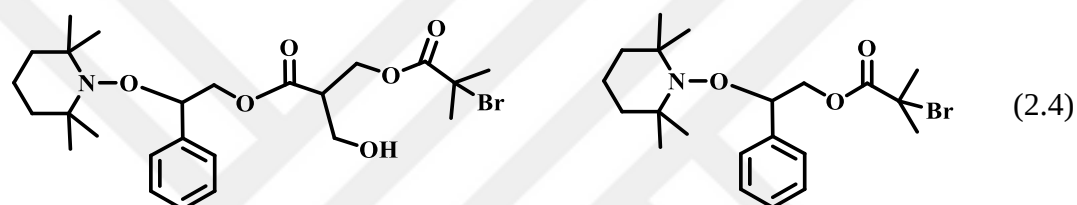
Nitroxide-mediated radical polymerization (NMP) is a one type of a C/LRP technique that allows the synthesis of well-defined, functional and complex macromolecular architectures. The NMP process has a similar mechanism to the use of iniferters and the pioneering iniferter work was reported by Otsu in 1982 provided the basis for the development of LFRP and it is interesting to note the similarity between the iniferter mechanism and living free radical mechanism [107].

$$\begin{array}{c}
 \text{wavy P}_n\text{-X} \xrightleftharpoons[k_{\text{deact}}]{k_{\text{act}}} \text{wavy P}_n^\bullet + \text{X}^\bullet \\
 \text{monomer} \xrightarrow{k_p} \text{wavy P}_m \xrightarrow{k_t} \text{wavy P}_{n+m}
 \end{array} \quad (2.3)$$

$\text{X}^\bullet =$

TEMPO (2,2,6,6 tetramethyl-piperidinyloxy)

14

two radicals in the right stoichiometry. By using the unimolecular initiator, the molecular weight can be properly controlled, because the number of initiating sites per polymeric chain is determined. Moreover, unimolecular initiators can afford the polymerization of a wide variety of monomers, such as styrene, methacrylates, acrylates, acrylamides, dienes, and acrylonitrile. The variable nature of these initiators can also be used to control the synthesis of block copolymers from a wide selection of monomers. This technique has also some limitations. The upper molecular weight limit with the appropriate stoichiometric values is between 150 000 and 200 000. The MWD is generally lower than 1.20 but become broader upon enhancing molecular weight, indicating the presence of termination reactions. The structure of the typically used unimolecular initiators for NMP can be seen in Scheme 2.4.



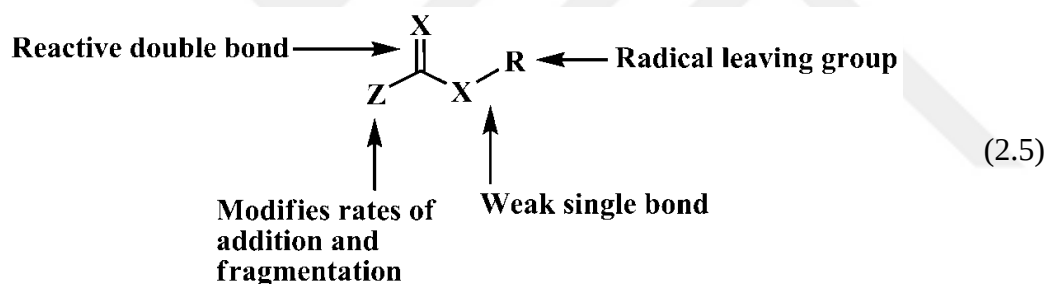
The structure of the nitroxides strongly affects their ability to efficiently mediate C/LRPs of various monomers. Different nitroxides have been developed and used for NMP, many of which have proved to be far superior to the TEMPO type, giving better molecular weight distributions in addition to faster polymerizations.

Compared with other reversible-deactivation radical polymerization methods, NMP possesses several advantages, such as easier product purification and an excellent functional group tolerance since no metal complex is used [109]. Although NMP is one of the simplest methods of living free radical polymerization, it has many disadvantages. Many monomers will not polymerize due to the stability of the dormant alkoxyamine that forms. Also, since the reaction is kinetically slow, high temperatures (110 °C) are often required [92].

The first true stable radical-mediated polymerization method, NMP, was demonstrated by Solomon, Rizzardo and Moad in 1982 [110] that the reversible end capping of the propagating chain ends by nitroxide free radicals, like TEMPO. In their patent, they explained the use of nitroxides and alkoxyamines as a route to control the radical polymerization of a range of monomers, including acrylates and styrenics.

2.2.3 Reversible addition-fragmentation chain transfer polymerization (RAFT)

Reversible addition-fragmentation chain transfer (RAFT) is another method of controlled radical polymerization, based upon a degenerative transfer system between active and dormant species. A typical RAFT-mediated polymerization consists of chain transfer agent (CTA), monomer, and initiator. As shown in Scheme 2.5, certain dithio compounds $[S = C(-S - R)(-Z)]$ with proper substituents $-R$ and $-Z$, which are used as CTA and allow the polymerization with living characteristics. Dithioesters, dithiocarbamates, trithiocarbonates, and xanthates are generally used as CTA to control molecular weights, molecular weight distributions, and even chemical composition [111, 112]. Transfer agents in this reaction contain moieties for both initiation and transfer which are generated in the presence of radicals. In addition, conventional radical initiators (AIBN and peroxides) are employed in this process, these compounds only serve as a radical source to drive reversible exchange reactions between active and dormant state.



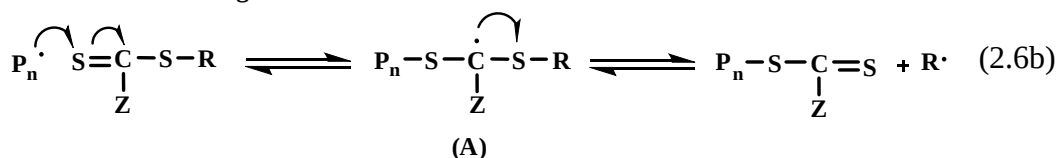
The generally accepted mechanism of the RAFT polymerization involves a series of addition-fragmentation steps as shown in Scheme 2.6. The mechanism of RAFT begins with a standard initiation step as homolytic bond cleavage of the initiator molecule yields a reactive free radical. This free radical then reacts with the monomer to produce the active center with additional monomer then adding in a sequential fashion to form a growing polymer chain ($P_n\bullet$). The propagating chain adds to the CTA to yield a radical intermediate. Fragmentation of this intermediate gives rise to either the original polymer chain ($P_n\bullet$) or to a new radical ($R\bullet$), which itself must be able to reinitiate polymerization. This free radical generates its own active center by reaction with the monomer and eventually a new propagating chain ($P_m\bullet$) is formed. At the very early stage of the polymerization, CTAs are consumed to ensure that all chains are initiated before propagation. Ultimately, chain equilibration occurs in which there is a dynamic equilibrium to be established between the active propagating

radicals ($P_n^\bullet$ and $P_m^\bullet$) and the dormant polymeric dithioester compounds [$P_n-S-C(Z)=S$ and $P_m-S-C(Z)=S$], thereby allowing all of the chains to grow at the same rate. A limited amount of termination does take place; however, the effect of termination of polymerization kinetics is negligible.

Initiation and propagation



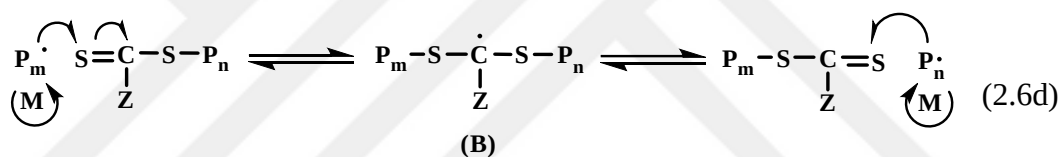
Addition to RAFT agent



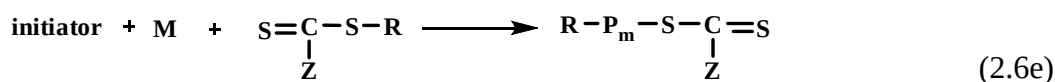
Reinitiation



Chain equilibration by reversible addition fragmentation



Overall



It is the most flexible technique with respect to monomer choice (styrene, acrylates, methacrylates, and derivatives) and functional group and impurity tolerance (-OH, -COOH, CONR₂, NR₂, SO₃Na, etc.,) and allows for the construction of well-defined polymeric materials with complex architectures [51, 113-115]. Moreover, a distinct advantage of RAFT polymerization is its relative simplicity and versatility, since conventional free radical polymerizations can be readily converted into a RAFT process by adding an appropriate RAFT agent while other reaction parameters can be kept constant [116]. A different types of architectures such as telechelic, block copolymers, graft copolymers, gradient copolymers, nano gels, stars, and dendritic structures can be synthesized by using RAFT polymerization [117-120].

2.3 Click Chemistry

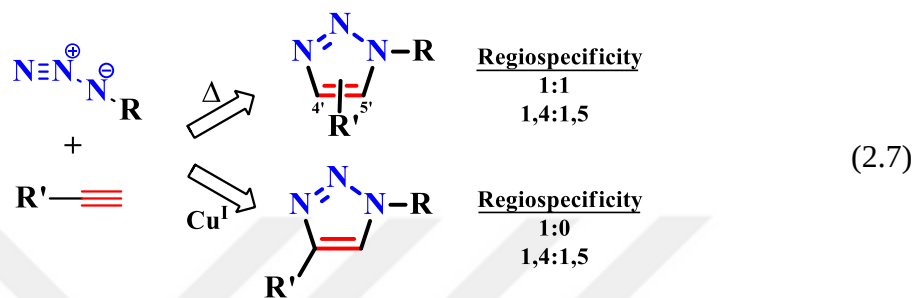
“Click chemistry” is a general concept, was defined by Sharpless and co-workers in 2001 [121] as a new way of categorizing organic reactions to building complex molecules from a few, straightforward, thermodynamically favorable reactions, occurring rapidly and selectively with each other in mild reaction conditions. Furthermore, according to Sharpless, click reaction must be modular, wide in scope, high yielding, creating only inoffensive by-products, be stereospecific and involve simple experimental procedure. The purification process of these reactions should be as simple as the synthesis procedure and, thus, nonchromatographic methods, that is, crystallization or distillation, are selected for isolation of the products.

Since their overwhelming success, click chemistry strategies have been rapidly investigated by the polymer science community. Nowadays there are several processes have been identified under this term such as nucleophilic ring opening reactions; non-aldol carbonyl chemistry; a family of thiol-based chemistries; and cycloaddition reactions. Among these selected reactions, copper(I)-catalyzed azide-alkyne (CuAAC), Diels-Alder cycloaddition reactions and thiol-ene reactions have gained much interest among the chemists not only the synthetic ones but also the polymer chemists. In this section, these most well-known of click reactions will be discussed along with another popular thiol based click reaction, thiol-*para* fluoro nucleophilic addition reaction.

2.3.1 Copper(I) catalyzed azide-alkyne cycloaddition (CuAAC) reaction

The copper(I) catalyzed azide-alkyne cycloaddition (CuAAC) reaction is derived from the original 1,3-dipolar cycloaddition of organic azides to terminal alkynes discovered by Huisgen et al. [122]. Sharpless et al. [121] defined this type of cycloaddition as the ideal click reaction and optimized this reaction via copper(I) catalysis. This type of click reaction can be characterized as highly efficient and specific, with the starting materials being very stable to other functional groups. Same year, the groups of Meldal [123] independently reported the use of a copper(I) catalyst to allow azide-alkyne cycloadditions to be conducted at low temperatures with high rates, efficiency, and (regio)specificity and the reaction principle has been employed in various fields of synthetic chemistry, i.e. medicinal chemistry, polymer chemistry, material chemistry, inorganic chemistry and, in particular, organic chemistry.

Even though the conventional Huisgen cycloaddition of azides and alkynes requires high temperatures (>110 °C) and long reaction times, resulting in a racemic mixture of 1,4- and 1,5-triazole products [124], CuAAC can occur at ambient temperature, is nearly solvent insensitive, with an extremely high tolerance of numerous functional groups and produces only the 1,4-regioisomer triazole [125]. Cu(I) catalysis directs the reaction to form the 1,4-regioisomer exclusively (Scheme 2.7) and increases the reaction rate up to 10^7 times [126], eliminating the need for elevated temperatures.



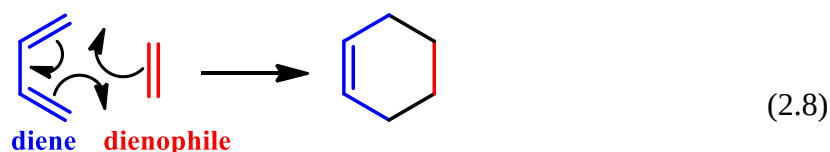
Although CuAAC click reaction was initially selected as a general concept for organic synthesis, this strategy also has a huge potential in polymer science for the preparation of well-defined functional polymeric building blocks either end-functionalized or side-functionalized at the chain. The discovery of this click reaction in polymer science by Hawker, Sharpless and coworkers, has had a significant effect on the construction of well-defined and complex macromolecular structures via click chemistry has been fully utilized [127]. Afterwards, the number of publications in this field has increased dramatically within the years.

2.3.2 Diels-Alder reaction

The Diels-Alder reaction is defined as the cycloaddition reaction between a conjugated diene and a second component, called dienophile to form a six membered ring in a regio- and stereo controlled way. The Diels-Alder reaction was discovered by Otto Diels and Kurt Alder in 1928, and they were awarded the Nobel Prize in Chemistry in 1950 for discovering this useful transformation [128]. The discovery of this reaction has had a significant impact on mechanistic and synthetic organic chemistry [129].

The reaction is classified as a $[4\pi + 2\pi]$ cycloaddition; 4 and 2 identify both the number of π electrons involved in the electronic rearrangement and the number of atoms originating unsaturated six-membered ring. The driving force of the reaction is the formation of new σ bonds which are known to be energetically more stable than π

bonds. The reorganization of the π electrons in the two starting compounds are transformed into two new sigma bonds and one new π bond all take place in a concerted manner as illustrated in Scheme 2.8.

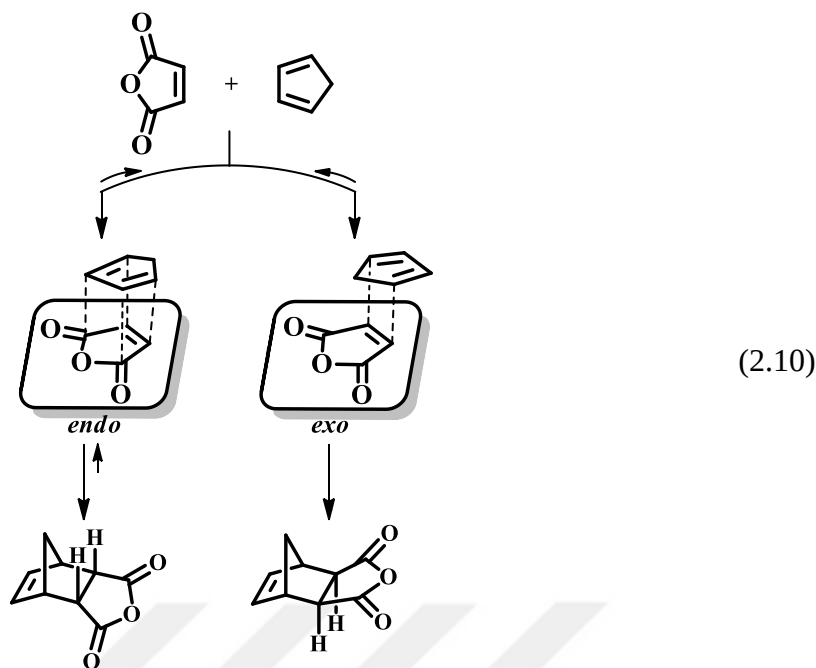


A great variety of conjugated dienes and dienophiles can be used for building simple and complex molecules. Typically, the Diels-Alder reaction works best when either the diene is substituted with electron donating functional groups (like -OR, -NR₂, etc) or when the dienophile is substituted with electron-withdrawing functional groups (like -CN, -CO, -COOR, -NO₂, etc).

The basic requirement is that the conjugated dienes must have *cisoid* conformation in order to participate in the Diels-Alder reaction Scheme 2.9. Rigid transoid structures of dienes that are more stable, so they are unreactive in the Diels-Alder reactions [130]. Additionally, cyclic conjugated dienes, which are locked into the rigid *cisoid* form, are particularly more reactive than the open chain dienes.



A unique type of stereoselectivity is observed in Diels-Alder reactions when the diene is cyclic. The reaction of an annulated diene usually yields a mixture of the *endo* and *exo* addition products with the *exo* product being the sterically less strained and thus thermodynamically more stable isomer. However, Diels-Alder reaction is known as highly selective reaction and quite often gives the *endo* product. This is the “*endo* rule”, first proposed by Alder [131]. In the reaction of maleic anhydride with cyclopentadiene, for example, the *endo* isomer is formed (the substituents from the dienophile point to the larger bridge) rather than the *exo* isomer (the substituents from the dienophile point away from the larger bridge) (Scheme 2.10).



The preference for *endo*-stereochemistry is “observed” in most Diels-Alder reactions. This occurs because the *exo* isomer, having less steric strain than the *endo*, is more stable, and because the Diels-Alder reaction is often reversible under the reaction conditions. Woodward, Hoffman, and Fukui showed that favorable interaction between the substituent π system and used molecular orbital theory to explain that overlap of the π orbitals on the substituents on the dienophile with π orbitals on the diene is favorable, helping to bring the two molecules together [132].

The use of a catalyst allows the cycloaddition to be carried out under mild conditions shorter reaction time at lower temperatures and, thus, allows to enhance the *endo*-*exo* selectivity; this has been attributed to changes in energy of molecular orbitals when complexed so that there is a lower activation energy [133]. The solvent also has an important effect on the rate of Diels-Alder reactions. The studies of solvent effects on the *endo*-*exo* selectivity of Diels-Alder reactions have displayed the significance of hydrogen-bonding interactions as well as this interactions in polar solvents tend to exclude nonpolar solutes and forces them together, resulting in higher effective concentrations [134].

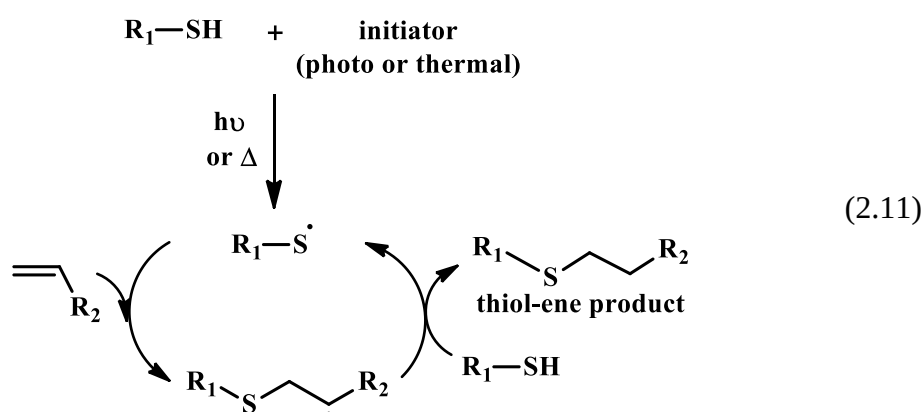
2.3.3 Thiol-ene reaction

Thiol-ene chemistry has been introduced as alternative click reaction [135] because the reaction has many of the attributes of the click reaction, for example, quantitative yields, rapid reaction rates, mild reaction conditions, and tolerant of various solvents

and functional groups. The thioether linkage, formed after thiol-ene reaction shows greater stability to a wide range of chemical environments, such as strong acid and basic media as well as oxidizing and reducing conditions.

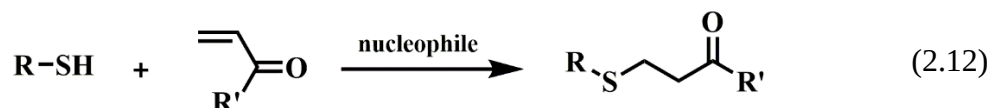
The radical addition of thiols to carbon-carbon double bonds is called as the thiol-ene reaction and discovered in the early 1900s by Posner [136-138]. The typically accepted mechanism of the thiol-ene free radical addition reaction, first proposed by Kharasch and coworkers in 1938 [139]. The thiol-ene reaction can be induced photochemically or thermally at ambient temperature without unwanted side reactions such as sulfenyl radical coupling [140-142]. Hawker and coworkers compared the thermal and photochemical initiation methods in model reactions and found the photoinitiated radical process proceeded with higher efficiency, requiring shorter reaction times for high conversion, and displayed better functional group tolerance [143].

Typically, the thiol-ene reaction proceeds through a chain radical polymerization process with initiation, propagation and termination steps, in Scheme 2.11. Initiation involves the treatment of a thiol with an initiator, under irradiation or heat, resulting in the generating a thiyl radical, $RS^\bullet$. Propagation step occurs in two step which involves first the direct addition of the thiyl radical to the $C=C$ bond producing an intermediate thioether carbon radical followed by chain transfer to a second molecule of thiol to give the thiol-ene addition product with the concomitant generation of a new thiyl radical. Termination is believed to occur through the radical-radical coupling processes of the thioether carbon and/or thiyl radicals.



Although thiol-ene click reaction has mainly been focused on a radical-mediated version to alkenes, this reaction can also proceed via Michael addition, especially when double bonds conjugated with electron-withdrawing groups (e.g. α , β -unsaturated

carbonyl compounds such as acrylate, maleimido, etc.) (Scheme 2.12). Liu and coworkers detailed the synthesis of norbornene–acrylate monomers was then treated with a series of thiols using nucleophilic thiol-Michael chemistry and subsequently evaluated their polymerisation behaviour via ring-opening metathesis polymerisation (ROMP) [144].

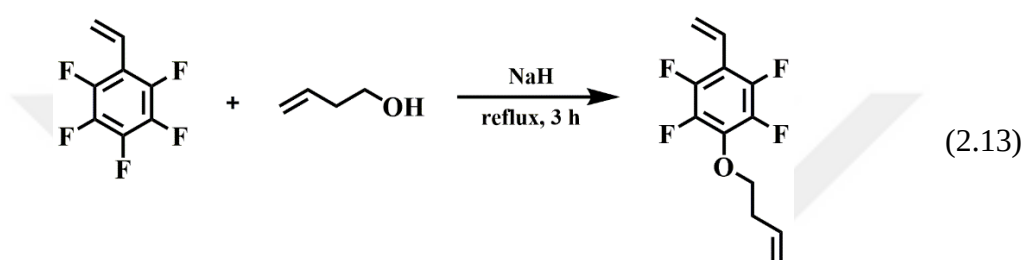


The thiol-ene click reactions, through either a radical or nucleophilic mechanism, provide efficient hydrothiolation routes across virtually any double bond [135, 145, 146]. Thiol-ene click reactions indeed have a promising future for the synthesis of not only for macromolecules but also small organic molecules and bioconjugates. These robust and efficient reactions have enormous benefits for the producing of polymeric structures. The great potential of thiol–ene chemistry was exploited by Killups et al. in the synthesis of poly(thioether) dendrimers [147], Chan and coworkers highlighted thiol-containing materials and their application in convergent star synthesis [148], Singha et al. reported the synthesis of polymer–peptide conjugates via a combination of ATRP and radical thiol–ene chemistries [149]. Recently, van Hensbergen, Burford and Lowe detailed the post-polymerisation modification of the backbone bonds in a ROMP homopolymer with a different thiols under photochemical radical mediated conditions [150], Altintas and coworkers demonstrated that light-induced thiol–ene coupling can proceed to terminal double bonds of various end functional polymers with a facile quantitative post-functionalization reaction [151]. The UV-induced crosslinking of unsaturated polymers (photocuring) by reaction with multifunctional thiols is currently employed in surface coating owing to a number of advantages over other curing methods. Biomaterials for application in medicine, especially dentistry, have been prepared by using this process. Consequently, numerous examples are summarized the power of thiol-ene chemistry [17, 145, 152-155].

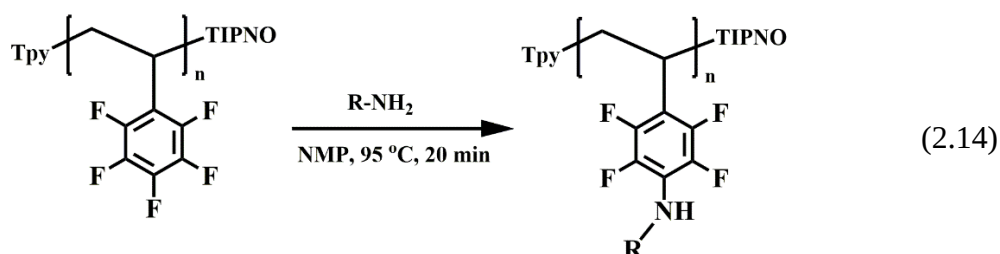
2.3.4 *Para*-fluoro addition reaction

It is well-known in organic chemistry that the labile *para*-fluorine substituents of pentafluorophenyl (C₆F₅) groups can undergo nucleophilic substitution reactions of various nucleophiles such as with primary and secondary amino groups in refluxing

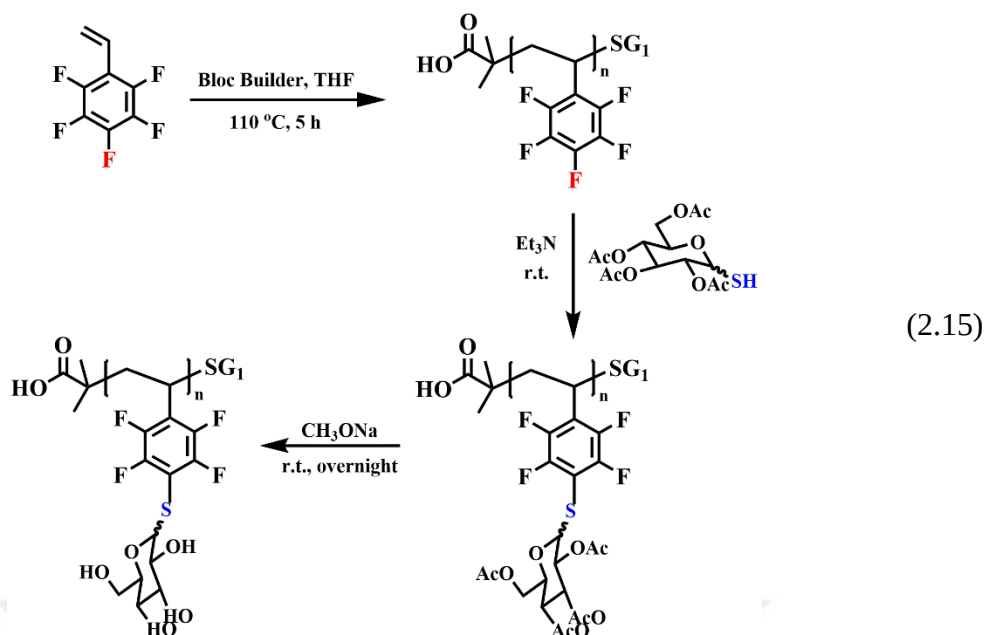
DMF or hexane, alkoxides in alcohol or THF and thiols in the presence of Et₃N in DMF with high yields [28, 156-159]. Wooley and coworkers demonstrated the synthesis of an amphiphilic crosslinked polymer network, consisting of a hyperbranched fluoropolymer and poly(ethylene glycol) for polymer coating purposes by nucleophilic substitution of the *para*-fluorine substituent by the amine functionalities [160, 161]. Same research group described a procedure for the preparation of alkene functionalized well-defined copolymers using RAFT polymerization technique. They synthesized various divinyl monomers using basic organic chemistry aspects, one of them is shown in Scheme 2.13 [162].



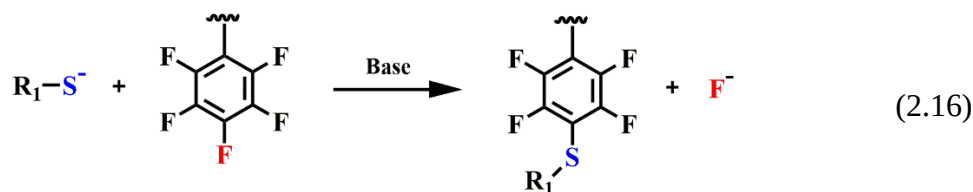
Hoogenboom and Schubert demonstrated the application of *para*-fluoro-amine click reaction on a terpyridine (Tpy) functionalized macromolecules to create well-defined multifunctional graft polymers (Scheme 2.14) [163].



Schubert et al. have shown a route to glycopolymers that combines NMP and metal-free click chemistry where thiol-glycoside was reacted under ambient conditions with pentafluorostyrene (PFS) moieties on the polymeric backbone utilizing thiol-*para* fluoro click reaction, as illustrated in Scheme 2.15 [33].



Although in essence these reactions are nucleophilic substitution reactions, most of these reactions are highly efficient and provide high yields under the employed conditions. In addition, a wide range of primary amines and thiols, which can be efficiently reacted with $-\text{C}_6\text{F}_5$ groups, are commercially available. The accessibility of the $-\text{C}_6\text{F}_5$ groups however is rather limited; obstructing the scope and modularity of the reaction. As can be seen from these properties, these reactions are applicable to most of the click chemistry requirements [30, 164]. General mechanism of thiol-*para* fluoro click reaction is shown in Scheme 2.16.

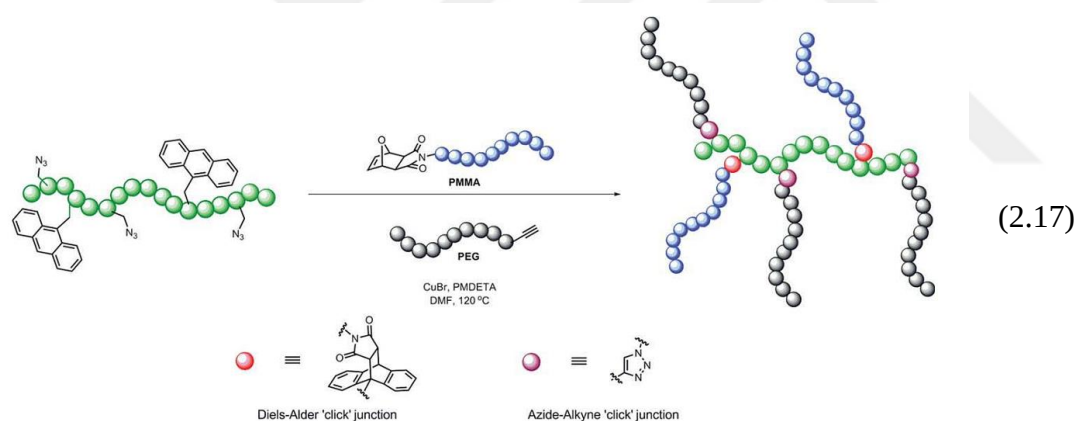


2.4 Orthogonal Multiple Click Reactions

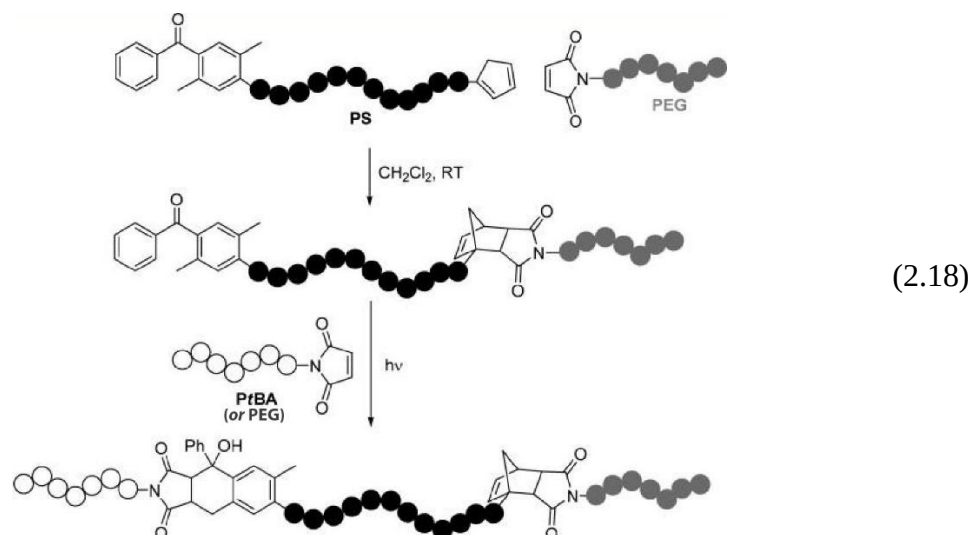
The functionalization of well-defined polymers after the successful achievement of polymerization techniques represents an ongoing field in macromolecular science for design and synthesis of well-defined complex macromolecular structures. Click reactions have the ability to create new polymers by introducing functionality at polymer chain ends or along the backbone and they are considered orthogonal as the components react together in high yield and in the presence of many other functional

groups. Thus, with increasing demands for the functionalization of complex macromolecular structures using robust, efficient, and orthogonal click chemistries prompted polymer chemists to search for alternative routes, such as a combination of click reactions with different natures, giving special properties with functional groups and chain architecture. The orthogonal multifunctionalization of polymers is important because one type click reaction itself is not capable of affording the target structures. Therefore, different click reactions have been employed in an orthogonal fashion to introduce multiple functional groups at different sites along a polymer backbone [34, 165-168].

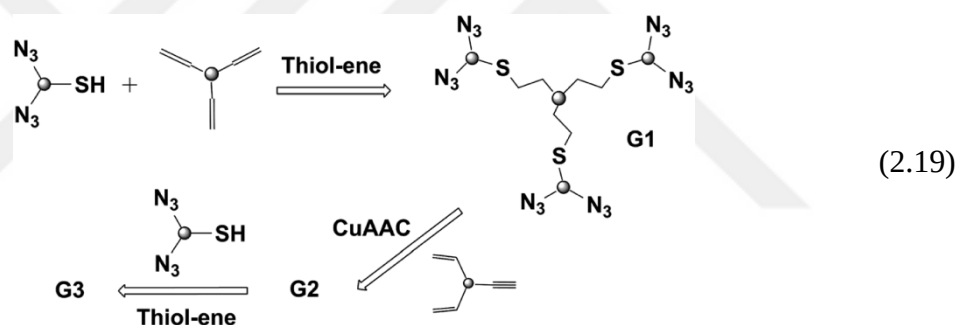
The remarkable success of the orthogonality of the CuAAC and Diels–Alder reactions in macromolecular chemistry was demonstrated by Tunca and coworkers to obtain ABC type triblock copolymers in a one pot fashion [169]. The approach was further extended to obtain well-defined heterograft copolymers via in situ use of these two orthogonal click reactions (Scheme 2.17) [129, 170].



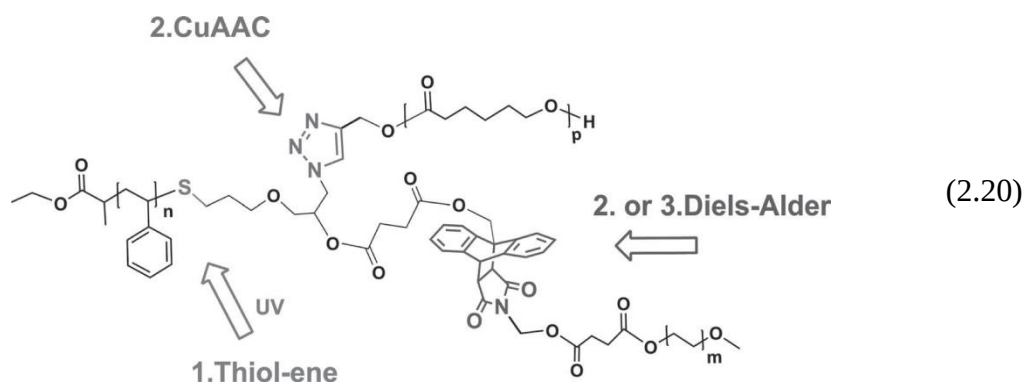
Recently, the group of Barner-Kowollik published novel ABA and ABC triblock copolymers by using the combination of photoinduced Diels-Alder reactions with thermal Diels-Alder reactions and azide alkyne click chemistry at ambient temperature (Scheme 2.18) [171].



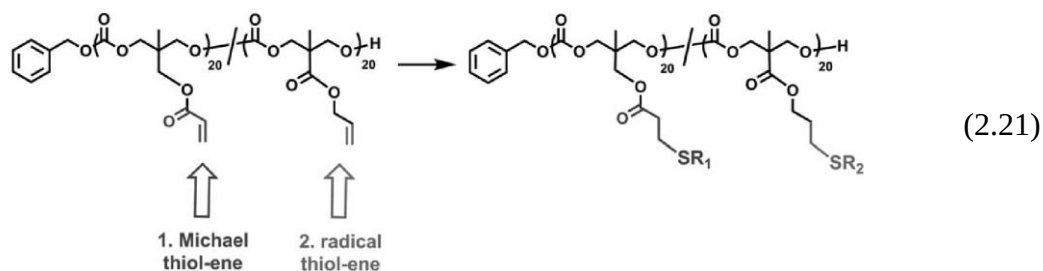
A combination of double click reaction strategy employing both thiol-ene and CuAAC was employed by Hawker and coworkers to accomplish the synthesis of high generation, high molecular weight dendrimers in a single day (Scheme 2.19) [172].



An interesting triple click reaction combination including the thiol-ene, Diels–Alder, and CuAAC reactions reported by Yagci and coworkers was applied to the formation of the ABC miktoarm star terpolymer containing PS, PCL, and PEG arms (Scheme 2.20) [173].



More recently, Tunca and Hizal et al. demonstrated the successful multifunctionalization of aliphatic polycarbonate with acrylate and allyl functional groups using sequential orthogonal reactions, nucleophilic thiol-ene coupling via Michael addition and photo-induced radical thiol-ene click reactions (Scheme 2.21) [174].



Weck group prepared random and alternating copolymers with varying degrees of alteration by free radical polymerization of 2,3,4,5,6-pentafluorostyrene (PFS) and propargyl functionalized styrene derivatives. Next, these copolymers are sequentially functionalized via CuAAC and nucleophilic substitution to functionalize PFS (Scheme 2.22) [29].



2.5 Star Polymers

Polymer properties are mainly influenced by the chemical composition and topology of the constituting macromolecules. Exciting developments in C/LRP and efficient coupling chemistry (e.g., click reaction) have allowed for the synthesis of polymeric materials with various architectures, e.g., block, brush, star, dendritic, and cyclic polymers, which recently attracted significant research interest for their various spectra of potential applications in life science and nanotechnology [175]. In addition to versatile polymerization chemistry, the synthesis of such complex macromolecules often requires the use of efficient and specific postpolymerization modification

techniques to incorporate functionality and to build novel structures by coupling preformed polymers. In this respect, click reactions are especially well conformed for such advanced macromolecular design. In this thesis, the design and synthesis of functional star type polymers will be detailed and discussed.

Star polymers are one example of branched macromolecules with a precisely controlled architecture containing multiple linear polymer chains connected at a central core. Star polymers have been widely studied for a long time because of synthetic challenges associated with preparing them and because these polymers offer different properties and behavior from those of corresponding linear polymers. The main feature of star polymers differing them from the linear analogues of identical molar masses, is their compact structure (smaller hydrodynamic volume and radius of gyration, and therefore lower viscosity), the multiple functionality and high solubility characteristics [8, 176]. The combination of their unique rheological properties and the ability to employ controlled polymerization techniques to obtain well-defined structures makes star polymers unique candidates for use in a variety of applications including drug delivery and advanced coatings. Their unique solution properties and high functionality also make them attractive building blocks for the preparation of nanostructured thin films [6, 177-179]. Depending on the chemical composition of the arm species, star polymers can be classified into two structural categories; homoarm (regular) and miktoarm (heteroarm) star types (Figure 2.1) [3, 5, 6, 180].

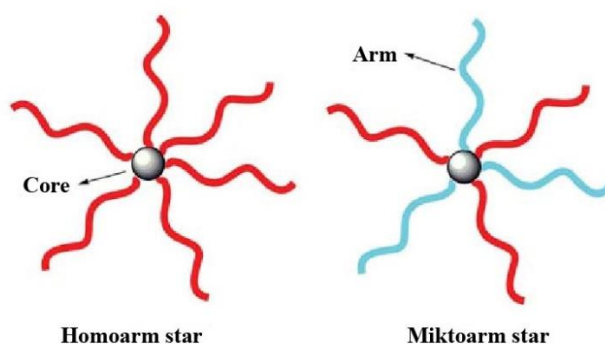


Figure 2.1 : Schematic representation of star polymer structures [6].

Homoarm star polymers consist of a symmetric structure comprising all arms have similar molecular weight and identical chemical structure although the arms could be homopolymers or copolymers. In contrast, a miktoarm star polymer contains two or more arm species with different chemical compositions and/or molecular weights [181]. In general, there are three synthetic approaches for the synthesis of star

polymers according to their formation sequence of core and arms; namely, “core-first”, “arm-first” and “coupling onto” approaches [6, 182]. Each of these approaches has associated advantages and disadvantages. The synthetic aspects of all approaches will be discussed in detail below.

2.5.1 “Core first” approach

In the “core-first” approach, multifunctional initiators are used for growing arms from a central core resulting in star macromolecules with preserved initiating functions at the chain end of each arm, which can be further used for chain extension with a second monomer to form star block copolymers (Figure 2.2).

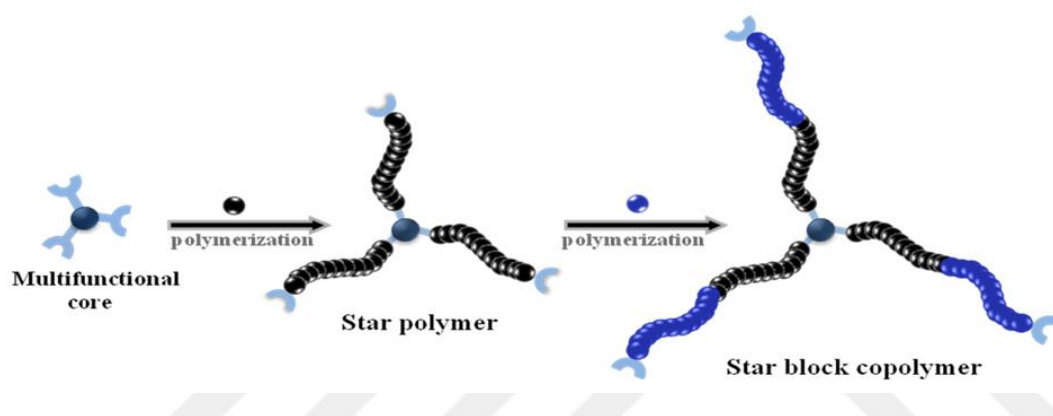


Figure 2.2 : Schematic representation of the synthesis of star and star block copolymers by “core-first” approach [179].

The “core-first” approach, allows for the preparation of well-defined star polymers with a precise number of arms, which can be controlled by the number of initiating functions present on the multifunctional initiator, provided that the initiating sites are of equal reactivity and the rate of initiation is higher than the rate of propagation. The main advantages of this approach are high star polymer yields and facile separation of the star polymer from the crude reaction mixture. However, this approach is not suitable to the preparation of miktoarm star polymers unless specially designed multifunctional initiators with orthogonal initiating functions are employed. The other limitation is the limited access to star cores with sufficient functionalities to give polymer stars with high arm numbers. Thus, generally low arm numbers (usually 3~8) are obtained. Furthermore, the molecular weight of the arms cannot be measured directly, although the number of arms can be indirectly determined via several methods, including end-group analysis, determination of branching parameters and isolation of the arms after cleavage. Additionally, broad molecular weight distribution

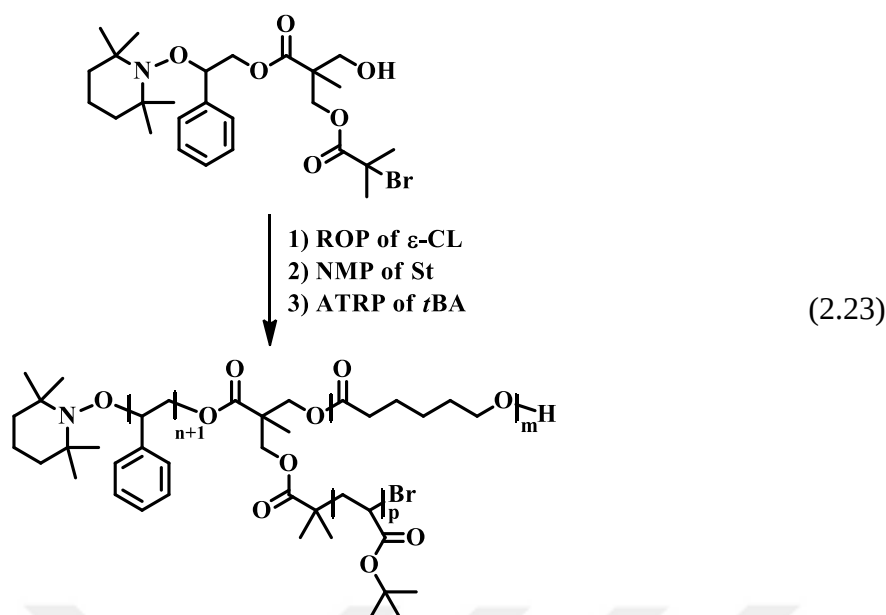
was observed because of the large amounts of initiating sites and high probability of radical-radical recombination. Therefore, the polymerizations are usually limited to low monomer conversion (<20%) to avoid star-star radical coupling reaction [183].

The first successful synthesis of homoarm star polymers by “core-first” method was reported by using anionic polymerization. For instance, Sawamoto et al. managed to carry out the synthesis of well-defined tri-arm poly(isobutyl vinyl ether) (PIBVE) star polymer using living cationic polymerization [184].

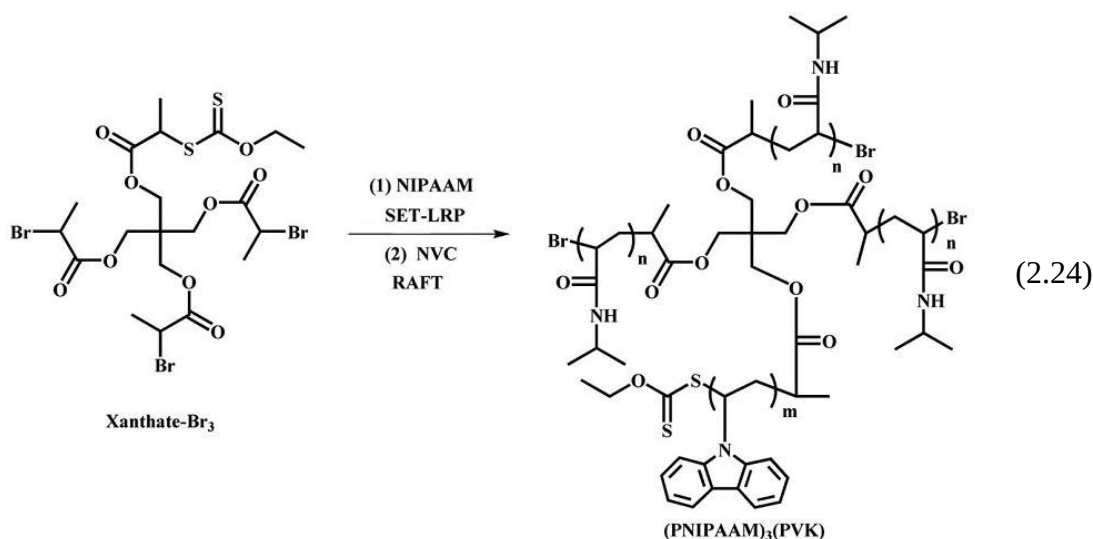
Several groups have shown that well-defined star polymers could be prepared by the combination of ATRP with other living polymerization systems using “core-first” technique [185-190]. Hawker and co-workers were tested NMP system for the synthesis of three arm PS, using trifunctional unimolecular initiator with hydrolysible core at high temperature [191].

It is convenient to prepare miktoarm star polymers by means of the employ one or several “living”/controlled radical polymerization methods. Because of the variety of polymerization methods and their accompanying choice of monomers, it is easy to see why the “core-first” technique is a versatile and efficient synthetic strategy in the formation of miktoarm star polymers.

Using the “core-first” method, Tunca and coworkers synthesized well-characterized ABC miktoarm star polymers by a combination of ROP, NMP and ATRP using a novel trifunctional initiator bearing a hydroxy group, an ATRP initiator, and a NMP initiator (Scheme 2.23) [192].



Recently, Zhang et. al. have synthesized amphiphilic A₃B miktoarm star copolymer poly(*N*-isopropylacrylamide)₃-poly(*N*-vinylcarbazole) ((PNIPAAm)₃(PVK)) by a combination of single-electron transfer living radical polymerization (SET-LRP) and RAFT polymerization and obtained thermoresponsive fluorescent micelles based on the self-assembly of this amphiphilic miktoarm star block copolymers in a selective solvent (Scheme 2.24) [193].



2.5.2 “Arm first” approach

In the “arm first” approach, a living polymer precursor is used as macroinitiator for the polymerization of a divinyl cross-linker (Figure 2.3). The resulting star polymers

have a unique three-dimensional globular architecture consisting of a densely cross-linked core surrounded by a large number of radiating arms.

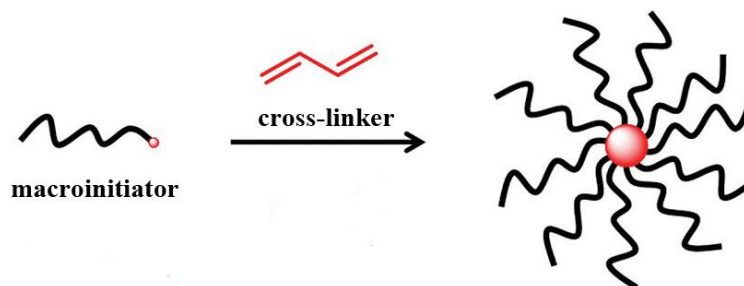


Figure 2.3 : Schematic representation of the “arm-first” approach for star polymer synthesis [179].

This method is more practical than the “core-first” and “coupling onto” approaches which require the complicated synthesis of the multifunctional agents. While the “core-first” and “coupling onto” methods based on multifunctional initiators or cores with an accurate number of functional groups can afford star polymers with the desired number of arms, the arm-first with divinyl compounds of linear polymers results in statistically distributed numbers of arms due to occurring cross-linking reactions.

The functionality of the stars prepared by “arm-first” approach can be determined by molecular weight measurements on the arms and the star product, but it is very difficult to predict and control the number of arms. The average number of arms attached to a star core depends on several experimental parameters, including the degree of polymerization (DP) and composition of the arm precursor, the chemical nature of cross-linker, the amount of cross-linker. Incomplete incorporation of linear arm precursors into the formed star is a common problem in this “arm-first” method, which could be explained by the loss of chain-end initiating sites or a buildup of steric hindrance around the core, as the coupling reactions proceed [194].

The star polymer synthesis based on the “arm-first” approach was first developed in a living anionic polymerization. Zilliox et al. first employed anionic polymerization to prepare star polymers in high yield via the cross-linking of living PS with divinylbenzene (DVB) [195]. On the other hand, the “arm-first” approach has been studied in living cationic polymerization. The successful preparation of star polymers was first reported by Kanaoka et al. and synthesized star-shaped polymers of alkyl vinyl ethers in high yield on the basis of the living cationic polymerization by the HI/ZnI_2 initiating system [196].

The discovery of the C/LRP methods had superseded the living ionic polymerisation methods mainly due to the less stringent reaction conditions and wide range of monomers. The first synthesis of star polymers with a cross-linked core by ATRP was reported by Matyjaszewski and coworkers [197]. PS macroinitiators were cross-linked by using various divinyl cross-linkers in anisole at 110 °C. The use of DVB led to the formation of star polymers with the best-controlled structure, as compared to other cross-linkers, such as ethylene glycol diacrylate (EGDA) and ethylene glycol dimethacrylate (EGDMA). The optimum molar ratio of DVB to PS macroinitiator was found between 5 and 15 for the formation of stars with high star yield. Following the preliminary study, same group synthesized the poly(*tert*-butyl acrylate) (PtBA) star polymers with high yields (up to 95%) by the same approach [198]. Sawamoto also applied the “arm-first” approach for the synthesis of star polymers containing poly(methyl methacrylate) (PMMA) arms using Ru-based catalyst complexes and various divinyl cross-linkers [199, 200]. Hadjichristidis was used the NMP process for the synthesis of PS star polymers by employing TEMPO as the persistent stable radical to mediate the NMP of St and subsequent cross-linking reaction using DVB as cross-linker [201]. RAFT, was also applied to the synthesis of star polymers with a cross-linked core by the “arm-first” approach. The first experimental proof of the synthesis of star polymers with a cross-linked core by RAFT was reported by Davis and coworkers [202] although the synthesized (PS)_n-polyDVB star polymers were largely uncontrolled with high polydispersity when the yield of the polymerization was high enough. While the synthesis of star polymers using the RAFT process certainly faces difficulties, the advantages are many and new types of polymers such as poly(vinyl alcohol) are obtainable [203, 204].

There are several parameters in an ATRP that should be controlled carefully in order to maximize the yield of stars and prevent star–star coupling reactions. The effects of type of cross-linker, cross-linker/macroinitiator molar ratio, macroinitiator DP, macroinitiator concentration, catalyst concentration, solvent nature, reaction temperature, and reaction time on the structure and yield of core cross-linked star polymers prepared via ATRP were investigated in several reports.

The proposed mechanism for the formation of multiarm star polymers by “arm-first” approach is shown in Figure 2.4. The reaction starts with the addition of the cross-linker to the macroinitiator chain ends to form short block copolymers. The block

copolymers can then react with more cross-linker, macroinitiators or with the pendent vinyl groups present on other block copolymers. As more and more of the block copolymers link together they begin to form a star polymer with a lightly cross-linked core. If the cores of these star polymers are sterically accessible to each other then star–star coupling can occur resulting in the formation of higher molecular weight macromolecules. Simultaneously, block copolymers and macroinitiators could also add to these lightly cross-linked star polymers. Once the majority of the block copolymers have been immobilised into the star structure it is likely that intramolecular cross-linking within the stars dominates to afford multiarm star polymers with denser cross-linked cores [8].

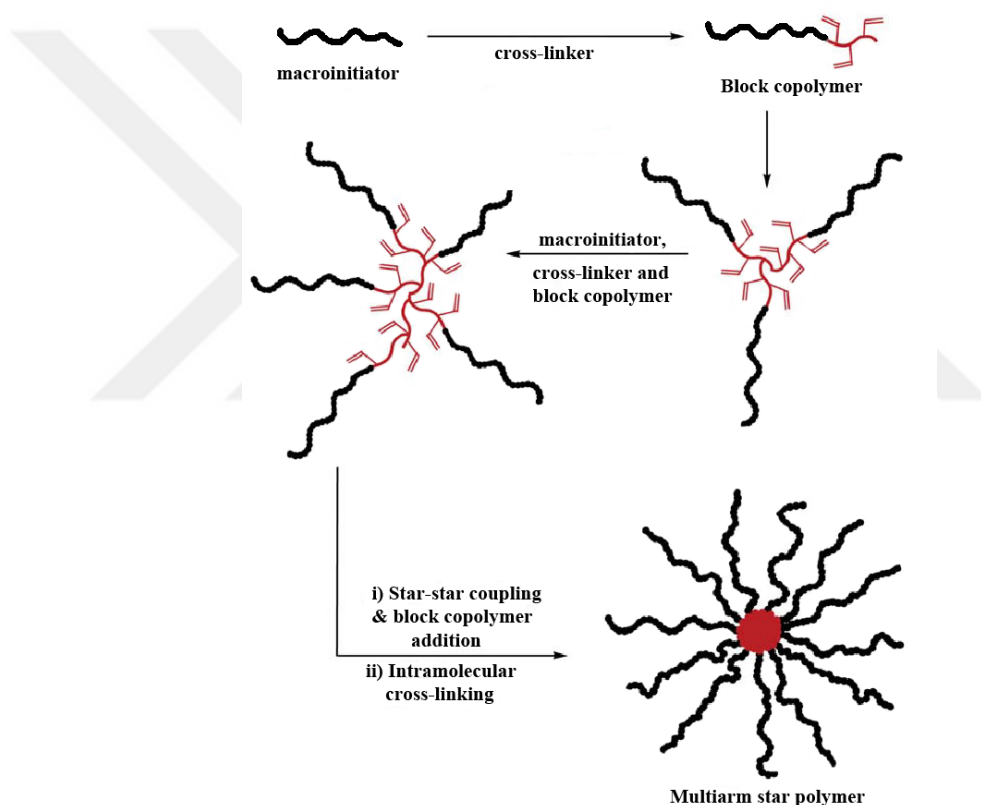


Figure 2.4 : Proposed mechanism for the formation of multiarm star polymers by “arm-first” approach [8].

It is likely that there are still preserved initiating sites present within the cores of the multiarm star polymers (i.e., alkyl halide groups in ATRP), and the star polymer can be used as a multifunctional initiator in the chain extension reaction with a different monomer to yield a miktoarm star copolymer. This combination method for synthesizing miktoarm star copolymers was termed the “in-out” method (Figure 2.5) [205, 206].

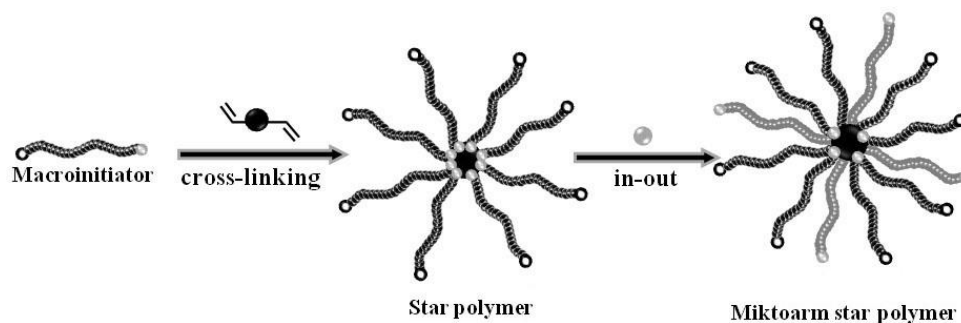


Figure 2.5 : Synthesis of miktoarm star polymers by “in-out” strategy [206].

The initiation efficiency of the star macroinitiator decreased with increasing arm length and structural compactness, thus it is conceptually impossible to synthesize a miktoarm star copolymer containing more than two kinds of arms using the “in-out” method. In order to synthesize miktoarm star copolymers with potentially any desired molar ratio and composition of the arms, Gao et al. reported a new strategy; one-pot ATRP cross-linking reaction with a mixture of different linear macroinitiators by a divinyl cross-linker (Figure 2.6) [207]. It was obtained a miktoarm star product with high molecular weight and high star yield.

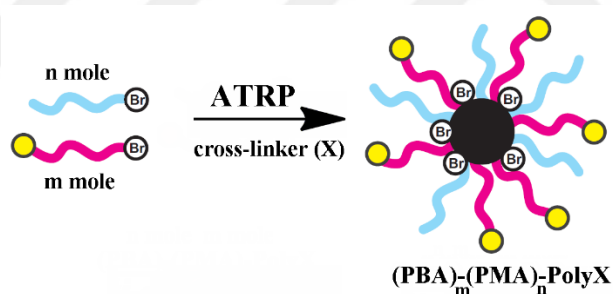
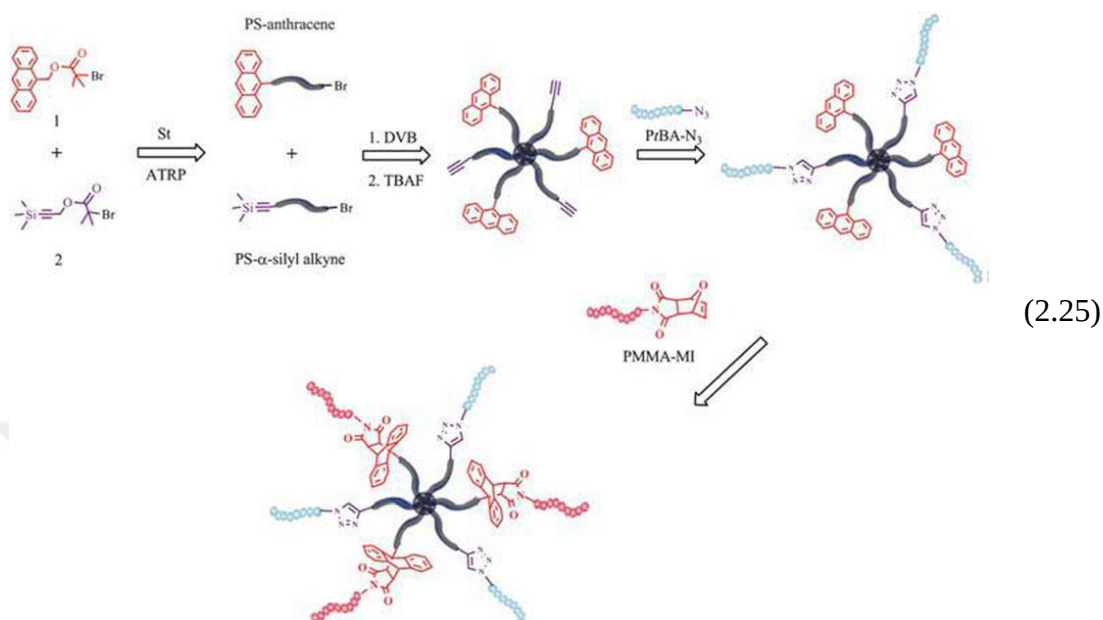


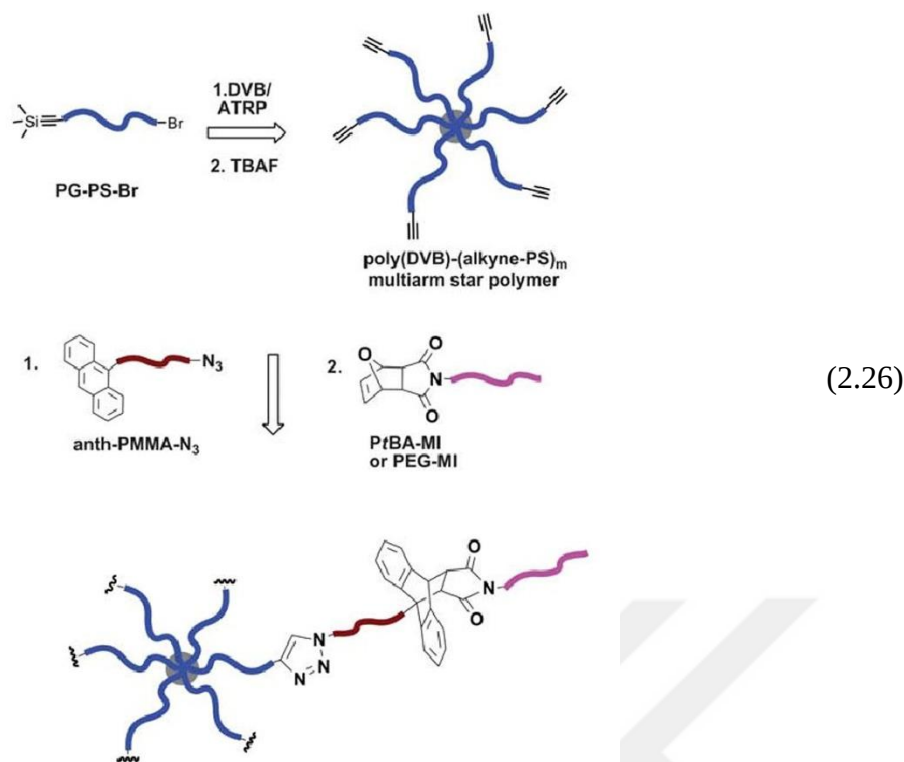
Figure 2.6 : Synthesis of miktoarm star copolymers by concurrently incorporation of the two linear macroinitiators [207].

In that sense, a particularly well-suited example comes from Tunca and coworkers [208] who have prepared multi-miktoarm star block copolymers based on the combination of “arm-first” approach via sequential double click reactions involving azide–alkyne and Diels–Alder, respectively. In this case, an α -silyl protected alkyne and α -anthracene end functionalized PS polymers were prepared by ATRP. Then, multiarm star PS with both alkyne and anthracene moieties at the periphery, (alkyne-PS)_n-polyDVB-(PS-anthracene)_n, was synthesized by a cross-linking reaction of DVB using these PS precursors as macroinitiators. Subsequently, the formation of multi-miktoarm star block copolymer (PtBA)_m-(PS)_n-polyDVB-(PS)_n-(PMMA)_k was

achieved via sequential azide–alkyne and Diels–Alder click reactions with PtBA–N₃ and α -maleimide terminated poly(methyl methacrylate) (PMMA–MI), respectively (Scheme 2.25).



It is important to note that the “arm-first” process leads to preparation of multifunctional star polymers when functional initiators are used for the synthesis of the arms. Indeed, this method provides an efficient route to prepare multiarm star homo and block copolymers. For this purpose, Tunca and coworkers reported the synthesis of multiarm star polymers with triblock terpolymer arms using a combination of ATRP and sequential double click reactions: azide–alkyne and Diels–Alder click reactions [209]. The synthetic strategy is given as follows: (PMMA)_n–(PS)_m–polyDVB multiarm star diblock copolymer was first obtained from an azide–alkyne click reaction of (alkyne-PS)_m–polyDVB multiarm star polymer with α -anthracene- ω -azide terminated PMMA (anth-PMMA–N₃), followed by a Diels–Alder click reaction of the anthracene groups at the star periphery with α -maleimide terminated poly (*tert*-butyl acrylate) (PtBA–MI) or α -maleimide terminated PEG (PEG–MI) leading to target multiarm star triblock terpolymers, (PtBA)_k–(PMMA)_n–(PS)_m–polyDVB and (PEG)_p–(PMMA)_n–(PS)_m–polyDVB (Scheme 2.26).



2.5.3 “Coupling-onto” approach

In the “coupling-onto” approach, a linear polymeric chain (arm), containing a reactive end group reacts with a multifunctional coupling agent (core) through the efficient organic reactions (Figure 2.7).



Figure 2.7 : Schematic representation of the synthesis of star polymers by “coupling-onto” approach [179].

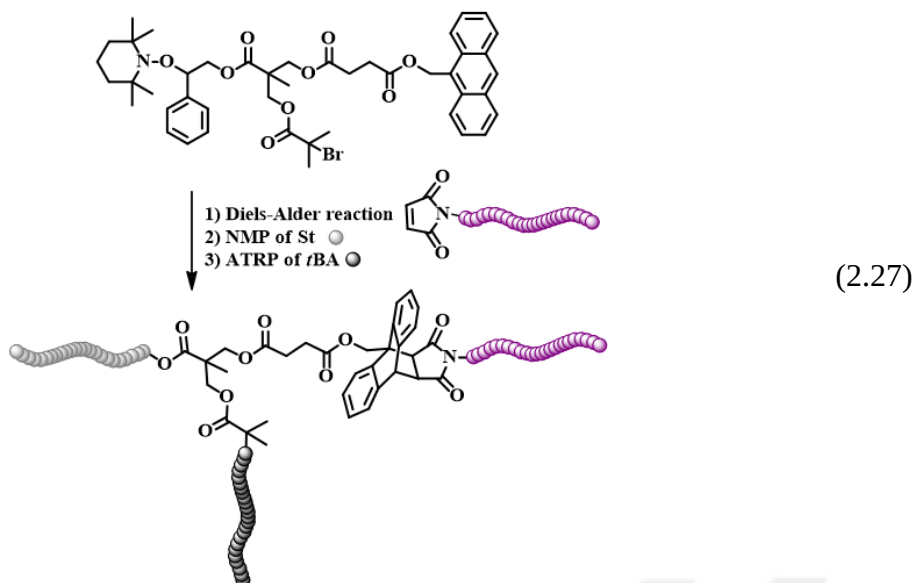
Theoretically, the functionalities on the coupling agents predetermine the arm numbers per star, although this method suffers from low coupling efficiency due to the slow reaction between the polymer chain end and the multifunctional core. In order to improve the coupling efficiency, the combination of C/LRP methods with highly efficient and orthogonal post-polymerization coupling reactions allowed for the

synthesis of well-defined star polymers, star block copolymers, and miktoarm star copolymers.

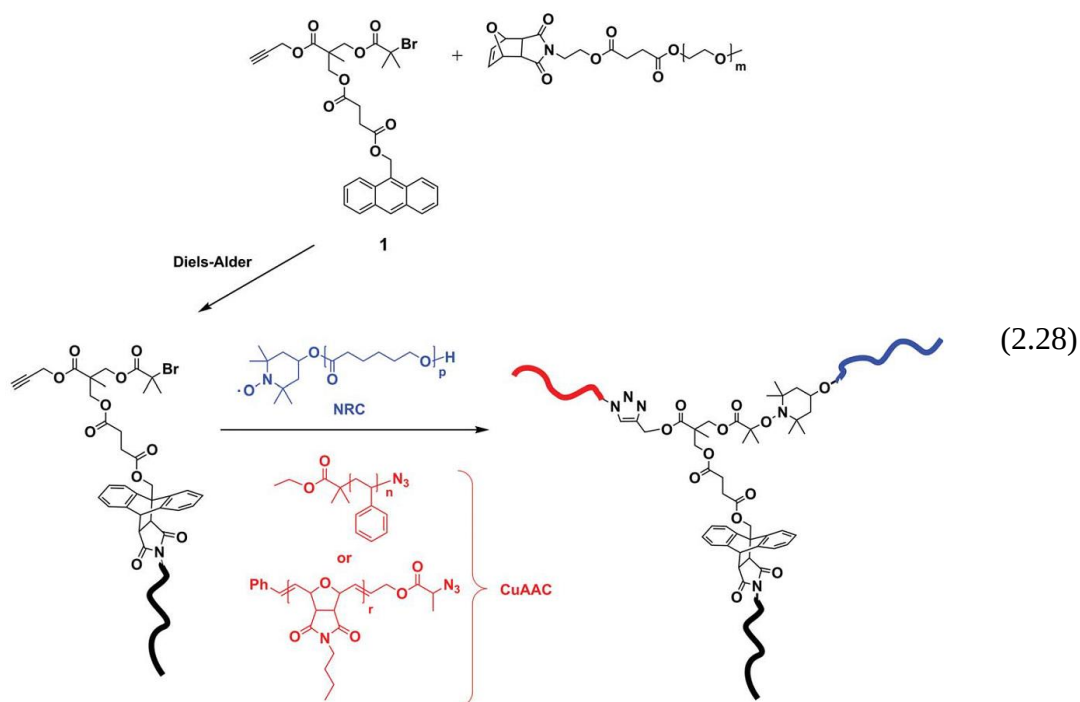
Matyjaszewski and coworkers were the first to describe the synthesis of star polymers with different arm numbers by “coupling-onto” method using a combination of ATRP and CuAAC click chemistry. In this case, the click coupling reactions between azido-terminated PS (PS-N₃) and alkyne-containing multifunctional coupling agents (bis-, tris- or tetra-alkyne) proved to be fast and highly efficient [210]. On the basis of similar principle, Tunca and coworkers were successfully applied Diels–Alder click reaction for the preparation of 3-arm star polymers (A₃) using furan protected maleimide end-functionalized linear precursors and trianthracene functional linking agent [211].

In the combination of the “core-first” and “coupling-onto” approaches, multifunctional initiators are used to grow arms via living polymerization techniques to yield the block copolymer with a functional group at its center. Matyjaszewski and coworkers reported the synthesis of three-arm star block copolymers by combining of core-first and coupling-onto strategies [212]. First, (PS-Br)₃ star polymers were synthesized by ATRP using the core-first method. The bromo groups were then transformed into azido groups via substitution reactions with NaN₃. The product, (PS-N₃)₃, was further used for click reactions with alkyne-terminated PEO chains (PEO-alkyne) and produced 3-arm star block copolymers (PS-*b*-PEO)₃ via the coupling-onto method.

The combinations of different C/LRP techniques have been used to prepare miktoarm star polymers. The group of Tunca has created an ABC type miktoarm star polymer by combining of Diels–Alder reaction, NMP, and ATRP. First, in Diels–Alder reaction, MI-PEG precursor was reacted with trifunctional core bearing anthracene moiety to give macroinitiator, which has convenient functional groups for NMP and ATRP. Then, NMP was used to grow St and ATRP for *t*BA was employed to yield the final ABC type miktoarm star terpolymer (PEG-PS-*Pt*BA) with controlled molecular weight and low polydispersity (Scheme 2.27) [213].



Recently, same approach was used again by the same group combining the Diels–Alder, CuAAC, and nitroxide radical coupling (NRC) click reactions to obtain 3-miktoarm star terpolymers. In this work, using coupling-onto methodology, Well-defined linear polymers with reactive functional end groups are simply attached to an orthogonally functionalized core (**1**) in a two-step reaction mode through triple click reactions (Scheme 2.28) [214].



2.6 Functionalized Polymers

The introduction of functional groups at the end or along the polymer chain can produce new materials that can be used as models to study complex architectures in polymer science. The most common methods for incorporating functional groups into polymer chains include the use of functional initiators and the post-polymerization transformation of end groups, each of which yields end group functionality. In addition, the direct polymerization of functional monomers yields pendant functionality (Figure 2.8) [4, 35, 46].

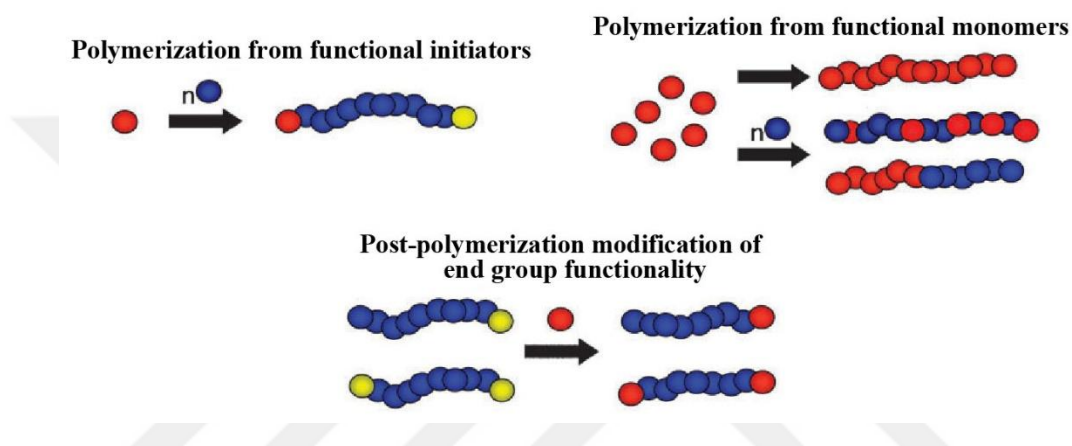


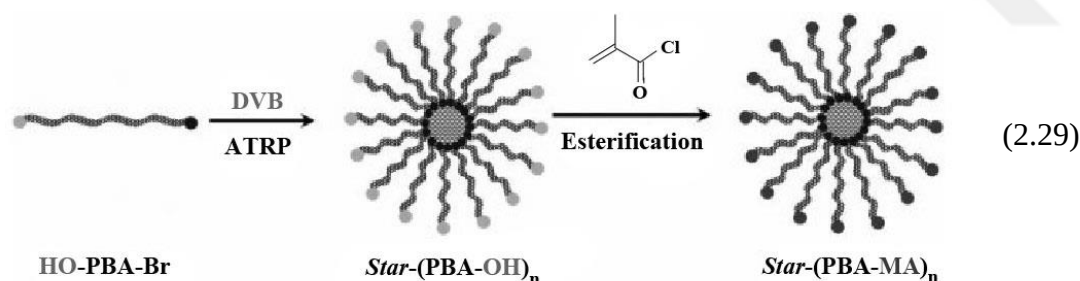
Figure 2.8 : Common strategies for incorporating functionality into polymer chains [35].

2.6.1 End-functional polymers

End-functional polymers are used for blend compatibilization during reactive processing and in many thermosetting compositions e.g. epoxy-functional polymers and functional materials form the basis of the majority of products prepared for dispersant, coating, adhesive, and sealant, etc. applications. Taking advantage of the tolerance of C/LRP processes for functional groups, a variety of functional polymers may be obtained. For example, the use of functionalized initiators guarantees the presence of the clickable group at the α -terminus of every polymer chain. This procedure ensures complete functionalization, provided that the functional initiator well-defined polymers with predictable molecular weights. Alternatively, the post-polymerization transformation of end groups can be used to conjugate of functional groups at the ω -terminus of a polymer chain. However, the post-polymerization transformation reaction should proceed with high efficiency because to separate of functionalized from non-functionalized polymer chains may be difficult. This method

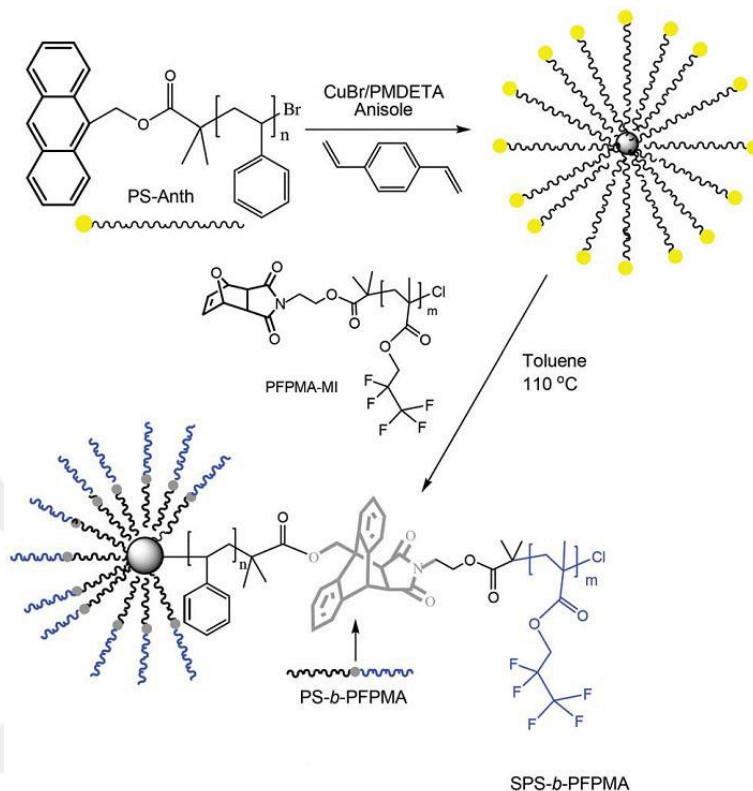
does not guarantee the desired functional group at the end of every polymer [35, 47, 215].

These methods have also been employed for the synthesis of functionalized star polymers. The polymerization of a monomer with a functionalized initiators for the preparation of end-group functionalised macroinitiators allow for the construction of peripherally functionalised star polymers. For example, Baek et al. synthesized a range of peripherally functionalised star polymers from α -functionalized PMMA macroinitiators via ATRP using amine, amide, ester and hydroxyl functionalized initiators [216]. Ohno et al. synthesized star polymers containing methacryloyl chain-end groups by esterification of the hydroxyl end-functional star polymers [217]. First, hydroxyl end-functional linear macroinitiator (MI) was prepared by ATRP using a functional initiator containing a hydroxyl group. The obtained linear MI was chain-extended and cross-linked with DVB using the arm-first method to obtain the hydroxyl end-functional star polymers. The hydroxyl groups on the star polymers were successfully converted into methacryloyl groups via esterification with methacryloyl chloride (Scheme 2.29).



More recently, Erdogan and coworkers synthesized well-defined novel multiarm star block copolymer ionomers containing hydrophobic fluorinated block at the periphery and partially sulfonated PS block at the core with varying ion exchange capacities [218]. First, multiarm star polymer with anthracene functionality as reactive periphery groups was prepared by a cross-linking reaction of DVB using α -anthracene end functionalized PS (PS-anthracene) as a macroinitiator. Thus, obtained multiarm star polymer was reacted with furan protected maleimide-end functionalized poly(2,2,3,3,3-pentafluoropropyl methacrylate) (PFPPMA-MI) resulting in the corresponding fluorinated multiarm star block copolymers via Diels–Alder click reaction. The third step involves the sulfonation reaction of phenyl ring of polystyrene

block with acetyl sulfate at 20 °C. After sulfonation reaction, the structures, molecular characterization and thermal properties of the multiarm star block copolymers were investigated (Scheme 2.30).



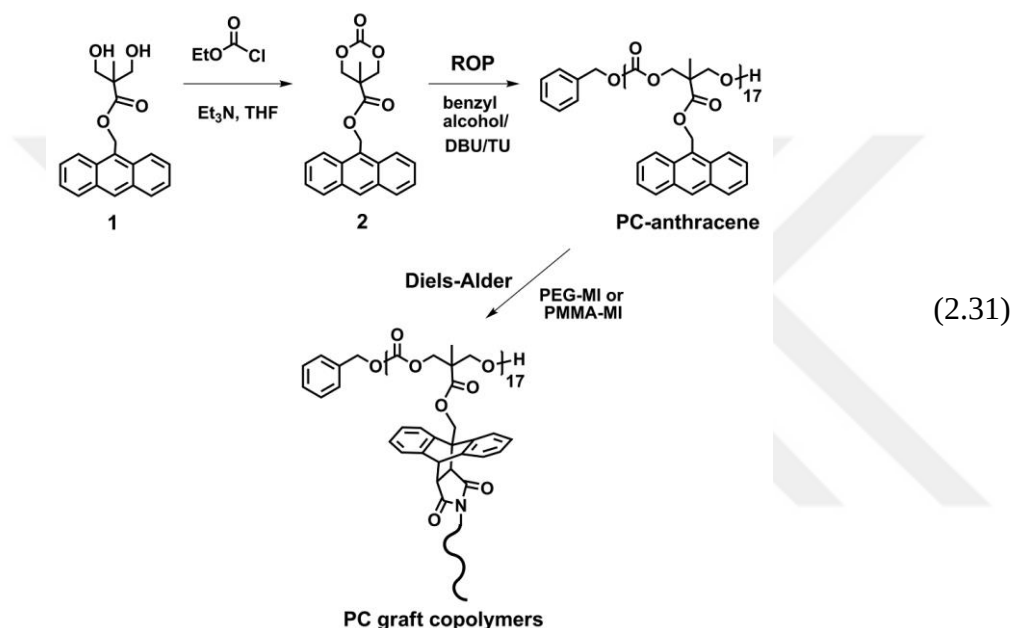
(2.30)

2.6.2 Pendant functional polymers

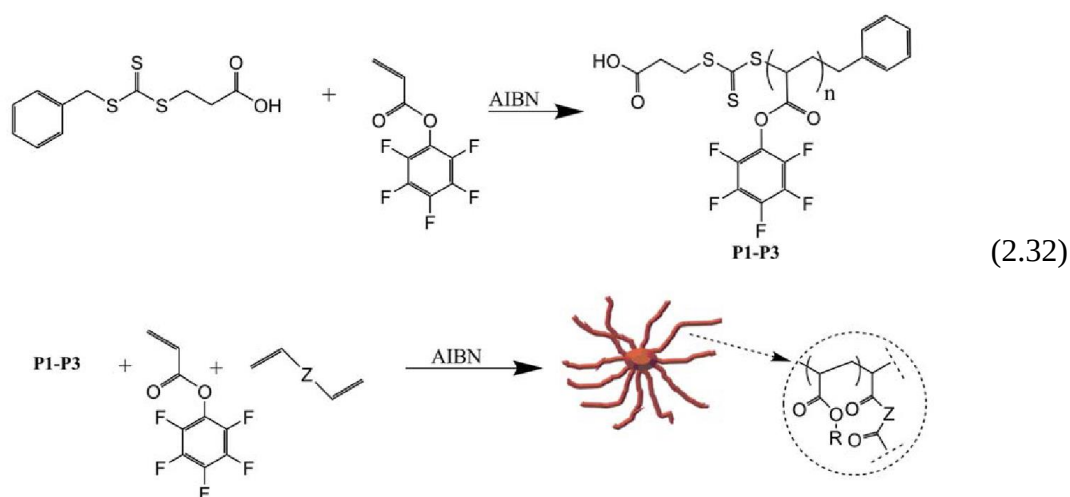
The incorporation of functionality throughout a polymer chain is generally accomplished by polymerizing a functional monomer. The direct polymerization of functional monomers can yield very high functional group densities throughout the polymer backbone, which can then be used further for preparing polymer brushes. This method provide the material used directly to exploit the properties provided by the functional group (hydrophilicity/phobicity, polarity, metal complexation, the elasticity etc.). A functionalized monomer guarantees the presence of the targeted functional group at every repeat unit in the polymer backbone, but this functional group may have to be protected if it interferes with the polymerization mechanism. The desired functional monomer may also not be commercially available [35, 46].

One of the first examples of this strategy was published by Sumerlin and coworkers [219]. A novel azido-containing monomer was directly polymerized and further

functionalized via CuAAC click chemistry with several model alkynes to prepare functional (co)polymers. Recently, Dag et. al. have prepared a novel anthracene-functionalized cyclic carbonate monomer followed by ROP of this monomer to prepare polycarbonate with pendant anthracene groups (PC-anthracene). Subsequently, the resulting PC-anthracene was grafted with a linear furan protected-maleimide terminated-poly(methyl methacrylate) (PMMA-MI) or poly(ethylene glycol) (PEG-MI) or a mixture of PMMA-MI and PEG-MI to yield well-defined PC graft or hetero graft copolymers using Diels–Alder click reaction (Scheme 2.31) [220].



The functionalised monomers have also been employed for the preparation of macroinitiators for the preparation of star polymers with arm functional groups. Davis and coworkers prepared star polymers bearing activated ester groups, via an arm first methodology. Arm polymers were prepared via RAFT polymerization of pentafluorophenyl acrylate monomer. Subsequently, the presence of pentafluorophenyl ester groups was exploited to attach amino compounds to yield functional star polymers with high yields (Scheme 2.32) [221].

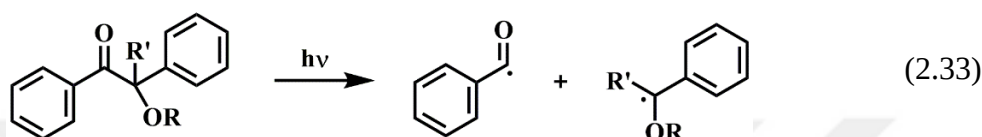


2.7 Polymeric Photoinitiators

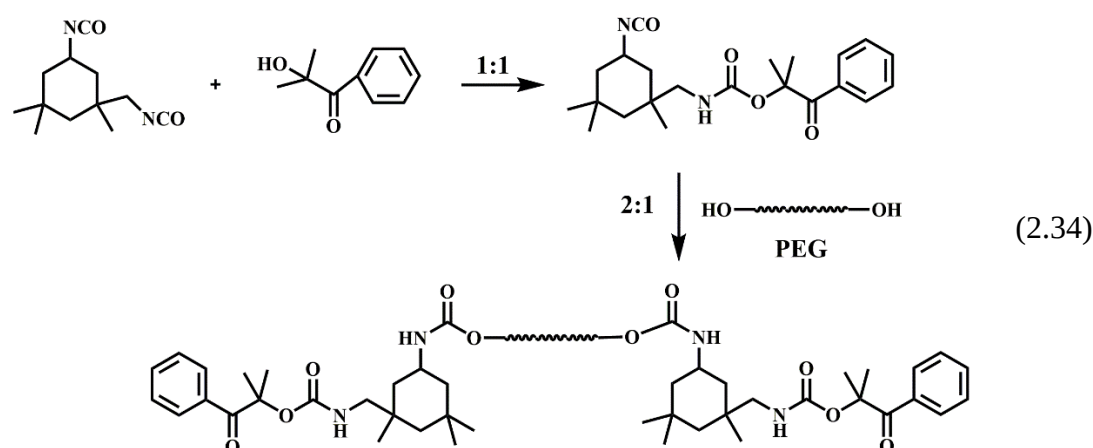
A photoinitiator is a compound added to a formulation to convert absorbed light energy, ultraviolet (UV) or visible light, into chemical energy in the form of initiating species, such as free radicals or cations. In the development of this technology, photoinitiator systems play a very important role. In order to get photoinitiator systems of high performance, one of the important ways is to develop polymeric photoinitiators, which have some advantages derived from polymeric structure, in comparison with low molecular weight analogues. Polymeric photoinitiators have received considerable interest in recent years, particularly in the field of UV curable coatings [38, 222]. Polymeric photoinitiators contain side chain or main chain photoinitiator moiety which generates free radicals upon absorption of UV light and are able to initiate polymerization and crosslinking of monomers and oligomers. Some practical aspects may favor the development of polymeric photoinitiators, such as solubility and compatibility within the formulations. In addition, odor and toxicity problems do not occur with polymeric photoinitiators owing to the low volatility of large molecules. Moreover, the low migration tendency of polymeric photoinitiators and of photoproducts brings about a reduced proneness to yellowing of cured coatings. Because of “polymer effect”, they are usually expected to display a higher efficiency with respect to the low molecular counterparts which results in a reduction of exposure time and increase of productivity. In many cases, polymeric photoinitiators were used to make tailor made block or graft copolymers [223, 224]. A variety of polymeric photoinitiators containing type I and type II free radical photoinitiators are described in the literature [36, 225, 226].

2.7.1 Type I polymeric photoinitiator

As for low molecular weight counterparts, Type I polymeric photoinitiators undergo a homolytic bond cleavage upon irradiation to yield free radicals. The majority of Type I polymeric photoinitiators are aromatic carbonyl compounds with appropriate substituents, which spontaneously undergo “ α -cleavage” often referred to as Norrish Type I reaction. Studies concerning the photochemical mechanism of fragmentation have led to the conclusion that efficient α -cleavage (Norrish Type I reaction) to generate benzoyl and α -alkoxybenzyl primary radicals (Scheme 2.33).

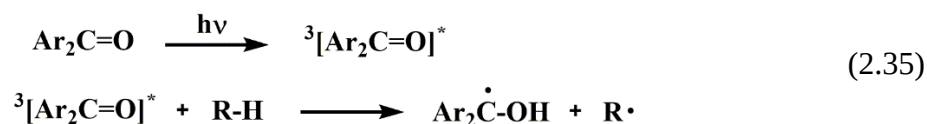


In many cases of Type I polymeric photoinitiators, photoactive groups are functional groups attached to polymer backbone. Another possibility is the attachment of photosensitive groups to monomers. In this case, polymeric photoinitiators are formed by polymerization or copolymerization with another monomer [227]. Benzoin ether based polymeric photoinitiators were synthesized by Angiolini and coworkers [228]. Degirmenci et. al applied ATRP technique to incorporate α -alkoxyphenyl ketone photoinitiator moieties at the end and at the middle of the polymer chain [229]. More recently, Huang and coworkers prepared amphiphilic polymeric photoinitiator based on 2-hydroxyl-2-methyl-1-phenylpropanone (Scheme 2.34) [230].

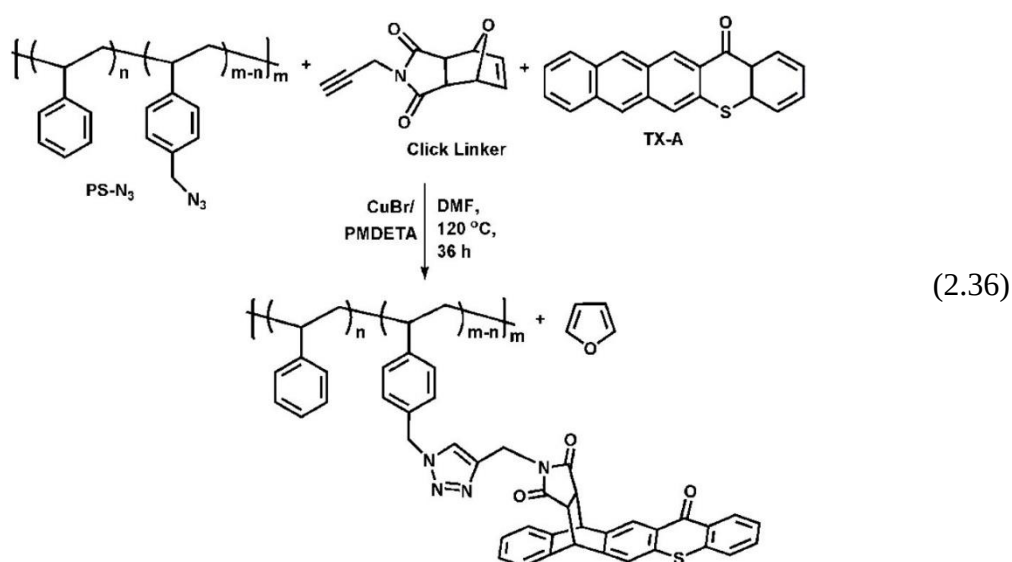


2.7.2 Type II polymeric photoinitiator

Type II photoinitiators undergo a bimolecular reaction where the triplet excited state of the photoinitiator interacts with a second molecule (a coinitiator) to generate free radicals. The mechanism of Type II photoinitiators is based on the aromatic ketones readily abstract hydrogen atoms from hydrogen donors, such as alcohols and tertiary amines (Scheme 2.35).

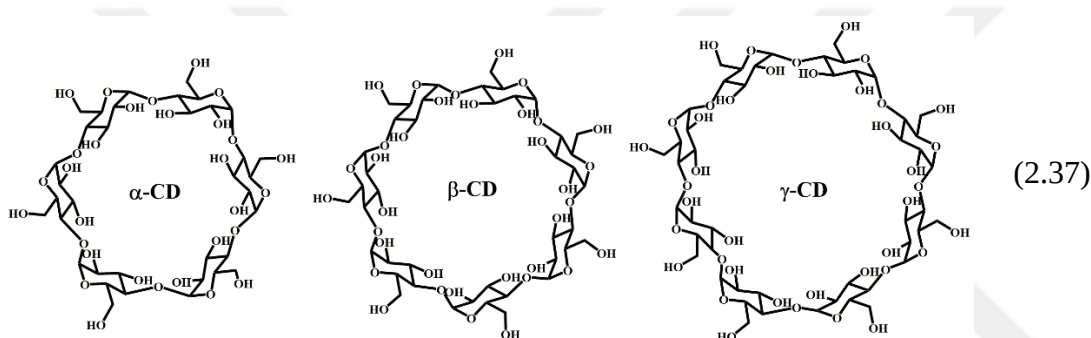


Regarding polymeric photoinitiators, examples with the ketone and the amine bound to polymer molecules can be cited [222]. Most of the Type II polymeric photoinitiators are based on benzophenone and derivatives, thioxanthone, quinones or benzyl moieties and require the presence of a coinitiator such as alcohols, ethers, amines, and thiols in the formulation to work [231-234]. Recently, Arsu and coworkers synthesized benzophenone containing monomeric and polymeric photoinitiators [37]. Gacal et. al developed polymeric photoinititors containing side-chain thioxanthone moieties by using two click reactions, namely Diels–Alder and CuAAC reactions (Scheme 2.36). The obtained polymeric photoinitiators were shown to initiate the free radical polymerization of different monomers via type II mechanism [235].

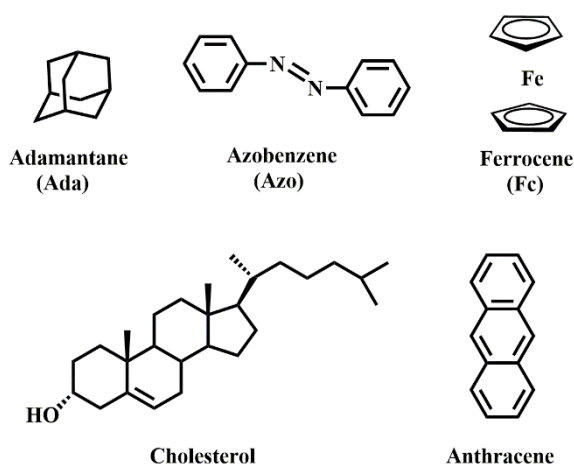


2.8 Supramolecular Polymers

Supramolecular polymers have gained special interest in recent years. Supramolecular polymer chemistry focuses on providing new complex polymeric materials through the incorporation of noncovalent interactions, such as hydrogen bonding, ligand–metal coordination, ionic interactions or “host–guest” inclusion complexation [236-238]. The binding ability of hosts and guests is mainly attributed to hydrophobic interactions and the complementary character of size and shape between their structures. Being the most widely used hosts, cyclodextrin and its derivatives (CDs) are a class of cyclic oligomers composed of glucopyranose units linked by α -1,4-glycosidic bonds (Scheme 2.37).

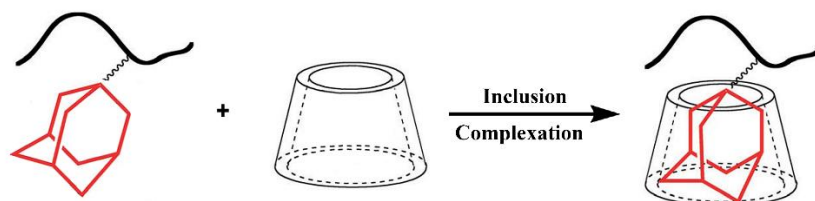


CDs are characteristic of a hydrophilic exterior surface and hydrophobic interior cavity, which can accommodate a wide range of hydrophobic molecules of appropriate size as the guest into its cavity to generate water soluble host–guest inclusion complexes by noncovalent bond. Among the three common CDs, α -CD is adaptable to form stable supramolecular complex with monocyclic aromatics, including azobenzene (Azo) and its derivatives; β -CD tends to interact with cholesterol, ferrocene (Fc), adamantane (Ada), Azo compound and some derivatives; γ -CD usually constructs supramolecular complex system with larger guest molecules, such as pyrene, anthracene, phenanthrene and so on. Some typical guest molecules are listed in Scheme 2.38. They can form inclusion complexes with hydrophobic guest molecules primarily in aqueous solution. This ability has been utilized in polymer science in various applications, such as drug delivery, nano-structures, supramolecular polymers, and self-healing materials [39, 178, 238-240].



(2.38)

Adamantane is one of the most important guests for β -CD due to its effective inclusion entrapment and high binding affinity (Scheme 2.39). Previous studies have showed that the association constant for Ada and β -CD is high in water (10^4 – 10^5 M^{-1}) [241, 242]. Recent years, polymeric systems based on β -CD and Ada have attracted extensive attention in medical and biological fields, especially in continuous drug release, targeted delivery and tissue engineering [243–245].



(2.39)

Stenzel and coworkers used this feature as a driving force to generate reversible comb-shaped polymers [246]. As a first step, macromolecular building blocks bearing either pendent β -CD moieties (P(β -CD)) or chain-end located Ada-functionalized poly(acrylic acid) (Ada-PAA) grafts have been prepared by RAFT polymerization. Subsequent self-assembly of macromolecular building blocks afforded the straightforward generation of hydrophilic supramolecular host–guest comb-shaped copolymer (Figure 2.9).

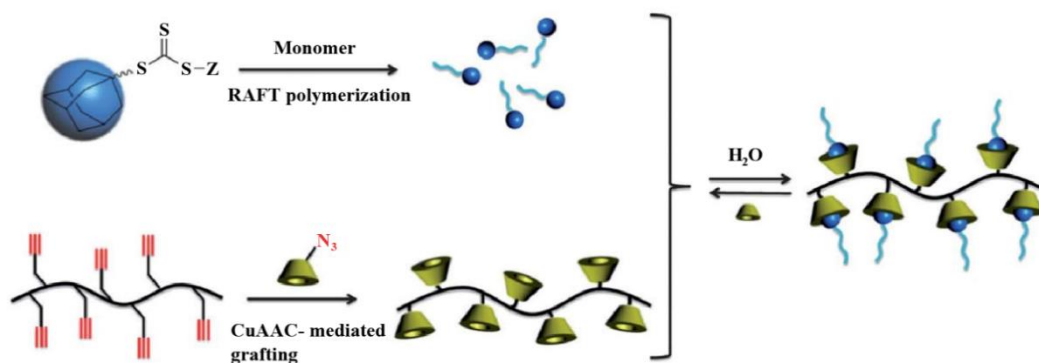


Figure 2.9 : General strategy toward the preparation of supramolecular comb-shaped polymers in water [246].

In 2008, Li et al. synthesized a β -CD core four-arm poly(*N*-isopropylacrylamide) PNIPAAm star polymer and functionalized PEGs with Ada groups at one or both of its ends. Thus they obtained non-covalently linked block copolymers with different architectures by inclusion complexation (Figure 2.10) [247].

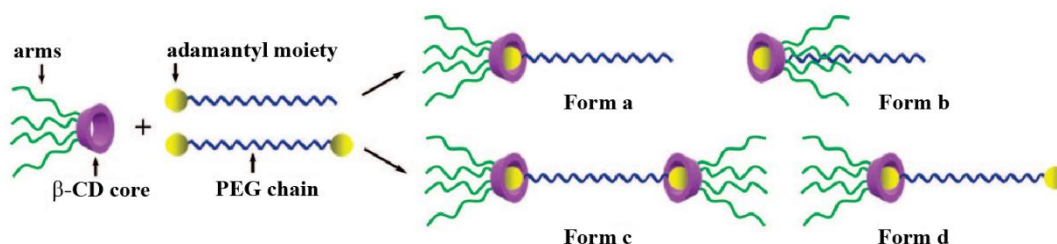


Figure 2.10 : Schematic representation of the inclusion complexes formed via “host-guest” interactions between β -CD-core star polymer and adamantyl-containing PEGs [247].

In 2009, Davis and coworkers published β -CD functionalized biodegradable star polymers via CD/cholesterol inclusion complexation [248]. Three armed star polymers were synthesized by RAFT polymerization using “core-first” approach and functionalized with cholesterol. Finally, the cholesterol functional star polymers were then used to form supramolecular structures via inclusion complex formation with β -CD (Figure 2.11).

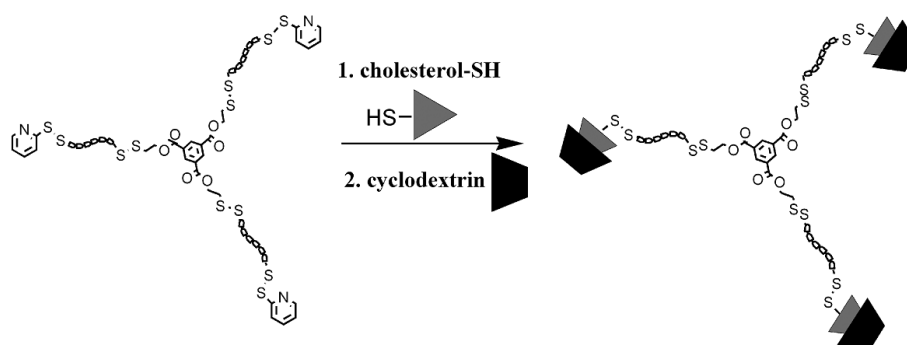


Figure 2.11 : Modification of three-armed stars with cholesterol and the subsequent formation of an inclusion complexation with β -CD [248].

Recently, Barner-Kowollik and co-workers reported a wide variety of novel macromolecular architectures including X- and H-shaped star block copolymers, ABA triblock copolymers, three-armed star polymers and miktoarm star polymers through CD/Ada host-guest interaction [249-252]. A similar approach was explored by Zhu et al. who reported the supramolecular ABC miktoarm star terpolymers based on host-guest inclusion complexation [253]. First, a hydrophilic diblock copolymer with two different blocks connecting to β -CD was prepared as the host, and the hydrophobic Ada-modified PMMA was the guest. Subsequently, a supramolecular ABC miktoarm star terpolymer was formed through the molecular recognition between β -CDs and adamantyl moieties via a simple mixing procedure (Figure 2.12).

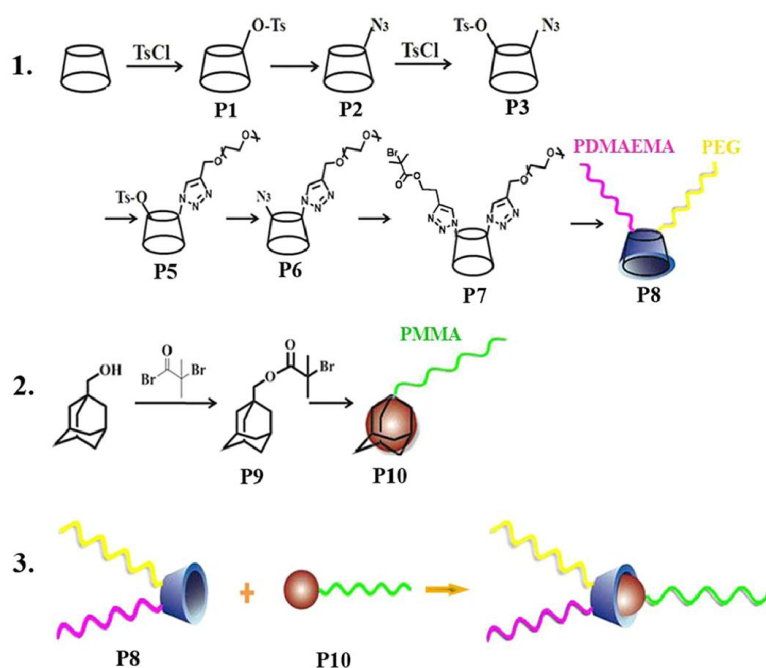


Figure 2.12 : Synthetic route to supramolecular ABC miktoarm star terpolymer [253].



3. EXPERIMENTAL PART

3.1 Materials

Styrene (St, 99% Aldrich) was passed through a basic alumina column to remove the inhibitor immediately before use. Divinylbenzene (DVB, 80%, Aldrich) was purified twice by passing through a column filled with basic alumina to remove the inhibitor. *N,N,N',N'',N''*-Pentamethyldiethylenetriamine (PMDETA, Aldrich) was distilled over NaOH prior to use. 2,3,4,5,6-Pentafluorobenzyl alcohol (98%, Aldrich), α -bromoisobutryl bromide (98%, Aldrich), triethylamine (Et₃N, 99.5%, Aldrich), allyl alcohol ($\geq 99\%$, Aldrich), *N*-acetyl-L-cysteine methyl-ester ($\geq 90\%$, Aldrich), 1-propanethiol (99%, Aldrich), *N,N'*-dicyclohexylcarbodiimide (DCC, 99%, Aldrich), 4-dimethylaminopyridine (DMAP, 99%, Aldrich), 4-pentynoic acid (98%, Aldrich), 1,6-hexanediol diacrylate (HDDA, 80%, Aldrich), 1-adamantanemethanol (99%, Aldrich), β -cyclodextrin ($\geq 97\%$, Aldrich), and CuBr (99.9%, Aldrich) were used as received. Poly(ethylene glycol) monomethylether (PEG-OH, $M_n = 550$, Acros, and $M_n = 5000$, Fluka) were dried by azeotropic distillation with anhydrous toluene. Dichloromethane (CH₂Cl₂) was purchased from Aldrich and used after distillation over P₂O₅. Tetrahydrofuran (THF; 99.8%, J.T. Baker) was dried and distilled over benzophenone-Na. *N,N*-Dimethylformamide (DMF, 99.8%, Aldrich) was dried and distilled under vacuum over CaH₂. Diethyl ether (99.7%, Aldrich), 1,4-dioxane (99.8%, Aldrich), methanol (99.8%, Aldrich) were used without further purification. Ethyl acetate (EtOAc), acetone and hexane were in technical grade and distilled prior to use. 2-Hydroxy-1,2-bis(4-(methylsulfonyl-phenyl)-ethanone (MTB) was synthesized by Dr. Duygu Sevinç Esen at Yildiz Technical University.

3.2 Instrumentation

¹H (500 MHz), ¹³C (125 MHz), and ¹⁹F NMR (470.4 MHz) spectra were recorded in CDCl₃ with Si(CH₃)₄ as internal standard or dimethylsulfoxide-*d*₆ (DMSO-*d*₆) as the solvent, using an Agilent VNMR 500 instrument. ROESY (Rotating frame

Overhauser Effect Spectroscopy) was performed on an Agilent VNMRs 500 instrument at 500 MHz. The conventional gel permeation chromatography (GPC) measurements were carried out with an Agilent instrument (Model 1100) consisting of a pump, refractive index (RI), and ultraviolet (UV) detectors and four Waters Styragel columns (guard, HR 5E, HR 4E, HR 3, HR 2), (4.6 mm internal diameter, 300 mm length, packed with 5 μ m particles) were used in series. The effective molecular weight ranges are 2000-4,000,000, 50-100,000, 500-30,000, and 500–20,000, respectively. THF was used as eluent at a flow rate of 0.3 mL/min at 30 °C and toluene was used as an internal standard. The apparent molecular weights of polymers were determined with a calibration based on linear PS standards using PL Caliber Software from Polymer Laboratories. Molecular weights of the samples which insoluble in THF were determined with DMF GPC, Agilent 1100 series, consisting of a pump, two Styragel columns (HR3 and HR2) (7.8 x 300 mm column), a differential refractive index (RI) detector with a DMF flow rate of 1.0 mL min⁻¹ at 35°C and toluene as an internal standard. The other GPC set-up (TD-GPC) with an Agilent 1200 model isocratic pump, four Waters Styragel columns (guard, HR 5E, HR 4, HR 3, and HR 2), and a Viscotek TDA 302 triple detector including RI, dual laser light scattering (DLS) (λ = 670 nm, 90° and 7°) and a differential pressure viscometer was conducted to measure the absolute molecular weights ($M_{w,TDGPC}$) in THF with a flow rate of 0.5 mL/min at 35 °C. Three detectors were calibrated with a PS standard having narrow molecular weight distribution (M_n = 115,000 g/mol, M_w/M_n = 1.02, $[\eta]$ = 0.519 dL/g at 35°C in THF, dn/dc = 0.185 mL/g) provided by Viscotek company. Data analyzes were performed with OmniSec 4.5 software from Viscotek Company.

DVB conversion was determined using the Agilent 6890N gas chromatograph, equipped with an FID detector using a wide-bore capillary column (HP5, 30 m x 0.32 mm x 0.25 μ m, J&W Scientific). Injector and detector were kept constant at 280 and 285 °C, respectively. The chromatographic conditions: Injector and detector were kept constant at 280 °C and 285 °C, respectively. Initial column temperature is 40 °C, finally reaching up to 120 °C at a heating rate of 40 °C/min.

FT-IR spectra were recorded on an Agilent Technologies Cary 630 FTIR instrument over the range 4000–500 cm⁻¹.

UV measurements were recorded using Shimadzu UV-1601 spectrophotometer in CH₂Cl₂.

Electrospray ionization-mass spectra (ESI-MS) were recorded on a Thermo Finnigan LCQ Decaquadropole ion trap mass spectrometer (Thermo Finnigan, San Jose, CA), equipped with an atmospheric pressure ionization source operating in the nebulizer assisted electrospray mode and was used in positive ion mode.

Dynamic light scattering (DLS) measurements were carried out in a Malvern Instrument Nano ZS using a He-Ne laser with a 633 nm wavelength, at an angle of 173 °C.

Photoinitiated polymerization was also followed by differential scanning calorimetry (Photo-DSC) using a DSC Q100 (TA Instruments). Appropriate sample mixtures (2.0 ± 0.1 mg) were placed on the sample trays and UV light was applied from a medium-pressure Hg lamp (15 mW/cm^2 at the sample). The measurements were performed in isothermal mode at room temperature under N_2 flow (50 mL/min). A reaction heat of conversion of acrylate double bonds of $\Delta H_0^{\text{theory}} = 86 \text{ kJ/mol}$ was used for calculating polymerization rates and conversions.

3.3 Synthesis Methods

(Pentafluorophenyl)methyl 2-bromo-2-methylpropanoate (**1**) [254], allyl 2-bromo-2-methylpropanoate (**2**) [255], 2-hydroxy-1,2-bis(4-(methylsulfanyl-phenyl)-ethanone (MTB) [256], 1-adamantane methyl-2-bromo isobutyrate (**5**) [253], mono-6-deoxy-6-(p-tolylsulfonyl)- β -cyclodextrin (β -CD-OTs) and mono-6-deoxy-6-azido- β -cyclodextrin (β -CD- N_3) [245] were prepared according to the literature.

3.3.1 Synthesis of (pentafluorophenyl)methyl 2-bromo-2-methylpropanoate (**1**)

2,3,4,5,6-Pentafluorobenzyl alcohol (2.00 g, 0.01 mol) and DMAP (0.61 g, 5.00 mmol) were dissolved in 80 mL of CH_2Cl_2 , and Et_3N (3.47 mL, 25.0 mmol) was added. The reaction mixture was then cooled to 0 °C. A solution of α -bromoisobutryl bromide (1.85 mL, 15.0 mmol) in CH_2Cl_2 (20 mL) was added dropwise within 30 minutes. The reaction mixture was stirred for 15 min. at 0 °C then overnight at room temperature. After filtration of insoluble salts, the filtrate was evaporated to dryness. The obtained crude product was dissolved in 100 mL of CH_2Cl_2 . After extraction with an aqueous solutions of 1M HCl and saturated NaHCO_3 in sequence, the organic phase was washed with deionized water then dried over anhydrous Na_2SO_4 and concentrated to give as a pale yellow oil. (Yield= 3.24 g, 75%). ^1H NMR (CDCl_3 , δ)

5.28 (s, 2H, CH_2 -fluorobenzyl), 1.91 (s, 6H, $\text{C}(\text{CH}_3)_2\text{-Br}$). ^{19}F NMR (CDCl_3 , δ) -141.78, -152.10, -161.44.

3.3.2 Synthesis of α -fluoro- ω -bromide end-functional PS (α -fluoro-PS)

α -fluoro- ω -bromide terminated PS (α -fluoro-PS) was prepared by ATRP of St at 110 °C. St (10.0 mL, 87.0 mmol), PMDETA (0.091 mL, 0.435 mmol), CuBr (0.062 g, 0.435 mmol), and **1** (0.151 g, 0.435 mmol) were added in a 50 mL of Schlenk tube, and the reaction mixture was degassed by three freeze-pump-thaw (FPT) cycles and left in vacuum. The tube was then placed in a thermostated oil bath at 110 °C for 30 min. The dark-green polymerization mixture was diluted with THF, passed through a basic alumina column to remove the catalyst, and precipitated in methanol. The polymer was dried for 24 h in a vacuum oven at 40 °C. ^1H NMR (CDCl_3 , δ) 7.31-6.25 (br, ArH of PS), 4.76-4.27 (br, 3H, CH_2 -fluorobenzyl and $\text{CH}(\text{Ph})\text{-Br}$), 2.24-0.91 (br, aliphatic protons of PS). ^{19}F NMR (CDCl_3 , δ) -141.84, -153.10, -161.77.

3.3.3 Preparation of (fluoro-PS)_n-polyDVB multiarm star polymer

α -Fluoro-PS macroinitiator (2.00 g, 0.381 mmol, $M_{n,\text{GPC}} = 5250$ g/mol), DVB (0.814 mL, 5.72 mmol), PMDETA (0.08 mL, 0.381 mmol), CuBr (0.055 g, 0.381 mmol) and anisole (18 mL) were charged to a Schlenk tube equipped with a magnetic stirrer bar under argon atmosphere. The first sample was quickly taken from the reaction mixture for GC measurement, before the reaction mixture was degassed by using three FPT cycles. The reaction flask was back-filled with argon and immersed in oil bath at 110 °C. At time intervals, the samples were taken from the reaction mixture with argon purged-syringe under positive argon atmosphere and then diluted with THF, purified by passing through short neutral alumina column to remove the copper salt and filtered through poly(tetrafluoroethylene) (PTFE) filter (0.2 μm pore size) prior to GC and GPC analyses. After 17 h at 95 % conversion, the reaction was stopped via exposure to air. The polymerization mixture was diluted with THF, filtered through a column filled with neutral alumina to remove the copper complex and the star polymer was precipitated in methanol. The crude product was dissolved in THF, precipitated into methanol/diethyl ether (1/3; v/v) and dried under vacuum at 40 °C for 24 h. ^1H NMR (CDCl_3 , δ) 7.48-6.32 (br, ArH of PS), 4.68-4.47 (br, 2H, CH_2 -fluorobenzyl), 2.32-0.87 (br, aliphatic protons of PS). ^{19}F NMR (CDCl_3 , δ) -141.88, -153.15, -161.82.

3.3.4 Synthesis of (PEG)_m-(PS)_n-polyDVB multiarm star block copolymer with-(fluoro-PS)_n-polyDVB multiarm star polymer and PEG chains

PEG-OH ($M_n = 550$) (27.70 mg, 0.05 mmol) was diluted with dry THF (30 mL) and deprotonated by the addition of NaH (2.40 mg, 0.06 mmol) over 20 min at 0 °C. (Fluoro-PS)_n-polyDVB multiarm star polymer (0.29 g, 1.06 μ mol, $M_{w,TD-GPC} = 276000$ g/mol) in dry THF (10 mL) was then added dropwise. The reaction mixture was heated at reflux for 3 h. After specified time, reaction mixture was cooled to room temperature, and concentrated under reduced pressure. Saturated NH₄Cl solution (50 mL) was slowly added, and the organic products were extracted in CH₂Cl₂ (30 mL $\times$ 3), which was then washed with water (50 mL) and dried over Na₂SO₄. The organic phase was concentrated to give the crude product, which was diluted with THF and precipitated in methanol. The recovered polymer was dried under vacuum at 40 °C for 24 h. ¹H NMR (CDCl₃, δ) 7.48-6.36 (br, ArH of PS), 4.67 (br, 2H, CH₂-fluorobenzyl), 3.67-3.62 (m, 4H, -OCH₂CH₂, repeating unit of PEG), 2.32-0.87 (br, aliphatic protons of PS). ¹⁹F NMR (CDCl₃, δ) -144.01, -157.10.

3.3.5 Preparation of N-acetyl-L-cysteine methyl-ester functionalized multiarm star polymer ((cysteine-PS)_n-polyDVB) via thiol-*para*-fluoro click reaction

In a typical synthesis, a round bottom flask was charged with (fluoro-PS)_n-polyDVB multiarm star polymer (0.29 g, 1.06 μ mol, $M_{w,TD-GPC} = 276000$ g/mol) in DMF (5 mL). Subsequently, Et₃N (12.2 mg, 0.12 mmol) and N-acetyl-L-cysteine methyl-ester (8.86 mg, 0.05 mmol) were added into the solution in this order and the flask was capped immediately. Reaction was conducted at room temperature for 4 h. When the reaction was completed, precipitated in methanol. The recovered polymer was dried under vacuum at 40 °C for 24 h. ¹H NMR (CDCl₃, δ) 7.48-6.36 (br, ArH of PS), 4.83 (m, CHNH of cysteine), 4.68 (br, 2H, CH₂-fluorobenzyl), 3.61 (s, 3H, CH₃OC=O of cysteine), 3.12 (m, 2H, NCHCH₂S of cysteine), 2.32-0.87 (br, CH₃C=O of cysteine and aliphatic protons of PS). ¹⁹F NMR (CDCl₃, δ) -133.08, -141.57.

3.3.6 Synthesis of allyl 2-bromo-2-methylpropanoate (2)

A solution of α -bromoisobutyryl bromide (3.15 mL, 0.025 mol) in CH₂Cl₂ (20 mL) was added dropwise to a solution of allyl alcohol (1.00 g, 0.017 mol), DMAP (1.04 g, 8.50 mmol), and Et₃N (4.72 mL, 0.034 mol) in CH₂Cl₂ (80 mL) at 0 °C. After complete

addition, the reaction mixture was allowed to stir for 1 h at 0 °C and overnight at room temperature. The formed triethylammonium bromide was filtered off and the solvent was removed in vacuum. The crude product was dissolved in CH₂Cl₂ and washed two times with a saturated aqueous NaHCO₃ and two times with distilled water (50 mL). The organic layer was dried with Na₂SO₄ and solvent was removed in vacuum, afforded a yellowish oil which was further purified by flash chromatography over silica gel eluting with hexane/EtOAc (6/1; v/v). The product was isolated as colorless oil. (Yield= 2.62 g, 74%). ¹H NMR (CDCl₃, δ) 6.01-5.90 (m, 1H, CH₂=CH), 5.40-5.27 (m, 2H, CH₂=CH), 4.68 (m, 2H, CH₂OC=O), 1.96 (s, 6H, C(CH₃)₂-Br). ¹³C NMR (CDCl₃, δ) 171.16, 131.52, 118.52, 66.36, 55.62, 30.83.

3.3.7 Model reaction between α-fluoro-PS and N-acetyl-L-cysteine methyl ester

The α-fluoro-PS (0.20 g, 38.1 μmol, *M_{n, GPC}*= 5250 g/mol, 1 equiv), N-acetyl-L-cysteine methyl-ester (0.042 g, 1.90 mmol, 5 equiv), DMPA (4.90 mg, 19.0 μmol, 0.5 equiv) and 1,4 dioxane (5 mL) were put into a Schlenk tube. The reaction mixture was degassed by three FPT cycles and left in vacuum. The mixture was irradiated by a photoreactor at 365 nm at room temperature. After 2 hours the resulted polymer was diluted with THF, and precipitated in methanol. This dissolution-precipitation procedure was repeated two times. The polymer was dried for 24 h in a vacuum oven at 40 °C. Yield = 0.17 g (85 %). ¹H NMR (500 MHz, CDCl₃, δ): 7.20-6.48 (br, ArH of PS), 4.68-4.44 (br, 3H, CH₂-fluorobenzyl and CH(Ph)-Br), 2.22-0.96 (br, aliphatic protons of PS). ¹⁹F NMR (470 MHz, CDCl₃, δ): -141.83, -153.05, -161.78.

3.3.8 Synthesis of α-allyl-ω-bromide end-functional PS (α-allyl-PS)

In a typical synthesis, St (10.0 mL, 87.0 mmol), PMDETA (0.091mL, 0.435 mmol), CuBr (0.062 g, 0.435 mmol) and **2** (0.09 g, 0.435 mmol) were added in a 50 mL of Schlenk tube and the reaction mixture was degassed by three FPT cycles and left in vacuum. After the tube was placed in a thermostated oil bath at 110 °C for 35 min, the dark green polymerization mixture was diluted with THF, passed through a basic alumina column to remove the catalyst, precipitated in methanol and dried for 24 h in a vacuum oven at 40 °C. ¹H NMR (CDCl₃, δ) 7.44-6.30 (br, ArH of PS), 5.70 (m, 1H, CH₂=CH), 5.28-5.09 (m, 2H, CH₂=CH), 4.58-4.37 (br, 1H, CH(Ph)-Br), 4.23-3.77 (m, 2H, CH₂=CH-CH₂OC=O), 2.42-0.86 (m, CH₂, CH and CH₃).

3.3.9 Model reaction between α -allyl-PS and 1-propanethiol

The α -allyl-PS (0.25 g, 32.0 μ mol, $M_{n,GPC}$ = 7800 g/mol, 1 equiv) was dissolved in DMF (5 mL). Subsequently, Et₃N (30.0 μ L, 0.48 mmol, 15 equiv) and 1-propanethiol (68.0 μ L, 0.32 mmol, 10 equiv) were added into the solution in this order and the flask was capped immediately. Reaction was conducted at room temperature for 4 h and precipitated in methanol. The recovered polymer was re-dissolved in THF and precipitated in methanol, filtered and dried under vacuum at 40 °C for 24 h. Yield = 0.23 g (92 %). ¹H NMR (CDCl₃, δ) 7.44-6.28 (br, ArH of PS), 5.71 (m, 1H, CH₂=CH), 5.27-5.09 (m, 2H, CH₂=CH), 4.58-4.37 (br, 1H, CH(Ph)-Br), 4.23-3.76 (m, 2H, CH₂=CH-CH₂OC=O), 2.42-0.87 (m, CH₂, CH and CH₃).

3.3.10 One-pot preparation of α -fluoro and α -allyl-end-functionalized PS mixture (α -fluoro-PS + α -allyl-PS)

St (20.0 mL, 0.175 mol), PMDETA (0.17 mL, 0.873 mmol), CuBr (0.124 g, 0.873 mmol), **1** (0.15 g, 0.435 mmol) and **2** (0.09 g, 0.435 mmol) were added in a 50 mL of Schlenk tube and the reaction mixture was degassed by three FPT cycles and left in vacuum. After the tube was placed in a thermostated oil bath at 110 °C for 40 min, the dark green polymerization mixture was diluted with THF, passed through a basic alumina column to remove the catalyst, precipitated in methanol and dried for 24 h in a vacuum oven at 40 °C. ¹H NMR (CDCl₃, δ) 7.22–6.30 (ArH of PS), 5.69 (s, 1H, CH₂=CH), 5.24-5.08 (br, 2H, CH₂=CH), 4.76-4.33 (m, 4H, CH₂-fluorobenzyl and CH(Ph)-Br), 4.23-3.75 (m, 2H, vinylic H), 2.32-1.07 (br, aliphatic protons of PS). ¹⁹F NMR (CDCl₃, δ) -141.88, -153.16, -161.82.

3.3.11 Preparation of (fluoro-PS)_m-polyDVB-(allyl-PS)_m multiarm star polymer bearing pentafluoro and allyl functionalities at the periphery

α -Fluoro-PS + α -allyl-PS (4.0 g, 0.77 mmol, $M_{n,GPC}$ = 5200 g/mol), anisole (36.6 mL), PMDETA (0.161 mL, 0.77 mmol), DVB (1.645 mL, 11.55 mmol), and CuBr (0.110 g, 0.77 mmol) were charged to a Schlenk tube equipped with a magnetic stirrer bar under argon. The first sample was quickly taken from the reaction mixture for GC measurement, before it was degassed by using three FPT cycles. The reaction flask was back-filled with argon and immersed in a 110 °C oil bath. At specified intervals, samples were taken from the reaction mixture with argon purged-syringe under

positive argon atmosphere. The samples were diluted with THF and purified by passing through short neutral alumina column to remove the copper salt and then filtered through PTFE filter prior to GC and GPC analyses. The reaction was stopped after 17 h at 95 % conversion via exposure to air. The reaction mixture was diluted with THF, then filtered through a column filled with neutral alumina to remove the copper complex and the star polymer was precipitated in methanol. The crude product was further purified via dissolution in THF and then precipitation in methanol/ diethyl ether (1/1) and gradually increased to (1/4; v/v) mixture to remove the unreacted chains. Finally, the polymer was dried under vacuum at 40 °C for 24 h. ¹H NMR (CDCl₃, δ) 7.47-6.30 (br, ArH of PS), 5.73 (m, 1H, CH₂=CH), 5.27-5.07 (m, 2H, CH₂=CH), 4.70-4.43 (m, 2H, CH₂-fluorobenzyl), 4.24-3.76 (m, 2H, vinylic H), 2.35-0.83 (br, aliphatic protons of PS). ¹⁹F NMR (CDCl₃, δ) -141.83, -153.08, -161.76.

3.3.12 Thiol-*para*-fluoro click reaction with 1-propanethiol and (fluoro-PS)_m-polyDVB-(allyl-PS)_m multiarm star polymer

The (fluoro-PS)_m-polyDVB-(allyl-PS)_m multiarm star polymer (0.60 g, 2.70 μmol, *M*_{w,TD-GPC}= 222000 g/mol) was dissolved in DMF (5 mL). Subsequently, Et₃N (90.0 μL, 0.648 mmol) and 1-propanethiol (40.0 μL, 0.432 mmol) were added into the solution in this order and the flask was capped immediately. Reaction was conducted at room temperature for 4 h and precipitated in methanol. The recovered polymer was re-dissolved in THF and precipitated in methanol, filtered and dried under vacuum at 40 °C for 24 h. Yield = 0.51 g (84 %). ¹H NMR (CDCl₃, δ) 7.48-6.28 (br, ArH of PS), 5.71 (m, 1H, CH₂=CH), 5.27-5.08 (m, 2H, CH₂=CH), 4.75-4.44 (m, 2H, CH₂-fluorobenzyl), 4.23-3.75 (m, 2H, vinylic H), 2.60–2.35 (br, 2H, SCH₂CH₂CH₂), 2.32-0.84 (m, CH₂, CH and CH₃). ¹⁹F NMR (CDCl₃, δ) -134.35, -142.45.

3.3.13 Radical thiol-ene click reaction between *N*-acetyl-L-cysteine methyl-ester and (propyl-PS)_m-polyDVB-(allyl-PS)_m multiarm star polymer

The (propyl-PS)_m-polyDVB-(allyl-PS)_m multiarm star polymer (0.20 g, 0.847 μmol, *M*_{w,TD-GPC}= 236000 g/mol), *N*-acetyl-L-cysteine methyl-ester (0.026 g, 0.118 mmol), DMPA (1.52 mg, 6.00 μmol) and 1,4 dioxane (5 mL) were put into a Schlenk tube. The reaction mixture was degassed by three FPT cycles and left in vacuum. The mixture was irradiated by a photoreactor at 365 nm at room temperature. After 2 hours

the resulted polymer was diluted with THF, and precipitated in methanol. This dissolution-precipitation procedure was repeated two times. The polymer was dried for 24 h in a vacuum oven at 40 °C. Yield = 0.17 g (83 %). ¹H NMR (CDCl₃, δ) 7.48-6.26 (br, ArH of PS), 4.85-4.68 (m, CHNH and CH₂-fluorobenzyl), 3.78-3.40 (m, CH₃OC=O and CH₂OC=O), 3.08-2.72 (m, NCHCH₂S and CH₂SCH₂), 2.45-2.30 (br, 5H, CH₃C=ONH and SCH₂CH₂CH₂), 2.22-0.78 (m, CH₂, CH and CH₃). ¹⁹F NMR (CDCl₃, δ) -134.31, -142.45.

3.3.14 Synthesis of 2-oxo-1,2-diphenylethyl 2-bromo-2-methylpropanoate (3)

In a 100 mL of round bottom flask were added benzoin (1.0 g, 4.71 mmol), Et₃N (0.98 mL, 7.06 mmol) and DMAP (0.29 g, 2.35 mmol) in 50 mL of CH₂Cl₂. The mixture was cooled to 0 °C, and a solution of α-bromoisobutryl bromide (1.52 g, 7.06 mmol) in 20 mL of CH₂Cl₂ was added dropwise (30 min) to the reaction mixture. The mixture was stirred for 15 min at 0 °C then for overnight at room temperature. After that time, the mixture extracted with cold 1 M HCl (50 mL), saturated aqueous NaHCO₃ (50 mL) and then with distilled water (50 mL), respectively. The aqueous layers were again extracted with CH₂Cl₂, and combined organic layers were dried over Na₂SO₄. The organic phase was evaporated under reduced pressure and the remaining product was crystallized from hexane to give α-bromide functional benzoin as white crystals. (Yield= 1.60 g, 80%). ¹H NMR (CDCl₃, δ) 7.94 (d, 2H, CH₂ of phenyl), 7.55–7.32 (m, 8H, CH₂ of phenyl), 6.85 (s, 1H, Ph-CH-C=O), 2.02 (d, 6H, C(CH₃)₂-Br).

3.3.15 Preparation of benzoin end-functional PS (Benzoin-PS)

α-Benzoin terminated PS (Benzoin-PS) was prepared by ATRP of St. In a 25 mL of Schlenk tube, St (10 mL, 87.3 mmol), PMDETA (0.091 mL, 0.436 mmol), CuBr (0.062 g, 0.436 mmol), and **3** (0.151 g, 0.436 mmol) were added and the reaction mixture was degassed by three FPT cycles and left in argon. The tube was then placed in an oil bath thermostated at 110 °C for 30 min. The polymerization mixture was diluted with THF, passed through a neutral alumina column to remove the catalyst, and precipitated in methanol. The polymer was dried for 24 h in a vacuum oven at 40 °C. ¹H NMR (CDCl₃, δ) 7.70 (br, 2H, ArH of benzoin), 7.32-6.23 (br, ArH of PS and benzoin), 5.88 (br, 1H, Ph-CH-C=O), 4.43 (br, 1H, CH (Ph)-Br), 2.26-0.77 (br, aliphatic protons of PS).

3.3.16 Synthesis of multiarm (Benzoin-PS)_m-polyDVB star polymer

Benzoin-PS macroinitiator (1.80 g, 0.321 mmol, based on $M_{n, GPC}$), DVB (0.687 mL, 4.82 mmol), PMDETA (0.069 mL, 0.321 mmol), CuBr (0.047 g, 0.321 mmol) and anisole (13.0 mL) were charged to a schlenk tube equipped with a magnetic stirrer bar under argon atmosphere. The first sample was quickly taken from the reaction mixture for GC measurement, before the reaction mixture was degassed by using three FPT cycles. The reaction flask was back-filled with argon and immersed in oil bath at 110 °C. At time intervals, the samples were taken from the reaction mixture with argon purged-syringe under positive argon atmosphere and then diluted with THF, purified by passing through short neutral alumina column to remove the copper salt and filtered through PTFE filter (0.2 µm pore size) prior to GC and GPC analyses. After 20 h at 90 % of DVB conversion, the reaction was stopped via exposure to air. The polymerization mixture was diluted with THF, filtered through a column filled with neutral alumina to remove the copper complex and the star polymer was precipitated in methanol. The crude product was dissolved in THF, precipitated into methanol/diethyl ether (1/4; v/v) and dried under vacuum at 40 °C for 24 h. ¹H NMR (CDCl₃, δ) 7.79 (br, 2H, ArH of benzoin), 7.42-6.24 (br, ArH of PS and benzoin), 5.89 (br, 1H, Ph-CH-C=O), 2.26-0.78 (br, aliphatic protons of PS).

3.3.17 Synthesis of 2-hydroxy-1,2-bis(4-(methylsulfanyl-phenyl)-ethanone

(MTB)

In a 100 mL of round bottom flask was added potassium cyanide (0.65 g, 10 mmol) in 10 mL of water. A solution of 4-methylthiobenzaldehyde (3.05 ml, 23 mmol) in 20 mL of ethanol was added dropwise to the reaction mixture. The reaction mixture was stirred at room temperature for 10 minutes and then reflux for 3 hours. After 3 hours, the reaction solution was cooled in an ice bath. The organic residue was filtered and washed two times with distilled water and purified by three recrystallization cycles from ethanol. M_p : 106 °C, Yield: 20%, ϵ_{313} =18800 L mol⁻¹ cm⁻¹. ¹H NMR (CDCl₃, δ) 7.80-7.10 (m, 8H, aromatics), 5.84 (s, 1H, CH), 4.54 (d, 1H, OH), 2.45 (s, 6H, CH₃). IR (KBr): 3427 (OH), 1665 (C=O), 1250 (C-O) cm⁻¹. GC-MS (70 eV) m/e: 304 g/mol.

3.3.18 Synthesis of 1,2-bis(4-(methylthio)phenyl)-2-oxoethyl 2-bromo-2-methylpropanoate (4)

In a 100 mL of round bottom flask were added MTB (0.25 g, 0.82 mmol), Et₃N (0.171 mL, 1.23 mmol) and DMAP (0.05 g, 0.41 mmol) in 40 mL of CH₂Cl₂. The mixture was cooled to 0 °C and a solution of α -bromoisobutryl bromide (0.27 g, 1.23 mmol) in 20 mL of CH₂Cl₂ was added dropwise (30 min) to the reaction mixture. The mixture was stirred for 15 min at 0 °C then for overnight at room temperature. After that time, the mixture extracted with cold 1 M HCl (50 mL), saturated aqueous NaHCO₃ (50 mL) and then with distilled water (50 mL), respectively. The aqueous layers were again extracted with CH₂Cl₂, and combined organic layers were dried over Na₂SO₄. The organic phase was evaporated under reduced pressure and the remaining product was crystallized from hexane yielding **4** as white crystals. (Yield= 0.28 g, 65%). ¹H NMR (CDCl₃, δ) 7.84 (d, 2H, ArH of phenyl), 7.40-7.18 (m, 6H, ArH of phenyl), 6.76 (s, 1H, Ph-CH-C=O), 2.47 (d, 6H, SCH₃), 2.00 (d, 6H, C(CH₃)₂-Br).

3.3.19 Preparation of MTB end-functional PS (MTB-PS)

α -MTB terminated PS (MTB-PS) was prepared by ATRP of St. In a 25 mL of Schlenk tube, St (10 mL, 87.3 mmol), PMDETA (0.091 mL, 0.436 mmol), CuBr (0.062 g, 0.436 mmol), and **4** (0.191 g, 0.436 mmol) were added and the reaction mixture was degassed by three FPT cycles and left in argon. The tube was then placed in an oil bath thermostated at 110 °C for 30 min. The polymerization mixture was then diluted with THF, passed through a neutral alumina column to remove the catalyst, and precipitated in methanol. The polymer was dried for 24 h in a vacuum oven at 40 °C. ¹H NMR (CDCl₃, δ) 7.69 (br, 2H, ArH of MTB), 7.28-6.26 (br, ArH of PS and MTB), 4.41 (br, 1H, CH(Ph)-Br), 2.46 (s, 6H, SCH₃), 2.26-0.78 (br, aliphatic protons of PS).

3.3.20 Synthesis of multiarm (MTB-PS)_p-polyDVB star polymer

MTB-PS macroinitiator (2.00 g, 0.335 mmol, based on *M_n*,GPC), DVB (0.716 mL, 5.025 mmol), PMDETA (0.070 mL, 0.335 mmol), CuBr (0.048 g, 0.335 mmol) and anisole (13.8 mL) were charged to a schlenk tube equipped with a magnetic stirrer bar under argon atmosphere. The first sample was quickly taken from the reaction mixture for GC measurement, before the reaction mixture was degassed by using three FPT cycles. The reaction flask was back-filled with argon and immersed in oil bath at 110 °C. At time intervals, the samples were taken from the reaction mixture with argon

purged-syringe under positive argon atmosphere and then diluted with THF, purified by passing through short neutral alumina column to remove the copper salt and filtered through PTFE filter (0.2 μm pore size) prior to GC and GPC analyses. After 22 h at 91 % of DVB conversion, the reaction was stopped via exposure to air. The polymerization mixture was diluted with THF, filtered through a column filled with neutral alumina to remove the copper complex and the star polymer was precipitated in methanol. The crude product was dissolved in THF, precipitated into methanol/diethyl ether (1/4; v/v) and dried under vacuum at 40 $^{\circ}\text{C}$ for 24 h. ^1H NMR (CDCl_3 , δ) 7.69 (br, 2H, ArH of MTB), 7.50-6.24 (br, ArH of PS and MTB), 2.45 (s, 6H, SCH_3), 2.27-0.80 (br, aliphatic protons of PS).

3.3.21 Photopolymerization of MMA

Appropriate solutions of the MMA (4.68 $\text{mol}\cdot\text{L}^{-1}$) and multiarm (Benzoin-PS)_m-polyDVB star polymer or multiarm (MTB-PS)_p-polyDVB star polymer (certain O.D.) were dissolved in CHCl_3 and irradiated in a photoreactor equipped with 12 UV lamps irradiating at $\lambda=350$ nm for 60 minutes in air atmosphere. Polymers were obtained after precipitation in methanol and drying under vacuum. Conversions were calculated gravimetrically.

3.3.22 Photo-DSC procedure

Photopolymerization of 1,6-hexanediol diacrylate (HDDA) monomer investigated by using Photo-DSC with multiarm (Benzoin-PS)_m-polyDVB star polymer or (MTB-PS)_p-polyDVB star polymer using a DSC Q100 (TA Instruments). Appropriate sample mixtures (2 ± 0.1 mg) were placed on the sample trays and photopolymerization reactions were occurred at 0.5% (w/w) and 1% (w/w) photoinitiator concentration and different light intensities (20 mW/cm^2 and 40 mW/cm^2) at 25 $^{\circ}\text{C}$ and in inert atmosphere (Nitrogen flow: 50 mL/min).

3.3.23 Synthesis of 1-adamantane methyl-2-bromo isobutyrate (5)

1-Adamantane methanol (2.00 g, 0.012 mol), DMAP (0.73 g, 6.00 mmol), and Et_3N (3.35 mL, 0.024 mol) were dissolved in CH_2Cl_2 (120 mL) in an ice–water bath. After stirring for 0.5 h, α -bromoisobutyryl bromide (2.22 mL, 0.018 mol) in CH_2Cl_2 (30 mL) was added dropwise over 1 h. Subsequently, the reaction mixture was stirred at 0 $^{\circ}\text{C}$ for another 1 h and then at room temperature for 16 h. After removing the

insoluble salts by suction filtration, the filtrate was concentrated and then the crude product was dissolved in CH_2Cl_2 and extracted with HCl (3 M, 3×30 mL), deionized water (3×30 mL), NaOH (3 M, 3×30 mL), deionized water (3×30 mL) in sequence. The organic phase was dried over anhydrous Na_2SO_4 . After removing the solvents by a rotary evaporator, obtained as a yellowish oil which was further purified by flash chromatography over silica gel eluting with hexane/EtOAc (9/1; v/v). The product was isolated as a white solid (Yield= 3.22 g, 85%). ^1H NMR (CDCl_3 , δ) 3.77 (s, 2H, CH_2 -adamantyl), 2.01 (s, 3H, CH), 1.96 (s, 6H, $\text{C}(\text{CH}_3)_2\text{-Br}$), 1.71 (dd, $J = 27.8$ Hz, 6H, CH_2), 1.59 (s, 6H, CH_2).

3.3.24 Synthesis of mono-6-deoxy-6-(p-tolylsulfonyl)- β -cyclodextrin (β -CD-OTs)

Based on a literature procedure, in a 500 mL round bottom flask β -cyclodextrin (20.0 g, 17.6 mmol) was suspended in 250 mL 0.4 M sodium hydroxide (NaOH) aqueous solution. The flask was cooled to 0°C in ice bath. TsCl (13.4 g, 70.3 mmol) was added in slow portions over 10 min. After 45 min of stirring at 0°C , the precipitate was removed by filtration and the pH of the filtrate was adjusted to 8.5 by dropping HCl aqueous solution. Then the mixture was stirred for 1 h at room temperature. The resulting white precipitate was recovered by filtration and washed three times with water. The final product was dried in a vacuum oven at 60°C , yielding a white solid (8.83 g, yield: 40%). ^1H NMR ($\text{DMSO}-d_6$) δ 7.76 (d, $J = 8.3$ Hz, 2H, H-7), 7.45 (d, $J = 8.2$ Hz, 2H, H-8), 5.69 (br, 14H, OH-2,3), 4.83 (t, 5H, H-1), 4.77 (t, 2H, H-1), 4.47 (d, $J = 26.3$ Hz, 6H, OH-6), 4.37 (br, 2H, H-6'), 4.35 (br, 1H, H-5'), 3.81-3.08 (br, 26H, H-2,3,4,5,6 overlap with H_2O), 2.43 (s, 3H, H-9). FT-IR ν : 3316 (OH), 2924 (CH), 2160 (CH), 2030, 1358 (S=O), 1152 (S-O), 1077 (OH), 1023 (CH), 945, 841, 756 (OH), 684 (CH) cm^{-1} . ESI-MS: m/z 1312.2 [$\text{M} + \text{Na}^+$].

3.3.25 Synthesis of mono-6-deoxy-6-azido- β -cyclodextrin (β -CD- N_3)

β -CD-OTs (8.0 g, 6.2 mmol) was suspended in 100 mL water. After heating to 80°C , NaN_3 (2.0 g, 31.0 mmol) was added. The reaction mixture was stirred at 80°C for overnight. The reaction solution was cooled to room temperature and precipitated in 800 mL acetone. The resulting white precipitate was recovered by filtration and redissolved in 50 mL of water and precipitated again in acetone. The white solid was dried under vacuum at 60°C for 2 days (6.8 g, yield: 95%). ^1H NMR ($\text{DMSO}-d_6$) δ 5.72 (br, 14H, OH-2,3), 4.88 (s, H, H-1), 4.83 (d, 6H, H-1), 4.57-4.40 (br, 6H, OH-6),

3.86-3.50 (br, 28H, H-3,5,6,6'), 3.32 (br, 14H, H-2,4 overlap with H₂O). FT-IR ν : 3316 (OH), 2924 (CH), 2160 (C-C), 2102 (N=N), 1644 (C=C), 1364 (OH), 1152 (CN), 1077 (OH), 1025 (CH), 945, 853, 756 (NH), 704 (CH) cm^{-1} . ESI-MS: m/z 1182.3 [M + Na⁺].

3.3.26 Synthesis of alkyne end-functionalized PEG (Alkyne-PEG)

PEG-OH (M_n = 5000) (2 g, 0.4 mmol) was dissolved in 25 mL of CH₂Cl₂. 4-Pentynoic acid (0.118 g, 1.2 mmol) and DMAP (0.048 g, 0.4 mmol) was added successively. DCC (0.248 g, 1.2 mmol) was dissolved in 5 mL of CH₂Cl₂ was added to the solution in one portion. The reaction mixture was stirred overnight at room temperature. It was filtered, evaporated and the remaining product was dissolved in THF and precipitated into cold diethyl ether. This procedure was repeated two times. Finally, the polymer was dried for 24 h in a vacuum oven at 40 °C. Yield: 1.8 g (89%). ¹H NMR (CDCl₃, δ) 4.25 (t, 2H, PEG-OCH₂CH₂OC=O), 3.78 (t, 2H, PEG-OCH₂CH₂OC=O), 3.67-3.48 (m, 4H, -OCH₂CH₂, repeating unit of PEG, m, 2H, C=OOCH₂CH₂), 3.38 (s, 3H, PEG-OCH₃), 2.59-2.51 (m, 4H, CH $\equiv$ CCH₂CH₂C=O), 1.93 (t, 1H, CH $\equiv$ CCH₂CH₂C=O).

3.3.27 CuAAC click reaction of Alkyne-PEG with β -CD-N₃ (β -CD-PEG)

Alkyne-PEG (1.00 g, 0.19 mmol, M_n , NMR = 5180 g/mol) and β -CD-N₃ (0.456 g, 0.38 mmol) were dissolved in DMF (10 mL) in a Schlenk tube equipped with magnetic stirring bar. CuBr (0.0277 g, 0.4 mmol) and PMDETA (40.0 μ L, 0.19 mmol) were introduced under protection of nitrogen flow. The reaction tube was degassed by three FPT cycles, and placed in an oil bath thermostated at 60 °C for 2 days. The reaction mixture was exposed to air, and then the mixture was evaporated to dryness, and dissolved in CHCl₃ and precipitated in excess of cold diethyl ether. The white solid was redissolved in CHCl₃ and passed through a alumina column to remove copper catalysts. After removing the solvents, the residues were dissolved in 10 mL water and extracted with CHCl₃ to remove unreacted β -CD-N₃. The organic phase was dried over anhydrous Na₂SO₄. After evaporated to 5 mL, the final product was obtained by precipitation in excess of cold diethyl ether and drying in a vacuum oven at 40 °C for 24 h. Yield = 1.0 g (82 %). ¹H NMR (CDCl₃, δ) 7.78 (br, CH of triazole), 5.69 (br, 14H, OH-2,3), 5.02 (s, H, H-1), 4.82 (d, 6H, H-1), 4.56-4.43 (br, 6H, OH-6), 3.77-3.60 (br, 28H, H-3,5,6,6'), 3.58-3.25 (m, 4H, -OCH₂CH₂, repeating unit of PEG, br, 14H, H-2,4 overlap with H₂O), 3.23 (s, 3H, PEG-OCH₃).

3.3.28 Synthesis of adamantyl end-functionalized PS (ada-PS)

Adamantane end-functional PS (Ada-PS) was prepared by ATRP of St at 110 °C. St (10.0 mL, 87.0 mmol), PMDETA (0.091 mL, 0.435 mmol), CuBr (0.062 g, 0.435 mmol), and **5** (0.138 g, 0.435 mmol) were added in a 50 mL of Schlenk tube, and the reaction mixture was degassed by three FPT cycles and left in vacuum. The tube was then placed in a thermostated oil bath at 110 °C for 40 min. The dark-green polymerization mixture was diluted with THF, passed through a basic alumina column to remove the catalyst, and precipitated in methanol. The polymer was dried for 24 h in a vacuum oven at 40 °C. ¹H NMR (CDCl₃, δ) 7.20-6.25 (br, ArH of PS), 4.66-4.35 (br, 1H, CH(Ph)-Br), 3.35-3.00 (br, 2H, CH₂-adamantane), 2.32-0.82 (br, aliphatic protons of PS and adamantane).

3.3.29 Preparation of (ada-PS)_n-polyDVB multiarm star polymer

Adamantane-PS macroinitiator (1.50 g, 0.417 mmol), anisole (19.82 mL), PMDETA (87.0 μL, 0.417 mmol), DVB (0.890 mL, 6.25 mmol), and CuBr (0.060 g, 0.417 mmol) were charged to a Schlenk tube equipped with a magnetic stirrer bar under argon atmosphere. The first sample was quickly taken from the reaction mixture for GC measurement, before it was degassed using three FPT cycles. The reaction flask was back-filled with argon and immersed in a 110 °C oil bath. At time intervals, samples were taken from the reaction mixture with argon purged-syringe under positive argon atmosphere. The samples were diluted with THF and purified by passing through short neutral alumina column to remove the copper salt, and then filtered through PTFE filter (0.2 μm pore size) prior to GC and GPC analyses. After 18 h at 85 % conversion, the reaction was stopped via exposure to air. The reaction mixture was diluted with THF, and then filtered through a column filled with neutral alumina to remove the copper complex and the star polymer was precipitated in methanol. The crude product was dissolved in THF, and then reprecipitated in methanol–diethyl ether mixture (1/3 v/v). Finally, the polymer was dried under vacuum at 40 °C for 24 h. ¹H NMR (CDCl₃, δ) 7.24-6.24 (br, ArH of PS), 3.42-3.02 (br, 2H, CH₂-adamantane), 2.26-0.78 (br, aliphatic protons of PS and adamantane).

3.3.30 Preparation of supramolecular (CD-PEG)_p-(ada-PS)_n-polyDVB multiarm star block copolymer via CD/adamantane “host-guest” interaction

Adamantane end-functionalized multiarm star polymer ((ada-PS)_n-polyDVB; $M_{n,TD-GPC} = 74320 \text{ g mol}^{-1}$; 40.0 mg, 0.538 μmol , 1.0 eq.) was dissolved in DMF (3.0 mL) and added dropwise to a solution of β -CD end-functionalized PEG (β -CD-PEG; $M_{n,NMR} = 6130 \text{ g mol}^{-1}$; 42.9 mg, 6.994 mmol, 1.0 eq. per arm) in DMF (3.0 mL) under vigorous stirring. The resulting solution was dialysed (MW cut-off, 3.5 kDa) against a deionized water–DMF mixture. The water content was gradually increased from 30 % to 100 % over 3 day and the dialysis was continued with deionized water at room temperature. Finally, a white solid was produced by freeze-drying to yield the supramolecular (CD-PEG)_p-(ada-PS)_n-polyDVB multiarm star block copolymer in quantitative yield. Yield = 77.0 mg (93 %).

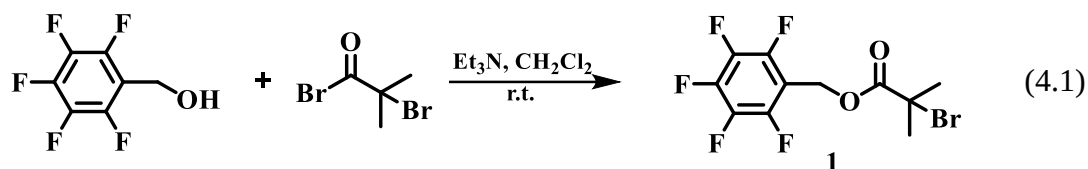
4. RESULTS AND DISCUSSION

As a general perspective, this thesis describes the design and synthesis of periphery functional well-defined multiarm star polymers. All studies include “arm first” approach that the initial synthesis of functional PS polymers, and following, cross-linking using DVB to prepare multiarm star polymers, has been accomplished by ATRP. Some of these star polymers were functionalized using a variety of thiol functional groups via click reactions to yield post-functionalized star polymers with predesigned chemical functionality. As part of our continuing interest in photoinitiating systems, some of these star polymers were used as polymeric photoinitiators. Finally, we focused on supramolecular interactions for the design and modify the our periphery functional multiarm star polymer.

4.1 Post-Functionalization of Multiarm Star Polymers via Nucleophilic Substitution of the *para*-Fluoro Substituent of Pentafluorophenyl Groups at the Periphery

In this study, a facile synthetic approach for the design of post-functionalized multiarm star polymers has been established by nucleophilic substitution reaction of *para*-fluoro phenyl groups with alcohols and thiols. For this purpose, pentafluoro functional multiarm star polymer, (fluoro-PS)_n-polyDVB, was created by ATRP of α -fluoro- ω -bromide terminated PS, (α -fluoro-PS), as macroinitiator in the presence of DVB as a bifunctional cross-linker. Obtained multiarm star polymer which is contain pentafluorophenyl groups throughout its structure was post-modified via nucleophilic substitution reactions.

Firstly, (pentafluorophenyl)methyl 2-bromo-2-methylpropanoate (**1**) was synthesized as an ATRP initiator via an esterification reaction between 2,3,4,5,6-pentafluorobenzyl alcohol and α -bromoisobutryl bromide in CH₂Cl₂ at room temperature (Scheme 4.1).



The ^1H NMR spectrum of **1** showed two singlets, methylene protons next to ester unit at 5.28 ppm, methyl protons next to Br at 1.91 ppm (Figure 4.1). ^{19}F NMR spectrum depicted in Figure 4.2. This spectrum demonstrates the presence of three different types of fluorine atoms that clearly supports the *ortho*, *meta* and *para* substitutions on the phenyl ring.

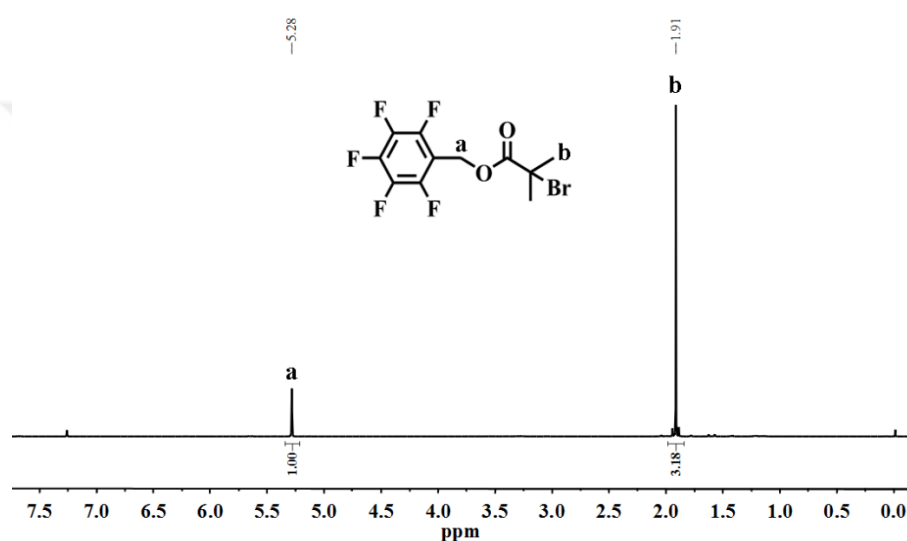


Figure 4.1 : ^1H NMR spectrum of (pentafluorophenyl)methyl 2-bromo-2-methylpropanoate (**1**) in CDCl_3 .

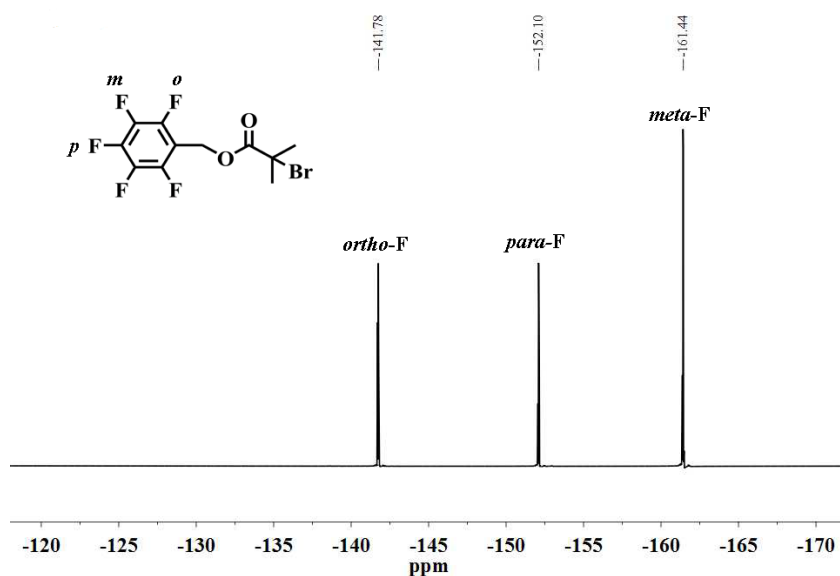
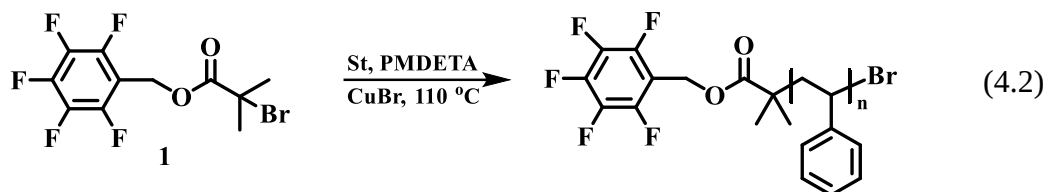


Figure 4.2 : ^{19}F NMR spectrum of (pentafluorophenyl)methyl 2-bromo-2-methylpropanoate (**1**) in CDCl_3 .

Then, α -fluoro- ω -bromide terminated PS (α -fluoro-PS) was prepared by ATRP of St using **1** as an initiator and CuBr/ PMDETA as catalyst at 110 °C (Scheme 4.2).



The NMR number-average molecular weight ($M_{n,NMR} = 5800$ g/mol) was calculated from a ratio of the integrated values of aryl protons of PS ($\delta 7.31$ - 6.25) to that of a signal at 4.76 - 4.27 ppm assignable to CH_2 -fluorobenzyl protons, while being included the molecular weight of initiator (347 g/mol) (Figure 4.3). The number-average molecular weight obtained by GPC ($M_{n,GPC} = 5250$ g/mol, relative to linear PS standarts) was almost consistent with $M_{n,NMR}$. Moreover, $M_w/M_n = 1.08$ calculated from GPC displays narrow molecular weight distribution.

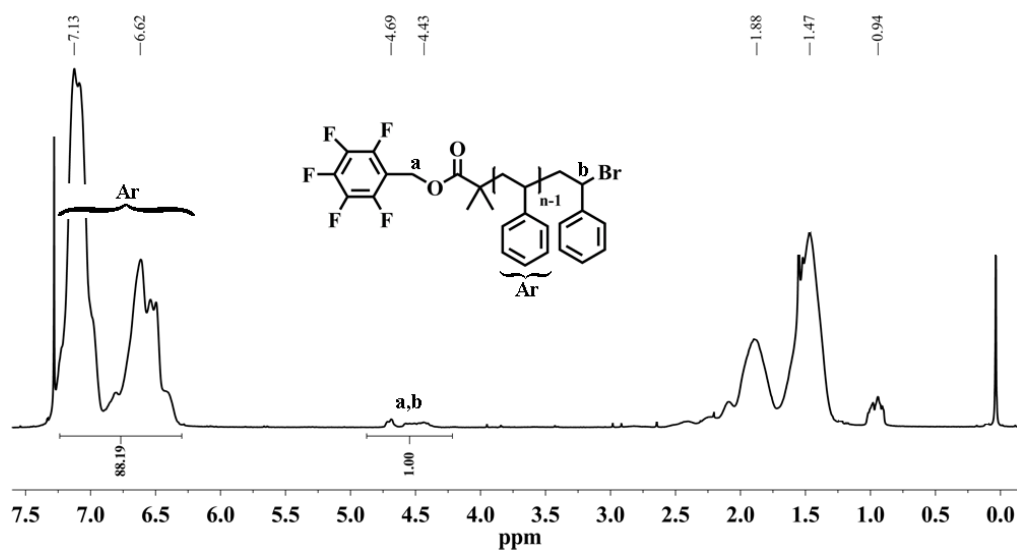


Figure 4.3 : ^1H NMR spectrum of α -fluoro-PS in $CDCl_3$.

In addition, we have measured ^{19}F NMR spectrum of the α -fluoro-PS to identify the fluoro groups. As illustrated in Figure 4.4, there are three peaks visible in the linear polymer, which correspond to fluoro atoms at the *ortho* (-141.84 ppm), *meta* (-161.77 ppm), and *para* (-153.10 ppm) positions.

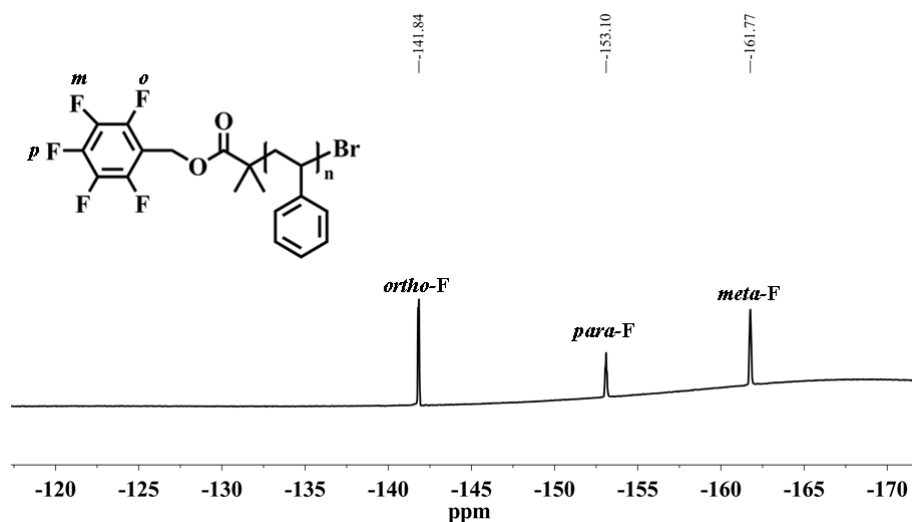
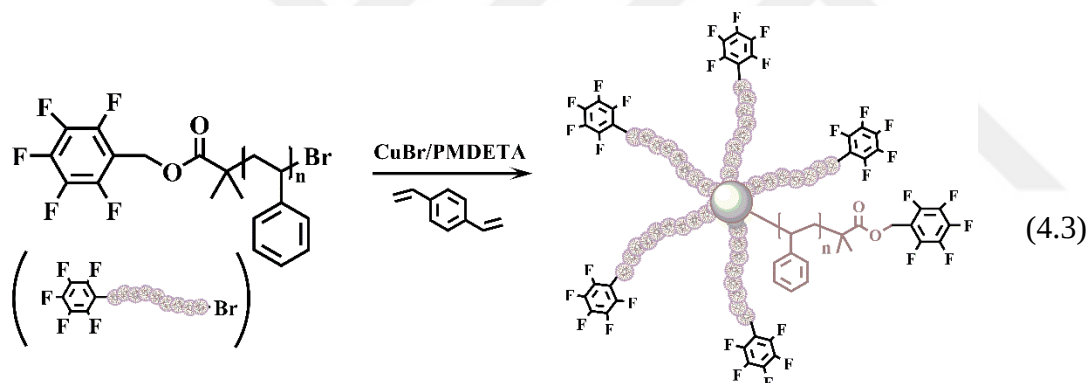


Figure 4.4 : ^{19}F NMR spectrum of α -fluoro-PS in CDCl_3 .

Thereafter, α -fluoro-PS was used as a macroinitiator DVB as cross-linker in ATRP condition at 110°C to give $(\text{fluoro-PS})_n$ -polyDVB multiarm star polymer (Scheme 4.3).



The progress of polymerization was followed by GC and GPC while taking samples at time intervals. We observed a peak originating from the α -fluoro-PS arms during the course of reaction process, where the peak gradually shifts toward higher molecular weight region and becomes monomodal as the polymerization proceeds, indicating that the molecular weight distribution becomes narrower. After 17 h, the reaction was stopped at 95% conversion and the reaction mixture was easily purified by two dissolution-precipitation cycles (THF-methanol/diethyl ether) to remove unreacted linear α -fluoro-PS. The relevant chromatograms and the purified multiarm star polymer are overlaid in Figure 4.5. A monomodal GPC trace and narrow molecular weight distribution for $(\text{fluoro-PS})_n$ -polyDVB multiarm star polymer were detected.

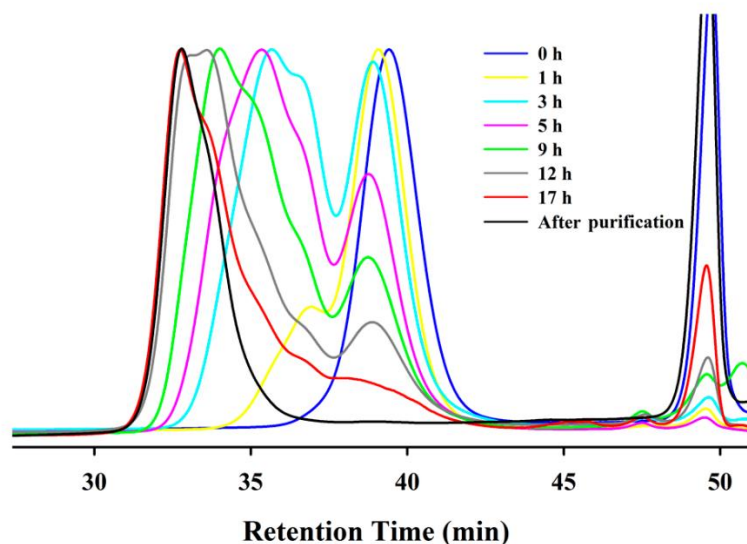


Figure 4.5 : Evolution of GPC traces of (fluoro-PS)_n-polyDVB multiarm star polymer using RI detector in THF at 30 °C ([DVB]₀/15 = [fluoro-PS]₀ = [CuBr]₀ = [PMDETA]₀ = 0.020 M in anisole at 110 °C).

The ¹H NMR spectrum of (fluoro-PS)_n-polyDVB showed aryl protons of PS at 7.48-6.32, methyl protons next to ester unit at 4.68-4.47 ppm (Figure 4.6). While the phenyl proton peaks from polyDVB core between 6.0 and 7.5 ppm are too broad to be detected because of the restricted rotation of the highly cross-linked polyDVB core [205].

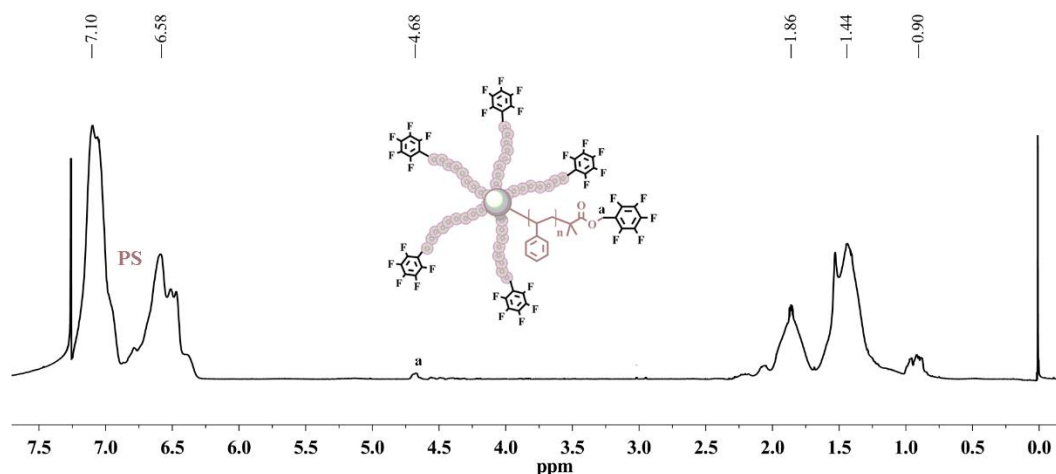


Figure 4.6 : ¹H NMR spectrum of (fluoro-PS)_n-polyDVB multiarm star polymer in CDCl₃.

The ¹⁹F NMR spectrum of (fluoro-PS)_n-polyDVB showed three peaks corresponding to fluoro atoms at the *ortho* (-141.88 ppm), *para* (-153.15 ppm), and *meta* (-161.82 ppm), respectively (Figure 4.7).

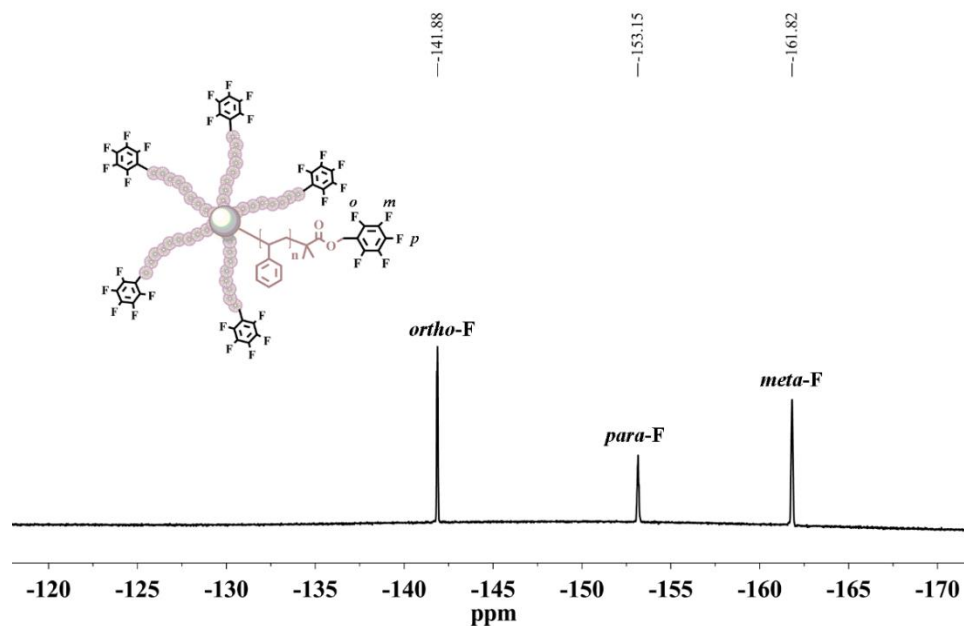


Figure 4.7 : ^{19}F NMR spectrum of (fluoro-PS) $_n$ -polyDVB multiarm star polymer in CDCl_3 .

It is noteworthy that star polymer have more compact structure than linear polymer of equivalent molecular weight and composition resulting in smaller hydrodynamic volume, for this reason, the absolute molecular weight of the polymer was also analyzed by a second GPC (Viscotek TDA 302 triple detector) system. Essentially, refractive index (RI), light scattering (LS) and differential viscometer detectors in TD-GPC instrument provides more advanced and accurate technique to measure the absolute molecular weight of star polymer, if refractive index increment (dn/dc) value of the analyzed polymer is known.

TD-GPC measurements of α -fluoro-PS and (fluoro-PS) $_n$ -polyDVB multiarm star polymer were carried out. The molecular weight values (M_w) of α -fluoro-PS and (fluoro-PS) $_n$ -polyDVB star polymer were obtained using TD-GPC instrument given in Table 4.1. It should be noted here that there is a huge discrepancy between the M_w values of the multiarm star polymer, measured by conventional GPC and TD-GPC that can be clearly seen in Table 4.1. However, this discrepancy is expected because of dense nature of the star polymers with respect to linear polymer of identical molecular weight leading to smaller hydrodynamic volume meaning low molecular weight polymers are obtained. As mentioned above, TD-GPC instrument provides more advanced and accurate technique to measure the absolute molecular weight of star polymers. Although, dn/dc value of linear PS is available, an attempt has been made to clarify the effect of cross-linked DVB core on the dn/dc value of multiarm PS

star polymer. Therefore, the dn/dc of (fluoro-PS)_n-polyDVB was measured by TD-GPC instrument and found to be 0.185 mL/g in THF at 35 °C, which is equal to that of linear PS. The weight average arm number (f) of multiarm (fluoro-PS)_n-polyDVB star polymer was calculated using the following equation 4.1 based on the absolute molecular weights (M_w) of multiarm star polymer.

$$f = \frac{WF_{\text{arm}} \times M_{w,\text{star}}}{M_{w,\text{arm}}} \quad (4.1)$$

$$= \frac{M_{w,\text{star}}}{M_{w,\text{arm}} + M_{\text{DVB}} \times \text{conv}_{\text{DVB}} \times [\text{DVB}]/[\alpha\text{-fluoro-PS}]}$$

Where WF_{arm} is the weight fraction of PS arm in the star polymer, $M_{w,\text{star}}$ and $M_{w,\text{arm}}$ are the absolute molecular weights of the (fluoro-PS)_n-polyDVB star and the α -fluoro-PS arm, respectively obtained from TD-GPC instrument introducing the predetermined $dn/dc = 0.185$ mL/g of PS to OmniSEC software, M_{DVB} is the molecular weight of DVB, $[\text{DVB}]/[\alpha\text{-fluoro-PS}]$ is a feed molar ratio of the DVB to α -fluoro-PS before cross-linking polymerization. The conversion of DVB (conv_{DVB}) was determined by GC. Thus, the f of multiarm (fluoro-PS)_n-polyDVB star polymer was calculated to be 37 and listed in Table 4.1. It is generally accepted that the intrinsic viscosity comparison of star polymer and its linear counterpart provides the most convenient method to elucidate the structure of star polymers, where g' is the contraction factor as given in equation 4.2.

$$g' = [\eta]_{\text{star}} / [\eta]_{\text{linear}} \quad (M = \text{constant}) \quad (4.2)$$

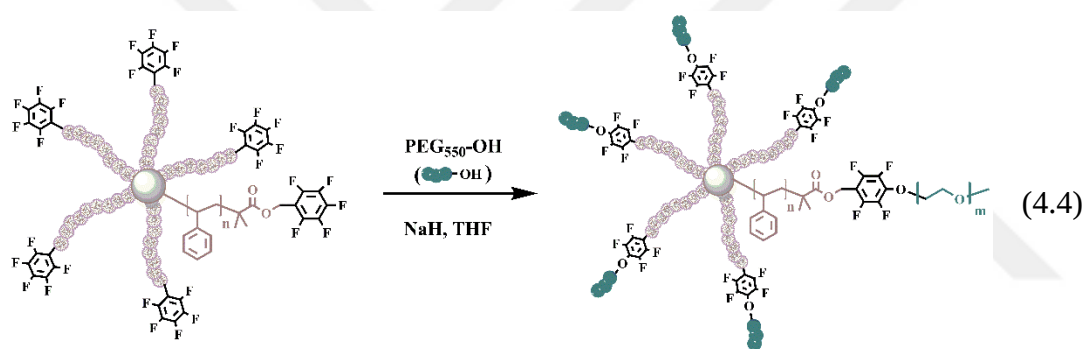
Where $[\eta]_{\text{star}}$ and $[\eta]_{\text{linear}}$ are the intrinsic viscosities of star polymer and the linear polymer with the same molecular weight and the composition, respectively [257]. It is also shown that in regular (equal arm length) star polymers, g' is related with the number of arms, f as follows:

$$\log g' = 0.36 - 0.8 \log f \quad (4.3)$$

Mark-Houwink-Sakurada (MHS) parameters K and a for linear PS were determined to be 1.44×10^{-4} dL/g and 0.707, respectively in THF at 35 °C using a series of linear narrow PS standards by TD-GPC. Then, using these parameters $[\eta]_{\text{linear}}$ was calculated to be 1.015 dL/g for a specified molecular weight ($M_w = 276000$) of linear PS. Moreover, the $[\eta]_{\text{star}}$ of (fluoro-PS)_n-polyDVB star polymer was measured to be 0.143

dL/g by the viscometer detector in TD-GPC. The number of arms, f was calculated to be 37 using equation 4.1 and in close agreement with that obtained from equation 4.2 and 4.3 [258]. Absolute molecular weight (M_w), M_w/M_n and hydrodynamic radius (R_h) for (fluoro-PS) $_n$ -polyDVB multiarm star polymer are given in Table 4.1.

Next, (PEG) $_m$ -(PS) $_n$ -polyDVB multiarm star block copolymer was achieved via nucleophilic substitution reaction of (fluoro-PS) $_n$ -polyDVB multiarm star polymer with the commercially available linear PEG₅₅₀-OH precursor in the presence of NaH in THF at reflux temperature for 3 h (Scheme 4.4). In this case, an excess of linear precursors (1.25 equiv.) was employed with respect to that of multiarm star polymer. The unreacted linear precursors were easily removed from the reaction medium due to their solubility in methanol. After purification, the obtained multiarm star block copolymers were characterized by ^1H NMR, ^{19}F NMR, TD-GPC and GPC.



From ^1H NMR spectrum of (PEG) $_m$ -(PS) $_n$ -polyDVB multiarm star block copolymer, characteristic signal at 3.65 ppm related with $\text{CH}_2\text{CH}_2\text{O}$ of PEG along with signals of PS block at 7.48-6.36 ppm confirmed a successful nucleophilic substitution reaction of PEG₅₅₀-OH with *para*-fluoro phenyl group of (fluoro-PS) $_n$ -polyDVB multiarm star polymer (Figure 4.8).

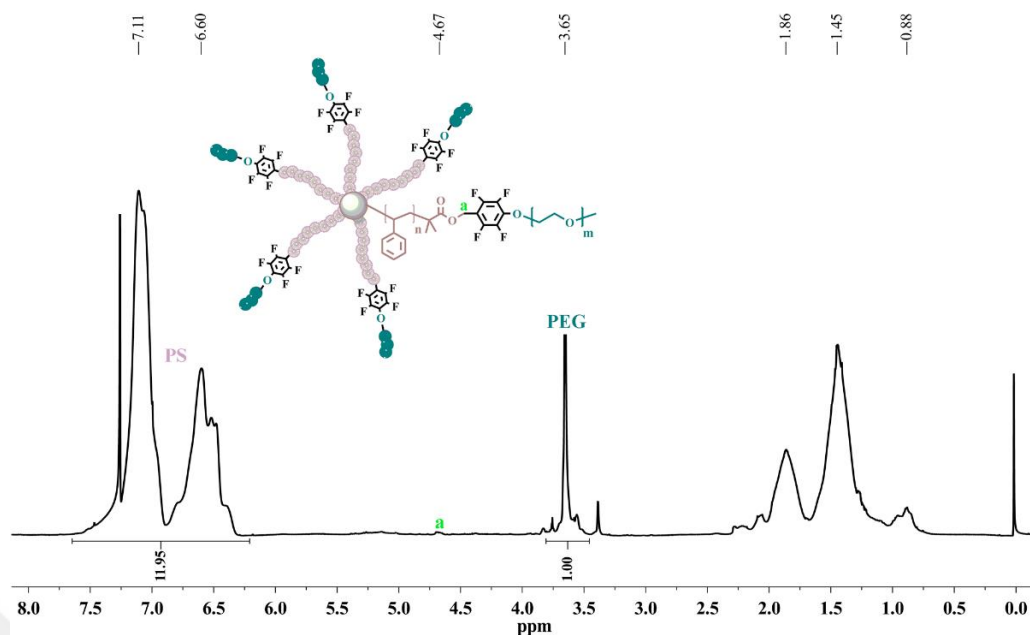


Figure 4.8 : ^1H NMR spectrum of $(\text{PEG})_m\text{-(PS)}_n\text{-polyDVB}$ multiarm star block copolymer in CDCl_3 .

Additionally, the ^{19}F NMR spectrum allowed for the confirmation that the nucleophilic substitution occurred in the para position because the *para*-F signal of (fluoro-PS) $_n$ -polyDVB multiarm star polymer (-153.15 ppm) fully disappeared with the introduction of two new *ortho*- (-144.01) and *meta*-F (-157.10) resonances upon the formation of $(\text{PEG})_m\text{-(PS)}_n\text{-polyDVB}$ multiarm star block copolymer (Figure 4.9).

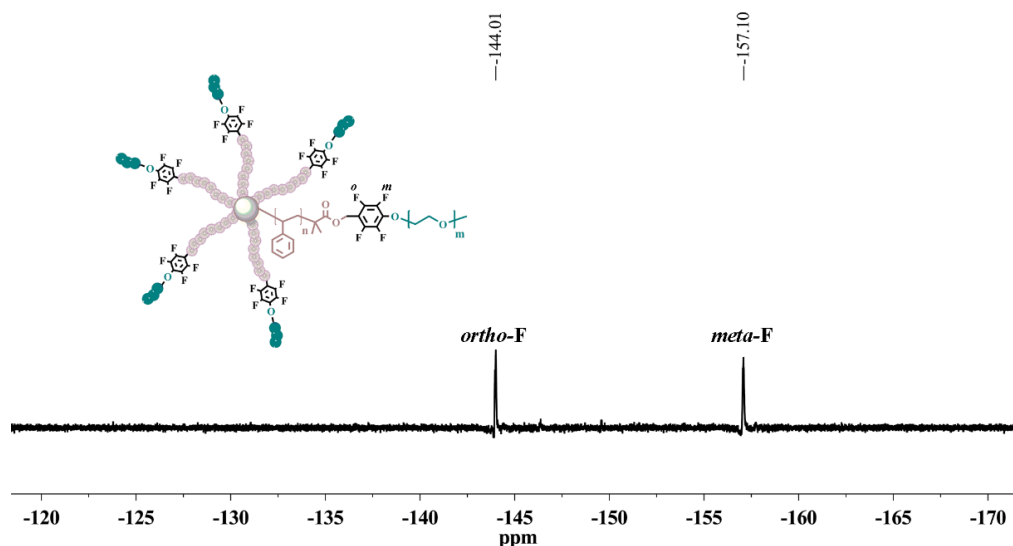


Figure 4.9 : ^{19}F NMR spectrum of $(\text{PEG})_m\text{-(PS)}_n\text{-polyDVB}$ multiarm star block copolymer in CDCl_3 .

In order to determine the absolute molecular weight of the $(\text{PEG})_m\text{-(PS)}_n\text{-polyDVB}$ multiarm star block copolymer, firstly the dn/dc value of the linear precursors of PS

and PEG were measured by TD-GPC instrument and found to be 0.185 mL/g and 0.078 mL/g, respectively. Meanwhile, it was shown that dn/dc value correlates linearly with composition of block copolymer in equation 4.4, given in literature [207].

$$(dn/dc)_{\text{block copolymer}} = x (dn/dc)_{\text{PS}} + y (dn/dc)_{\text{PEG}} \quad (4.4)$$

Where x and y are the weight fractions (w) of PS and PEG blocks from ^1H NMR according to the backbone protons. The weight fractions for the PS and PEG were determined to be 0.96 and 0.04, respectively from NMR. Using these weight fractions, $dn/dc = 0.180$ mL/g of star block copolymer was subsequently calculated. Thus, the obtained dn/dc is then introduced into the Omni-Sec software of TD-GPC for the calculation of M_w , M_p , M_w/M_n and R_h of the multiarm star block copolymer. Table 4.1 summarizes data obtained from both conventional GPC and TD-GPC.

GPC analysis of $(\text{PEG})_m\text{-(PS)}_n\text{-polyDVB}$ multiarm star block copolymer showed a monomodal trace, however, which shifted to higher retention time with respect to that of $(\text{fluoro-PS})_n\text{-polyDVB}$ multiarm star polymer (Figure. 4.10). This may be due to that adsorption of the PEG segment with stationary phase caused a shift to lower molecular weight region.

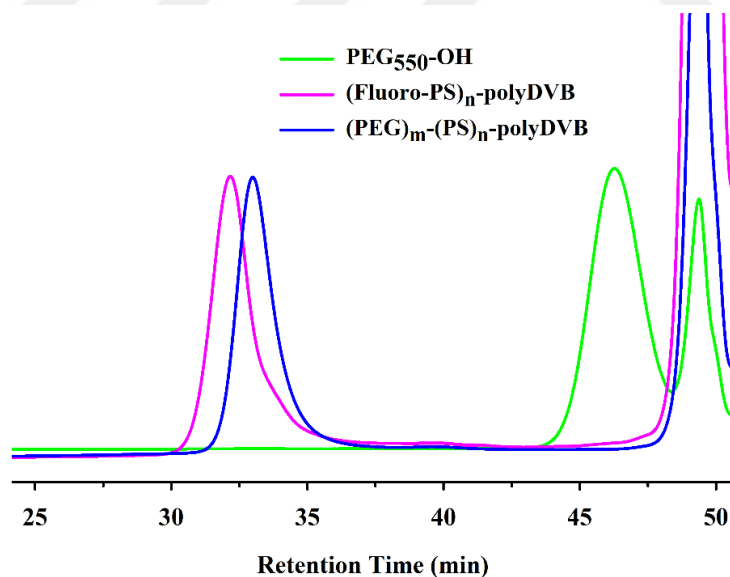
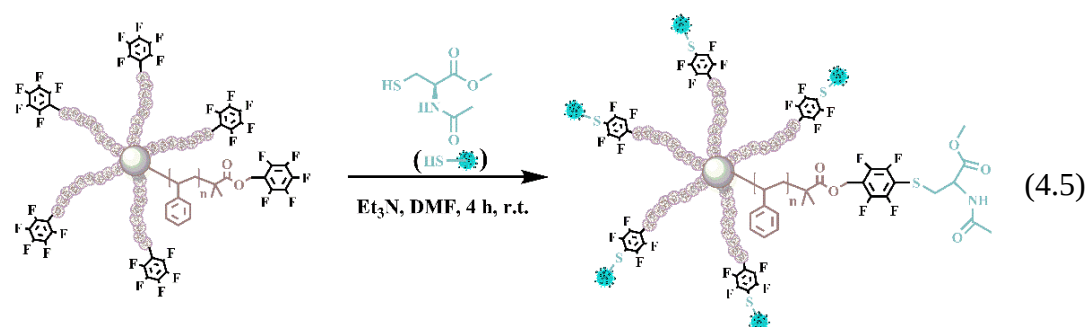


Figure 4.10 : GPC traces of $(\text{PEG})_m\text{-(PS)}_n\text{-polyDVB}$, $(\text{fluoro-PS})_n\text{-polyDVB}$ multiarm star polymer and linear $\text{PEG}_{550}\text{-OH}$ precursors using RI detector in THF at 30 °C.

In parallel, $(\text{fluoro-PS})_n\text{-polyDVB}$ multiarm star polymer was reacted with *N*-acetyl-*L*-cysteine methyl ester in the presence of Et_3N for 4 h at room temperature (Scheme

4.5). In this case, an excess of thiol compound (1.25 equiv. per arm) was employed with respect to that of multiarm star polymer.



^1H NMR spectroscopy indicated that new signals corresponding to the CHNH , $\text{CH}_3\text{OC}=\text{O}$, NCHCH_2S , and $\text{CH}_3\text{C}=\text{O}$, at 4.83, 3.61, 3.12, 1.85 ppm, respectively confirmed the structure of cysteine functionalized multiarm star polymer ((cysteine-PS) $_n$ -polyDVB) (Figure 4.11).

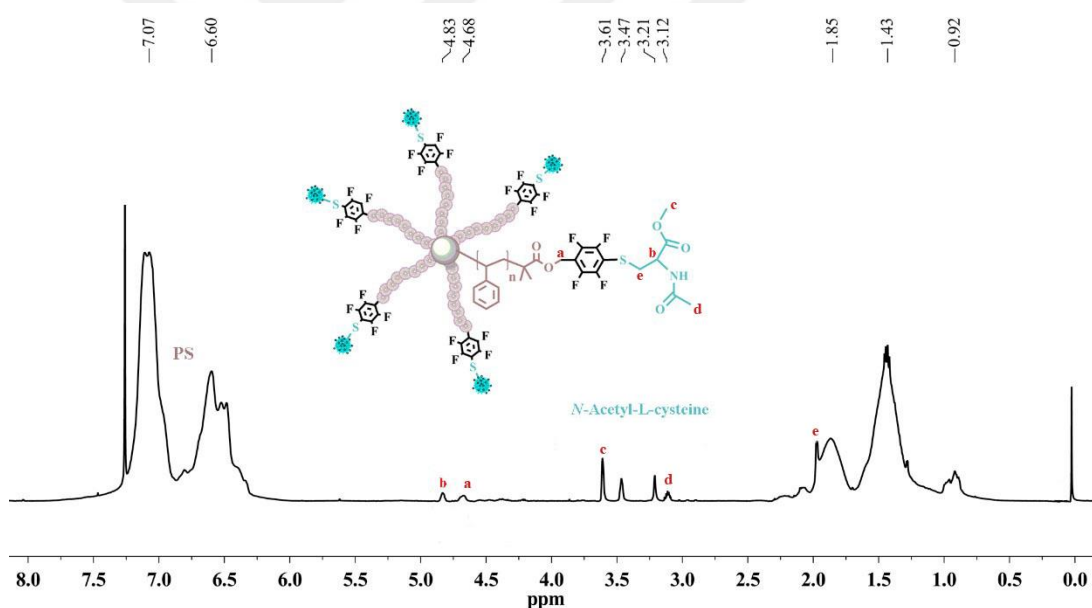


Figure 4.11 : ^1H NMR spectrum of (cysteine-PS) $_n$ -polyDVB multiarm star polymer in CDCl_3 .

Further evidence for (cysteine-PS) $_n$ -polyDVB multiarm star polymer formation was obtained by ^{19}F NMR spectroscopy (Figure 4.12). The completely disappearance of *para*-fluoro atoms at -153.15 ppm suggested that the efficiency and selectivity of the thiol-*para*-fluoro “click” reaction. Moreover, new *ortho* and *meta* fluoro signals were detected at -133.08 and -141.57 ppm, respectively.

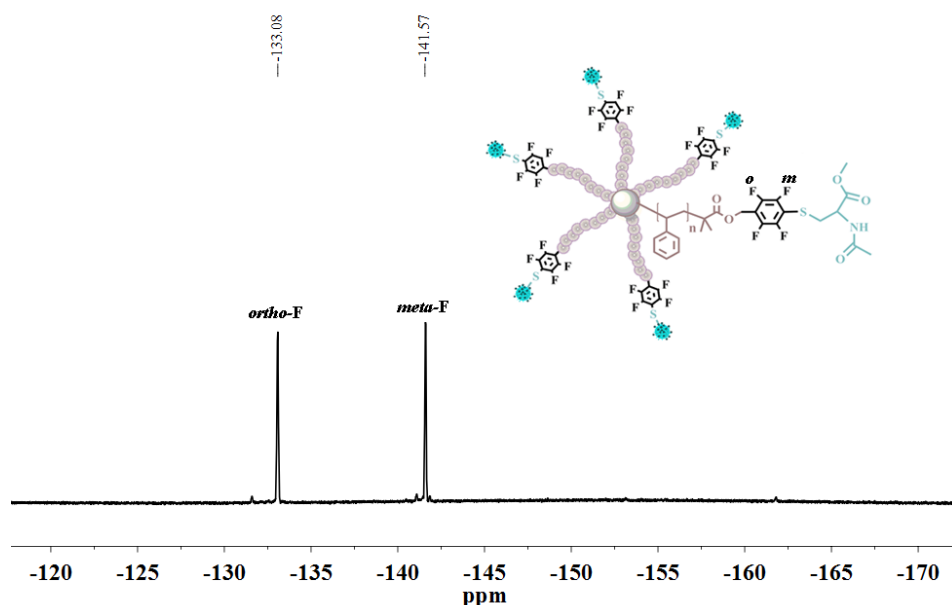


Figure 4.12 : ^{19}F NMR spectrum of (cysteine-PS) $_n$ -polyDVB multiarm star polymer in CDCl_3 .

GPC analysis of (cysteine-PS) $_n$ -polyDVB multiarm star polymer showed broad monomodal traces, which slightly shifted to higher retention time with respect to that of (fluoro-PS) $_n$ -polyDVB multiarm star polymer (Figure 4.13). This broadness might be attributed to supramolecular interaction of cysteine molecules each other.

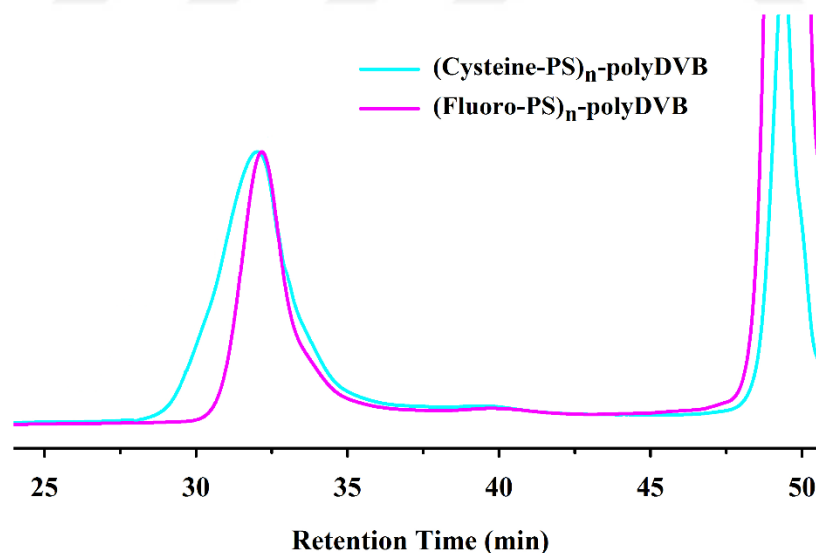


Figure 4.13 : GPC traces of (cysteine-PS) $_n$ -polyDVB and (fluoro-PS) $_n$ -polyDVB multiarm star polymer using RI detector in THF at 30 °C.

Table 4.1 : GPC and TD-GPC characterization of fluoro-end functionalized PS polymer, multiarm star polymer, and post-functionalized multiarm star (co)polymers.

Polymers	GPC ^a			TD-GPC						
	M_n (g/mol)	M_w (g/mol)	M_w/M_n	M_n (g/mol)	M_w (g/mol)	M_w/M_n	$[\eta]$ (dL/g)	R_h (nm)	dn/dc (mL/g)	f^d
α-fluoro-PS^b	5250	5650	1.08	4800	5500	1.13	0.071	1.82	0.185	-
(Fluoro-PS)_n-polyDVB^c	64800	73000	1.12	232000	276000	1.18	0.143	8.39	0.185	37(33) ^e
(PEG)_m-(PS)_n-polyDVB	45800	49900	1.09	266000	294000	1.10	0.129	8.30	0.180 ^f	-
(Cysteine-PS)_n-polyDVB	74240	101381	1.36	358000	425000	1.18	0.124	9.14	0.185	-

^a Determined by using GPC in THF at 30 °C relative to PS standards.

^b $[M]_0:[I]_0:[CuBr]:[PMDETA] = 200:1:1:1$; polymerization was carried out at 110 °C.

^c $[DVB]_0/15 = [\alpha\text{-fluoro-PS}]_0 = [CuBr]_0 = [PMDETA]_0 = 0.020$ M in anisole at 110 °C.

^d Calculated according to equation 4.1.

^e Calculated according to equations 4.2 and 4.3.

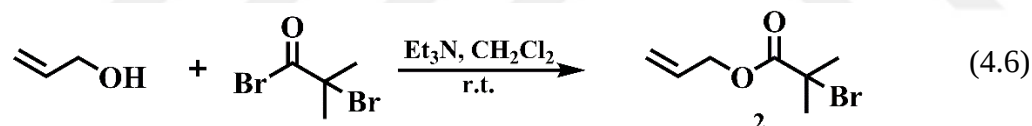
^f Calculated according to equation 4.4.

4.2 Synthesis of Hetero-Functionalized Multiarm Star Polymers via Sequential Thiol-*para*-Fluoro and Thiol-Ene Double Click Reactions

The objective of this study was to design and the synthesis of hetero-functionalized multiarm star polymers with highly efficient click reactions, which have been recently shown to be modular tools for polymer synthesis. For this purpose, a combination of “arm-first” method with sequential double click reactions, involving thiol-*para*-fluoro and radical thiol-ene, is presented as a new and an efficient approach for the synthesis of well-defined hetero-functionalized multiarm star polymer.

Towards this aim, a mixture of fluoro and allyl functional initiators was used in ATRP of St to give a mixture of macroinitiators, then employed in the formation of star polymers via “arm-first” approach. Next, different thiol groups were easily introduced into star polymer via sequential double click reactions.

Previously synthesized fluoro functional initiator (**1**) was also used for this study (Scheme 4.1). Linear allyl functional initiator (**2**) was synthesized through an esterification reaction via a similar method as described before (Scheme 4.6).



The structure was confirmed by ^1H NMR spectrum (Figure 4.14). A shift from 4.10 ppm of vinyl methylene protons of allyl alcohol to 4.68 (m, 2H, $\text{CH}_2\text{OC}=\text{O}$) ppm of methylene protons of **2** due to esterification reaction and singlet peak at 1.96 ppm assigned to $\text{C}(\text{CH}_3)_2\text{-Br}$ clearly indicated that **2** was achieved.

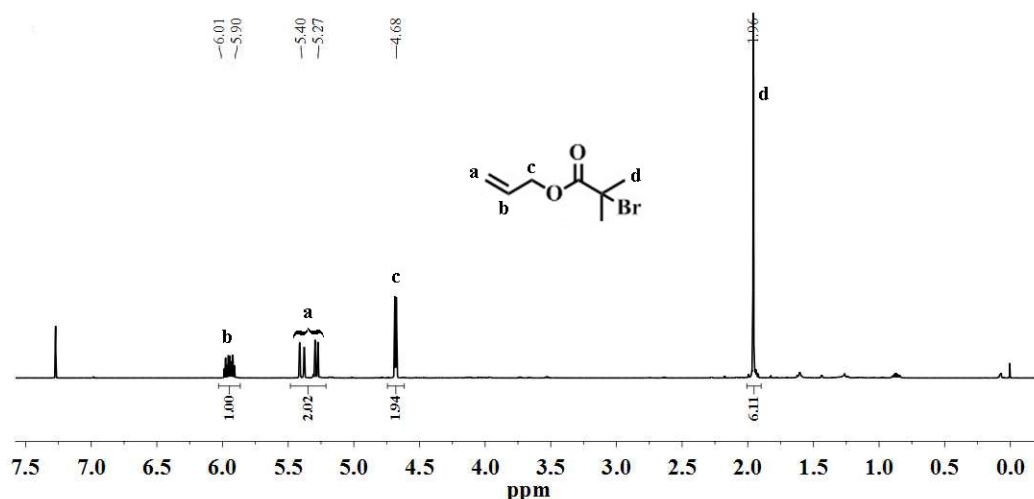
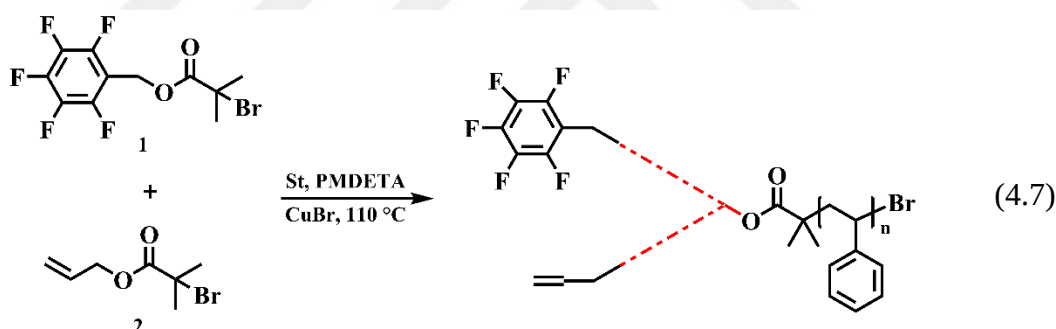


Figure 4.14 : ^1H NMR spectrum of allyl 2-bromo-2-methylpropanoate (**2**) in CDCl_3 .

The preparation of $(\text{fluoro-PS})_m\text{-polyDVB-(allyl-PS)}_m$ multiarm star polymer bearing pentafluoro and allyl functionalities at the periphery starts with the evolution of linear PS via ATRP of St, concurrently initiated by employing equal moles of **1** and **2** (0.435 mmol of each) in the presence of CuBr/PMDETA at $110\text{ }^\circ\text{C}$ for 40 min (Scheme 4.7).



From ^1H NMR spectrum, the percentage of pentafluoro and allyl moieties of linear PS were found to be 53 and 47 mol%, respectively, according to the ratio of integrated areas of allyl ($\text{CH}_2=\text{CH}$) at 5.24-5.08 ppm and CH_2 -fluorobenzyl group at 4.76-4.33 ppm (Figure 4.15).

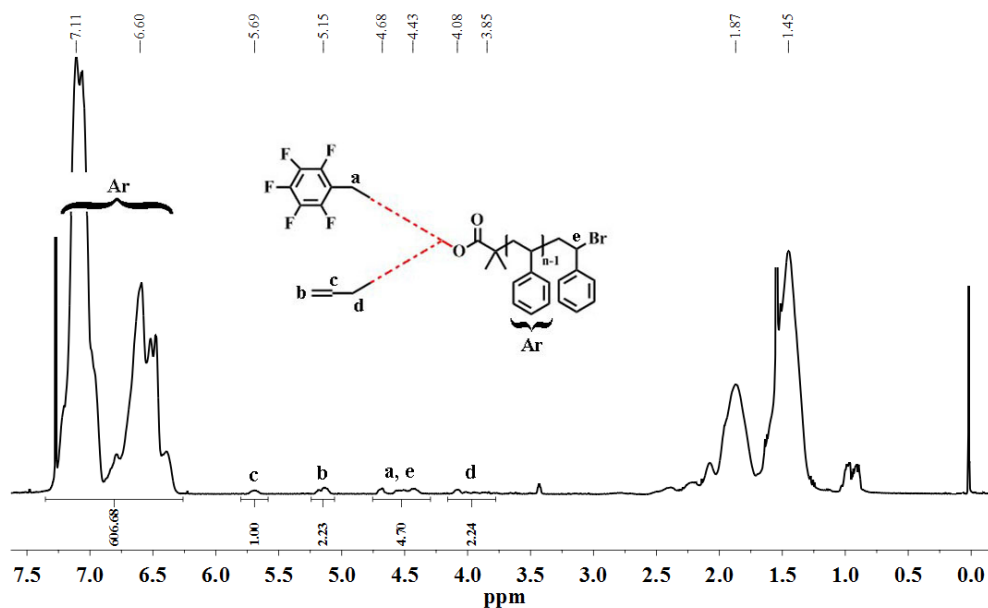


Figure 4.15 : ^1H NMR spectrum of mixture of linear α -fluoro-PS and α -allyl-PS in CDCl_3 .

Moreover, this ratio was so close to an equimolar feed ratio of **1** to **2** in the ATRP of St. The ^{19}F NMR spectrum of α -fluoro-PS and α -allyl-PS mixture demonstrated the expected three distinct signals around -141.88 (*ortho*), -153.16 (*para*) and -161.82 (*meta*) ppm (Figure 4.16).

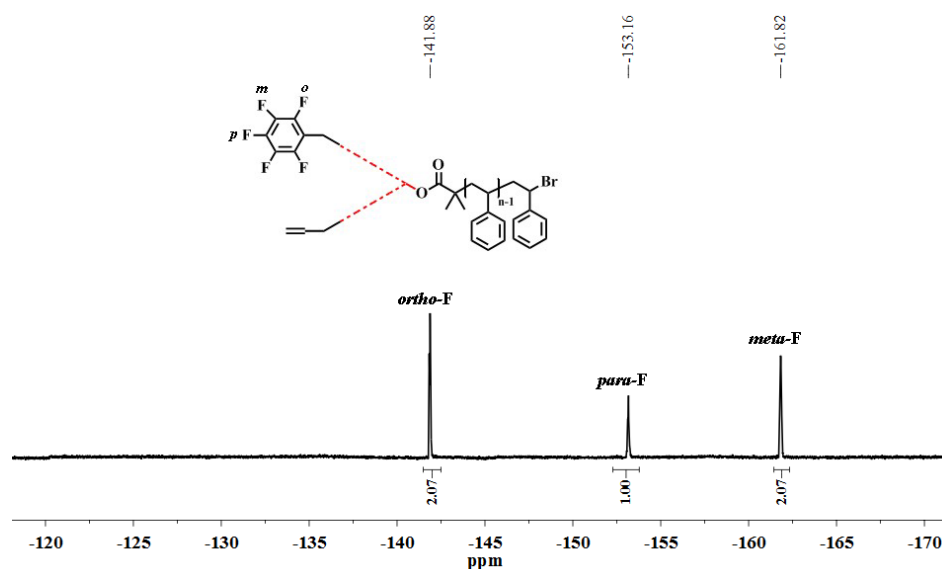
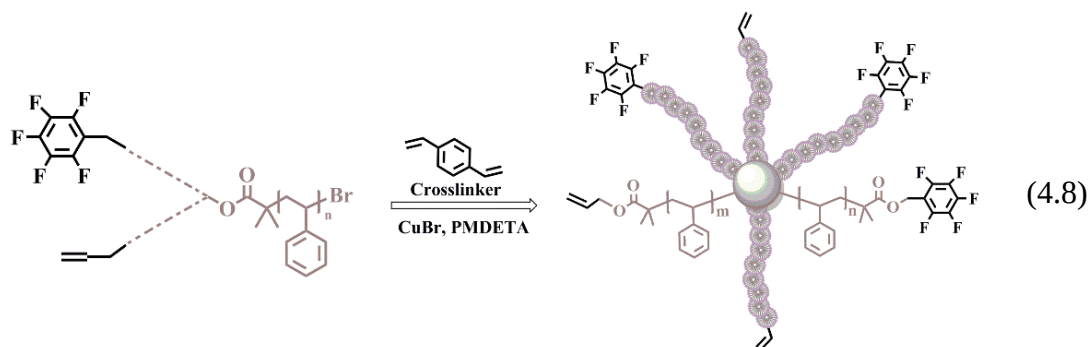


Figure 4.16 : ^{19}F NMR spectrum of mixture of linear α -fluoro-PS and α -allyl-PS in CDCl_3 .

Number average molecular weight ($M_{n,\text{GPC}} = 5200$) and polydispersity index ($M_w/M_n = 1.08$) of the polymer were determined by conventional GPC calibrated with PS standards in THF at 30 °C (Table 4.1) and fit well with those obtained by NMR ($M_{n,\text{NMR}}$

= 5600) and theoretical molecular weight ($M_{n,theo} = 5130$). Then, a mixture of α -fluoro-PS and α -allyl-PS was subsequently used as macroinitiator in ATRP of DVB catalyzed by PMDETA/CuBr at 110 °C for the preparation of (fluoro-PS)_m-polyDVB-(allyl-PS)_m multiarm star polymer (Scheme 4.8).



The progress of the reaction was monitored by GC and GPC via taking samples at specified time intervals. The semilogarithmic plot in Figure 4.17a was linear until 80% DVB conversion. A possible reason for the curvature at higher DVB conversion was that some alkyl bromide initiating sites inside the highly cross-linked polyDVB core became less accessible and less likely to be activated and react with DVB. The reaction was stopped after 17 h at 95% DVB conversion. At the same time, the unreacted DVB was nearly undetectable by GC analysis. The GPC curves at different reaction times are shown in Figure 4.17b. Star polymers were produced from the beginning of the reaction, as evidenced by the large shift of a new GPC elution peak to higher molecular weight region. The (fluoro-PS)_m-polyDVB-(allyl-PS)_m multiarm star polymer was purified by dissolution/precipitation in THF/MeOH-ether, respectively.

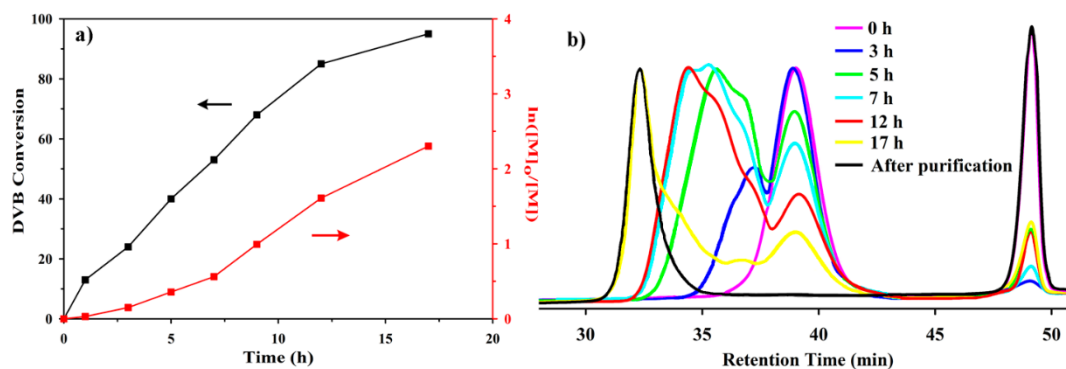


Figure 4.17 : a) Dependence of DVB conversion and $\ln([M]_0/[M])$ on reaction time and b) evolution of GPC traces during synthesis of (fluoro-PS)_m–polyDVB–(allyl-PS)_m star polymer using RI detector in THF at 30 °C. Experimental conditions: $([DVB]_0/15 = [fluoro-PS]_0 = [CuBr]_0 = [PMDETA]_0 = 0.023 \text{ M in anisole at } 110 \text{ °C})$. Linear PS standards were used for calibration of the THF GPC.

The refractive index increment value ($dn/dc=0.185 \text{ mL g}^{-1}$) of the analyzed multiarm star polymer is calculated experimentally and found to be equal to that of linear PS, and after introducing this value to OmniSec software, the absolute molecular weight of the (fluoro-PS)_m–polyDVB–(allyl-PS)_m multiarm star polymer was measured to be ($M_w=222000$) using TD-GPC (Table 4.2). Moreover, the number of arms (f) per molecule of the multiarm star polymer was calculated to be 30 using the equation 4.1 and found to be consistent with that obtained from equations 4.2 and 4.3.

Table 4.2 : The characterization of multiarm star polymer, heterofunctionalized multiarm star polymer, and result of linear polymer used in the synthesis of multiarm star polymer.

Polymers	GPC ^a			TD-GPC					
	M_n (g/mol)	M_w (g/mol)	M_w/M_n	M_n (g/mol)	M_w (g/mol)	M_w/M_n	$[\eta]$ (dL/g)	R_h (nm)	f^d
α-Fluoro-PS + α-allyl-PS^b	5200	5650	1.08	5100	5500	1.08	0.072	1.83	-
(Fluoro-PS)_m-polyDVB-(allyl-PS)_m^c	54000	63600	1.18	182000	222000	1.22	0.136	7.64	30(29) ^e
(Propyl-PS)_m-polyDVB-(allyl-PS)_m	54500	63000	1.15	212000	236000	1.11	0.152	8.18	-
(Propyl-PS)_m-polyDVB-(cysteine-PS)_m	51100	62300	1.22	232700	250500	1.08	0.154	8.40	-

^a Determined by using GPC in THF at 30 °C relative to PS standards.

^b $[M]_0:[I]_0:[CuBr]:[PMDETA] = 200:1:1:1$; polymerization was carried out at 110 °C.

^c $[DVB]_0/15 = [\alpha\text{-allyl-PS} + \alpha\text{-fluoro-PS}]_0 = [CuBr]_0 = [PMDETA]_0 = 0.023$ M in anisole at 110 °C.

^d Calculated according to equation 4.1.

^e Calculated according to equations 4.2 and 4.3.

The ^1H NMR analysis of the multiarm star polymer reveals the same ratios of pentafluoro and allyl moieties at the periphery (53 and 47 mol%, respectively) using similar NMR assignments for the mixture of linear PS given above are realized (Figure 4.18a). Given this percentage, the number of arms per star molecule containing pentafluorophenyl and allyl moieties is calculated to be 16 and 14, respectively. The ^{19}F NMR spectra of the multiarm star polymer exhibited three peaks corresponding to the fluorine atoms at the *ortho* (-141.83 ppm), *para* (-153.08 ppm), and *meta* (-161.76 ppm) positions, respectively (Figure 4.18b).

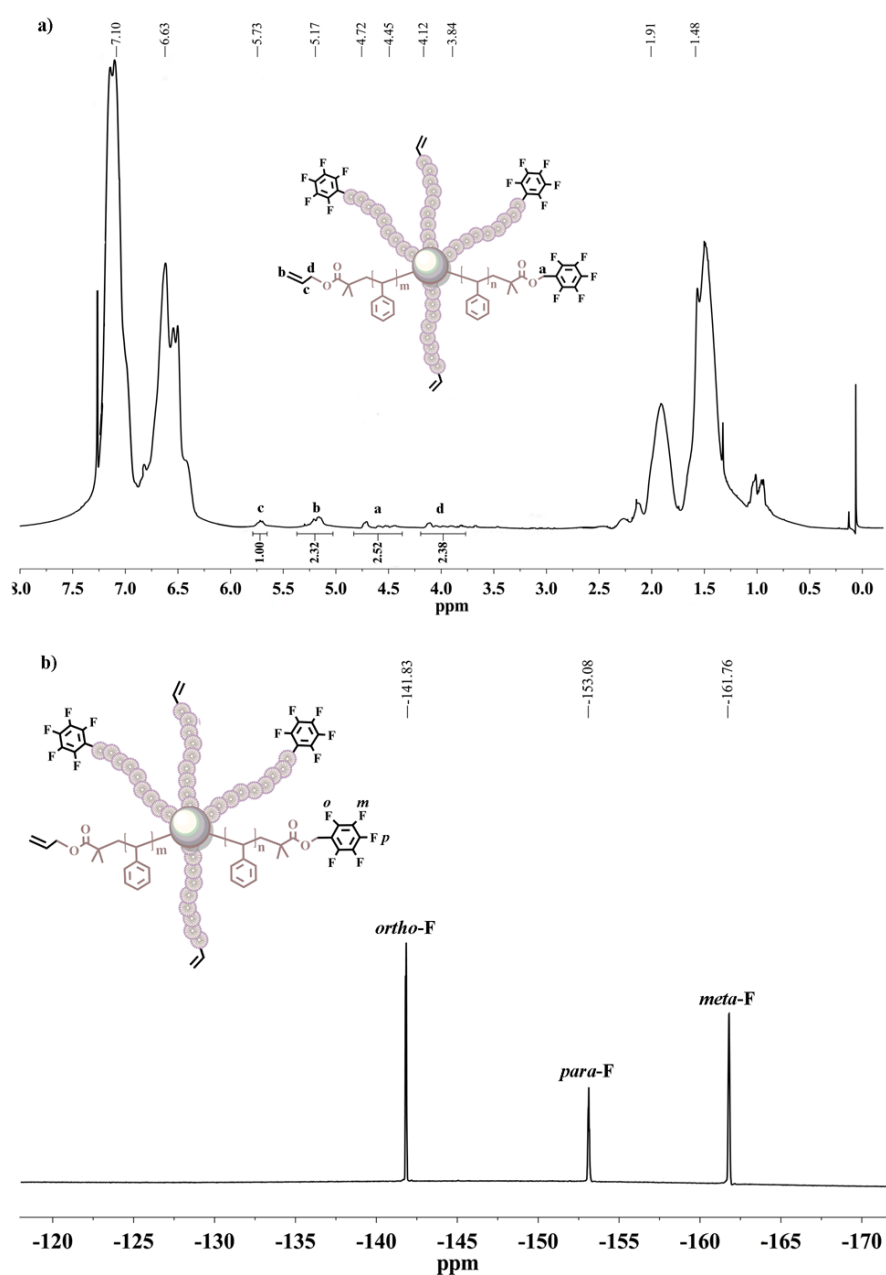


Figure 4.18 : ^1H NMR spectrum (a) and ^{19}F NMR spectrum (b) of (fluoro-PS)_m–polyDVB–(allyl-PS)_m multiarm star polymer in CDCl₃.

Before starting the modification of multiarm star polymer, two model experiments were designed in order to prove the orthogonality of the click reactions. Here, the idea is based on if allyl or pentafluorophenyl (particularly *para* fluorine atom) groups are stable during the nucleophilic substitution or radical addition reactions, respectively, since the reverse of these strategies are already well-known to proceed. To this end first, linear PS with allyl (α -allyl-PS) and pentafluorophenyl (α -fluoro-PS) end groups were prepared. Both reactions were prepared by ATRP of St using CuBr/ PMDETA as catalyst system at 110 °C with **1** (Scheme 4.9) and **2** (Scheme 4.10) as initiators, respectively. All polymerization conditions and results of the linear polymers used in the model reactions were tabulated in Table 4.3.

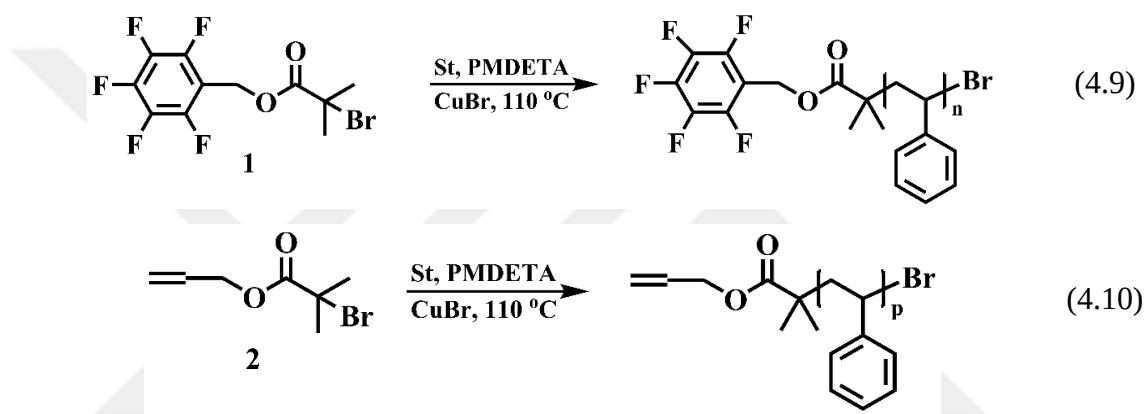


Table 4.3 : The conditions and results of linear polymers used in the model reactions.

Polymer	Ini	Time (min)	Conv. ^b (%)	$M_{n,\text{GPC}}^c$ (g/mol)	M_w/M_n^e	$M_{n,\text{theo}}^d$ (g/mol)	$M_{n,\text{NMR}}$ (g/mol)
α -fluoro-PS ^a	1	30	23	5250	1.08	5100	5800 ^e
α -allyl-PS ^a	2	210	34	7800	1.09	7300	7900 ^f

^a $[M]_0:[I]_0:[\text{CuBr}]:[\text{PMDETA}] = 200:1:1:1$; polymerization was carried out at 110 °C.

^b Determined by gravimetrically.

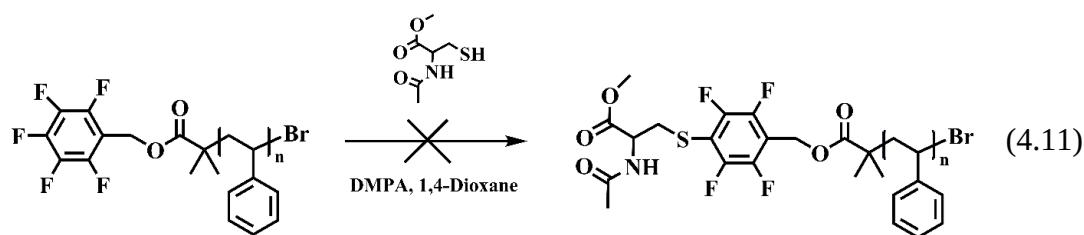
^c Determined by using conventional GPC (RI detection) in THF at 30 °C relative to PS standards.

^d $M_{n,\text{theo}} = ([M]_0/[I]_0) \times \text{conversion \%} \times \text{MW of monomer} + \text{MW of initiator}$.

^e $M_{n,\text{NMR}} = DP_n \times \text{conversion \%} \times \text{MW of monomer} + \text{MW of initiator}$. (DP_n of α -fluoro-PS was calculated to be 53 by comparing integration areas of signal at 7.17-6.46 (ArH of PS) to that of CH_2 -fluorobenzyl and CH(Ph)-Br at 4.69-4.43 ppm)

^f $M_{n,\text{NMR}} = 7900$ ($M_{n,\text{NMR}} = DP_n \times \text{conversion \%} \times \text{MW of monomer} + \text{MW of initiator}$. (DP_n of allyl-PS was calculated to be 74 by comparing integration areas of signal at 7.44-6.30 (ArH of PS) to that of $\text{CH}_2=\text{CH}$ at 5.70 ppm)

Next, α -fluoro-PS was reacted with *N*-acetyl-L-cysteine methyl ester (5 equiv) along with DMPA as a photoinitiator, irradiated by UV light at wavelength 365 nm for 2 h at room temperature (Scheme 4.11).



After purification, the polymer was characterized by ^{19}F NMR (Figure 4.19a) as well as GPC (Figure 4.19b). Completely identical ^{19}F NMR results, without loss or additional signals particularly related to the *para* position, were detected indicating the fluorine atom at *para* position remained intact during the radical process. Similarly, overlay GPC traces of α -fluoro-PS demonstrated no tail or high molecular weight shoulder under this experimental condition.

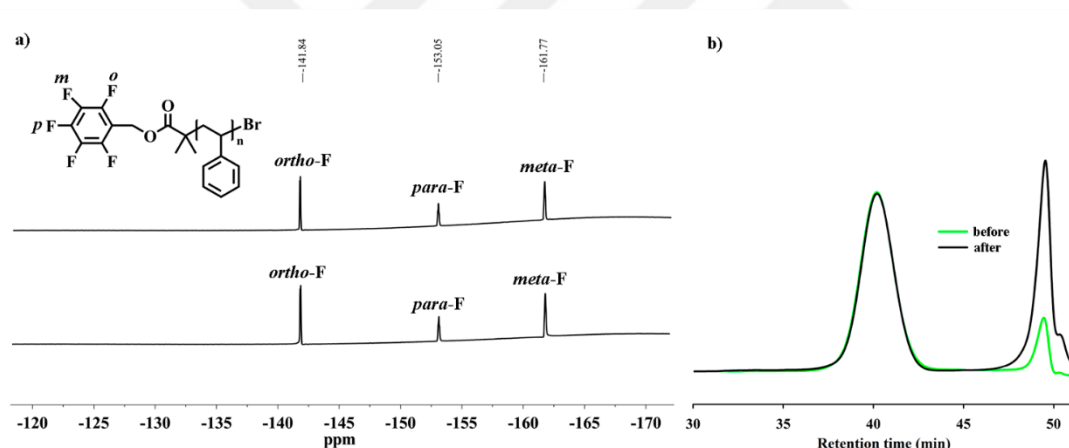


Figure 4.19 : ^{19}F NMR spectra (a) of model α -fluoro-PS before (top) and after (bottom) the reaction with *N*-acetyl-L-cysteine methyl ester. GPC traces (b) of model α -fluoro-PS before (green) and after (black) the reaction with *N*-acetyl-L-cysteine methyl ester.

^1H NMR spectrum showed a small loss of integral values of aromatic protons of PS before and after the radical addition reaction (Figure 4.20). The methine proton next to the bromine end group of PS could be reacted with cysteine molecule under this radicalic conditions.

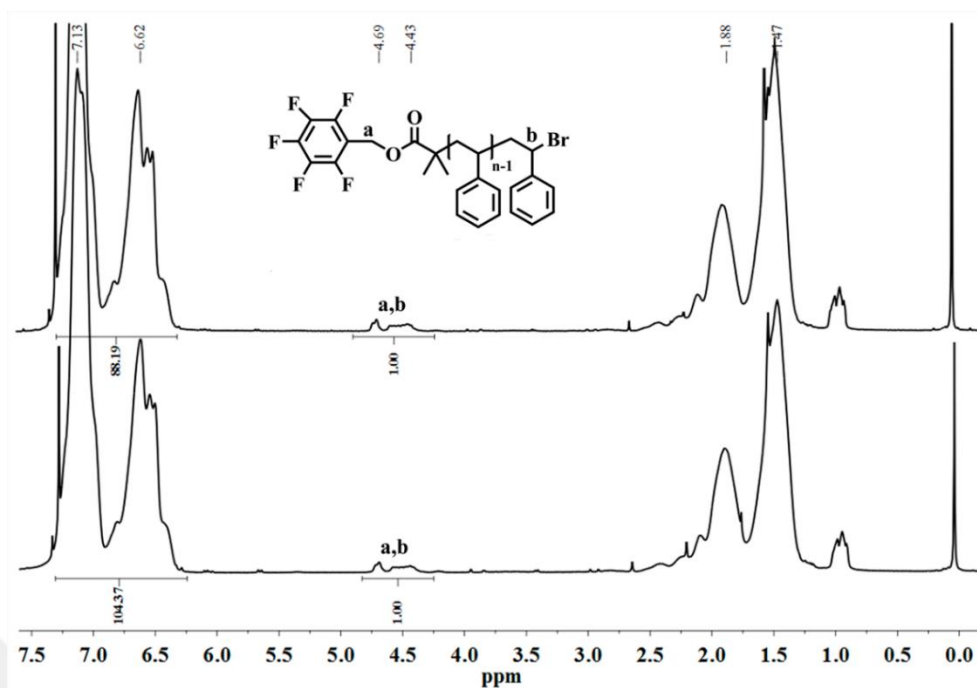
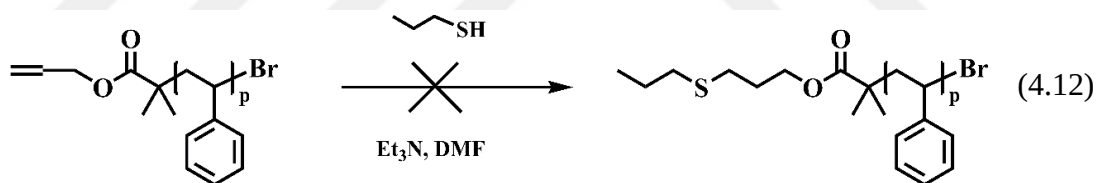


Figure 4.20 : ^1H NMR spectra of α -fluoro-PS before (top) and after (bottom) the model reaction in CDCl_3 .

In parallel, α -allyl-PS was reacted with large excess of 1-propanethiol (10 equiv) and Et_3N (15 equiv) in DMF for 4 h at room temperature (Scheme 4.12).



After purification, the polymer was characterized by ^1H NMR and GPC (Figure 4.21). As can be seen in Figure 4.21a, the integral ratios of allyl proton at 5.70 ppm to the aromatic protons of PS before and after the reaction was almost same suggesting the allyl group was intact during the reaction. However, a small loss of integral values of methine proton next to the bromine end group of PS was observed which could be attributed to the nucleophilic substitution of the bromine with 1-propanethiol under this experimental condition. Moreover, identical GPC traces of α -allyl-PS were obtained before and after the reactions (Figure 4.21b) which also supported the reaction was clear.

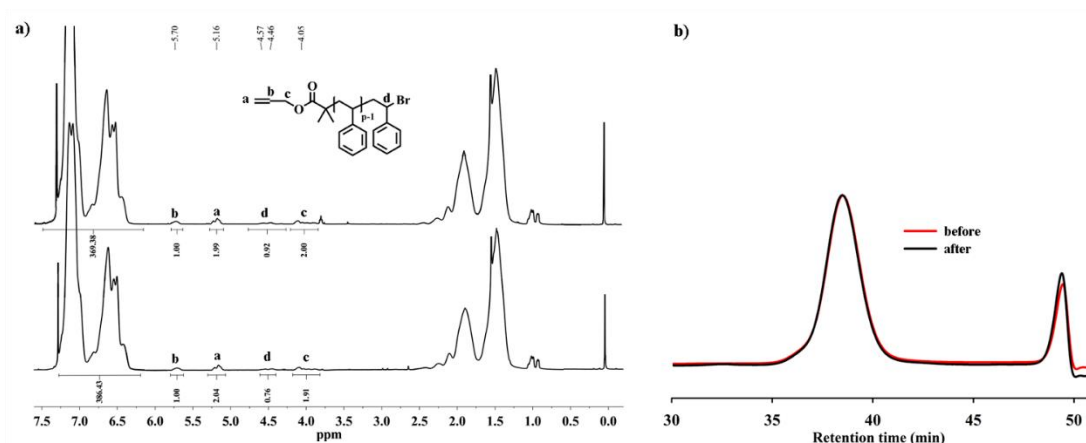


Figure 4.21 : ^1H NMR spectra (a) of model α -allyl-PS before (top) and after (bottom) the reaction with 1-propanethiol. GPC traces (b) of model α -allyl-PS before (red) and after (black) the reaction with 1-propanethiol.

It was concluded from the model experiments that the order of reaction routes, allyl or pentafluorophenyl, was not decisive for the modification of (fluoro-PS) $_m$ -polyDVB-(allyl-PS) $_m$ multiarm star polymer. Thus, multiarm star polymer was first reacted with 1-propanethiol (10 equiv per pentafluorophenyl) in the presence of triethylamine (1.5 fold with respect to 1-propanethiol) through thiol-*para*-fluoro click reaction. The reaction was performed at room temperature in DMF for 4 h. After that time, the solution was precipitated in methanol and purified by re-dissolution in THF and precipitation in methanol, yielding (propyl-PS) $_m$ -polyDVB-(allyl-PS) $_m$ multiarm star polymer. The nucleophilic substitution reaction was achieved with high yields, and the reaction kinetic was monitored online with ^{19}F NMR spectroscopy. As illustrated in Figure 4.22, the three signals related to fluorine atoms at *ortho*, *meta*, and *para* positions were gradually decreased, and completely disappeared after 4 h. Moreover, new *ortho* and *meta* fluoro peaks were detected at -134.35 ppm and -142.45 ppm, respectively (Figure 4.22).

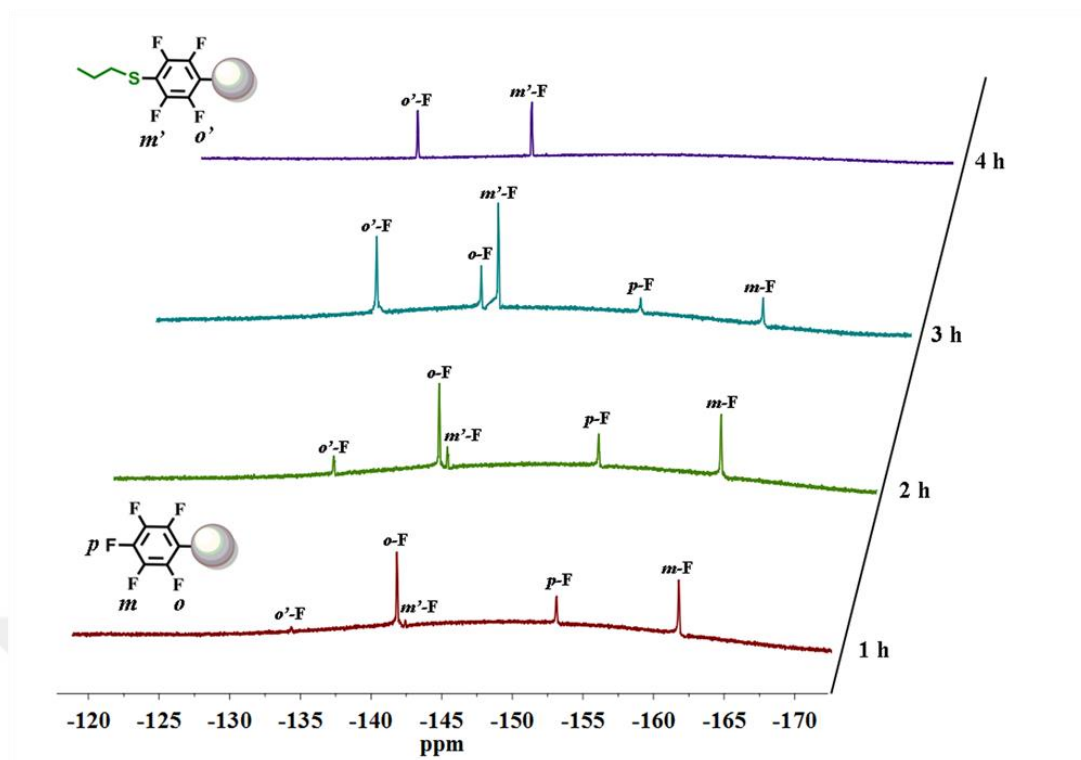


Figure 4.22 : ^{19}F NMR spectra for the online measurement of the thiol-*para*-fluoro click reaction between (fluoro-PS)_m-polyDVB-(allyl-PS)_m multiarm star polymer and 1-propanethiol in CDCl_3 . Purple round represents the all multiarm star polymer except one perfluoro functionality.

Nevertheless, ^1H NMR spectroscopy showed no change in the spectrum after thiol-*para*-fluoro click reaction due to overlap of all aliphatic protons (Figure 4.23).

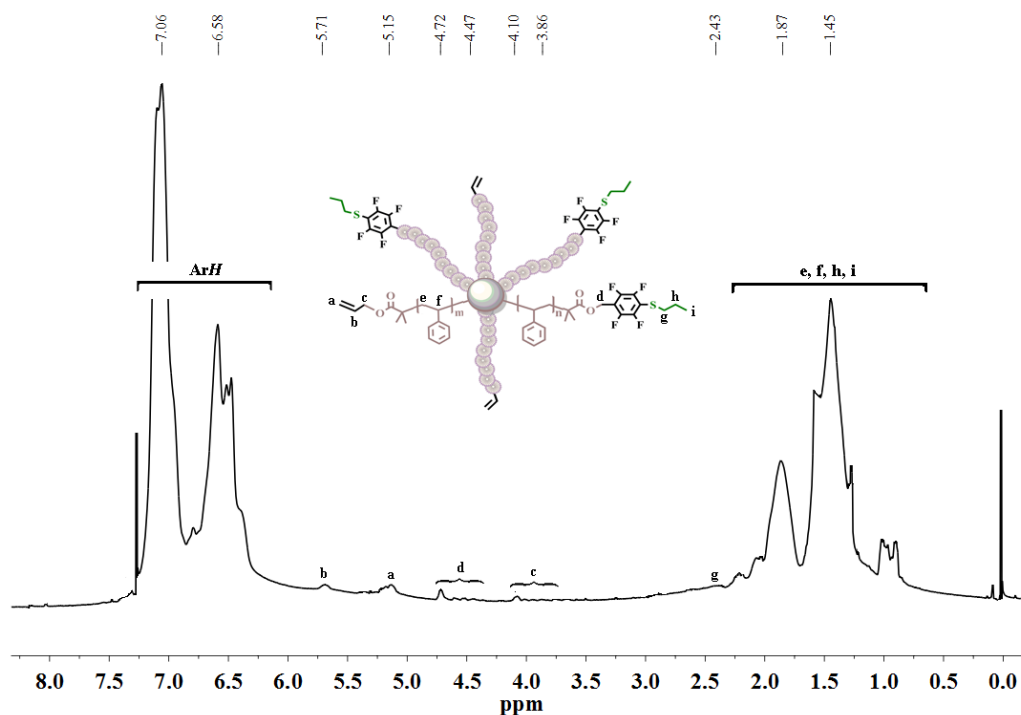


Figure 4.23 : ^1H NMR spectrum of (propyl-PS) $_m$ -polyDVB-(allyl-PS) $_m$ multiarm star polymer after thiol-*para*-fluoro click reaction of (fluoro-PS) $_m$ -polyDVB-(allyl-PS) $_m$ multiarm star polymer and 1-propanethiol in CDCl_3 .

Next, thiol-ene click reaction was performed for the post-functionalization of (propyl-PS) $_m$ -polyDVB-(allyl-PS) $_m$ multiarm star polymer by simply reacting allyl groups at the periphery and *N*-acetyl-L-cysteine methyl ester. The thiol-ene click reaction was carried out in the presence of five fold molar excess of *N*-acetyl-L-cysteine methyl ester with respect to allyl functionality in the star molecule, irradiated by UV light at wavelength 365 nm at room temperature for 2 h using DMPA as a photoinitiator. The ^1H NMR spectrum of the obtained hetero-functionalized (propyl-PS) $_m$ -polyDVB-(cysteine-PS) $_m$ multiarm star polymer is given in Figure 4.24. The complete disappearance of the allyl signals at 5.71 and 5.15 ppm and the appearance of new signals corresponding to the CHNH , $\text{CH}_3\text{OC}=\text{O}$, NCHCH_2S , SCH_2CH_2 , and $\text{CH}_3\text{C}=\text{ONH}$ at 4.81, 3.76, 2.93, and 2.39 ppm, confirms the new structure.

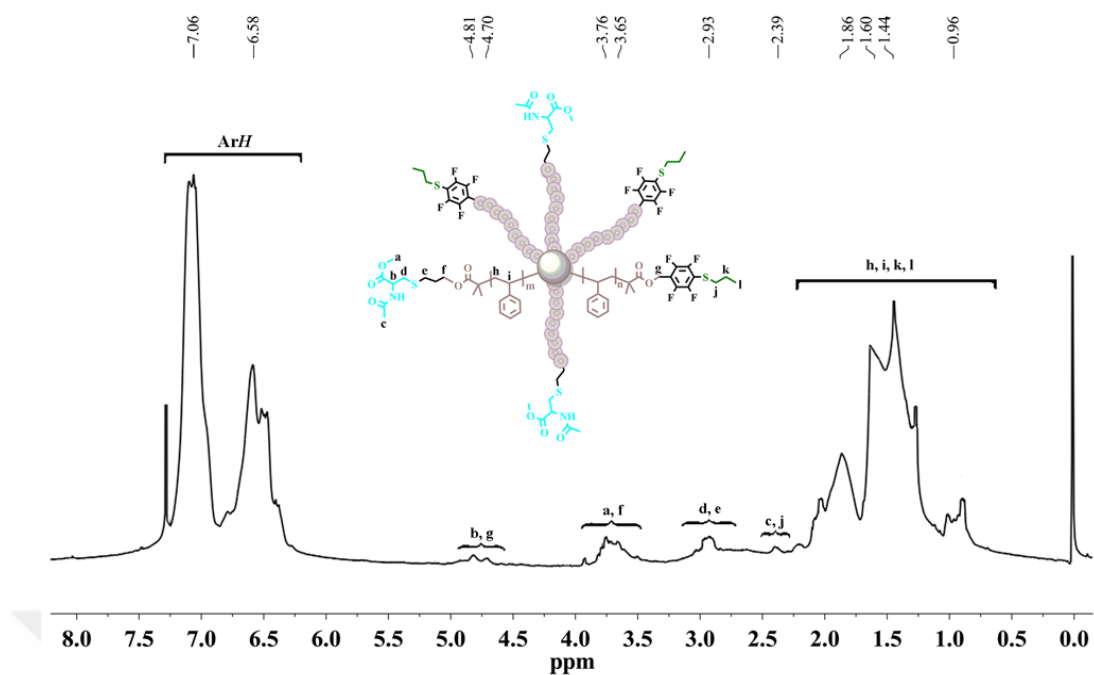


Figure 4.24 : ^1H NMR spectrum of hetero-functionalized (propyl-PS) $_m$ -polyDVB-(cysteine-PS) $_m$ multiarm star polymer in CDCl_3 .

Besides, ^{19}F NMR spectroscopy demonstrated no change in the spectrum, indicating that the *ortho*-F and *meta*-F groups were stable during radical thiol-ene reaction (Figure 4.25).

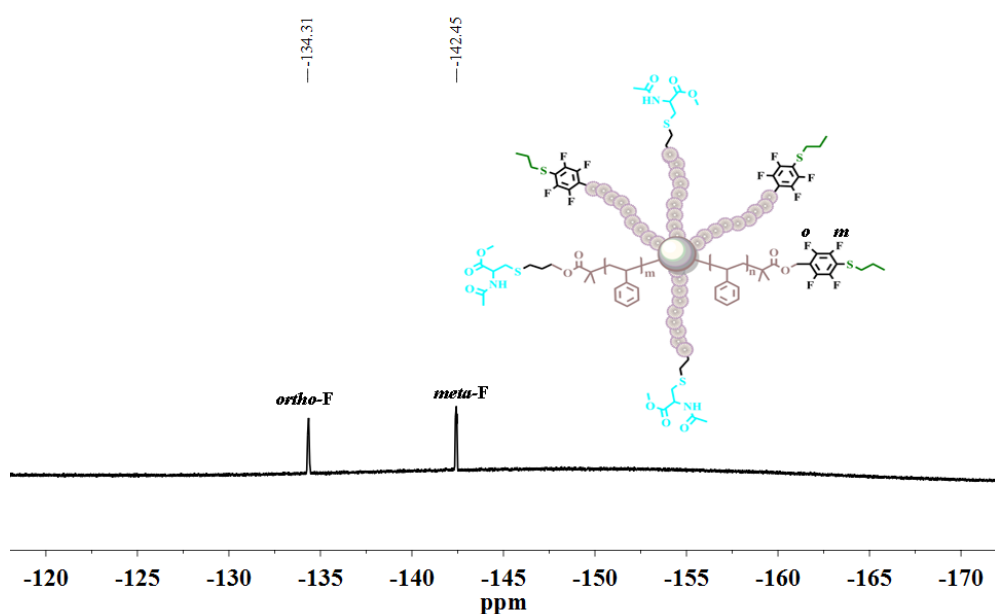


Figure 4.25 : ^{19}F NMR spectrum of hetero-functionalized (propyl-PS) $_m$ -polyDVB-(cysteine-PS) $_m$ multiarm star polymer in CDCl_3 .

Moreover, the absolute molecular weights of multiarm star polymers as well as linear PS are collected in Table 4.2 and the corresponding GPC overlay traces are given in

Figure 4.26. After the click reactions a slight increase in M_w values of (propyl-PS)_m-polyDVB-(allyl-PS)_m and (propyl-PS)_m-polyDVB-(cysteine-PS)_m multiarm star polymers was detected from TD-GPC results. The former was found to be ($M_w=236000$) and the latter was ($M_w=250500$) using same dn/dc value (0.185 mL g^{-1}) as in unfunctionalized multiarm star polymer.

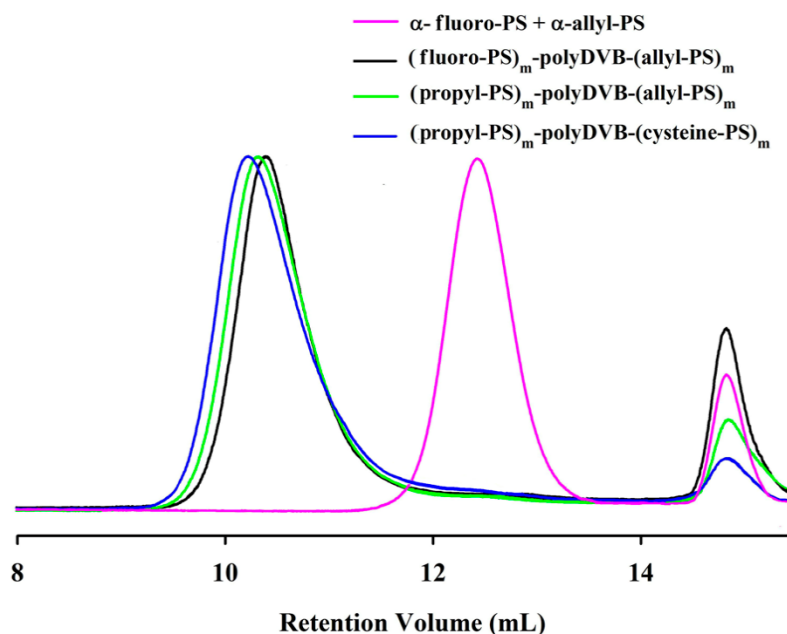


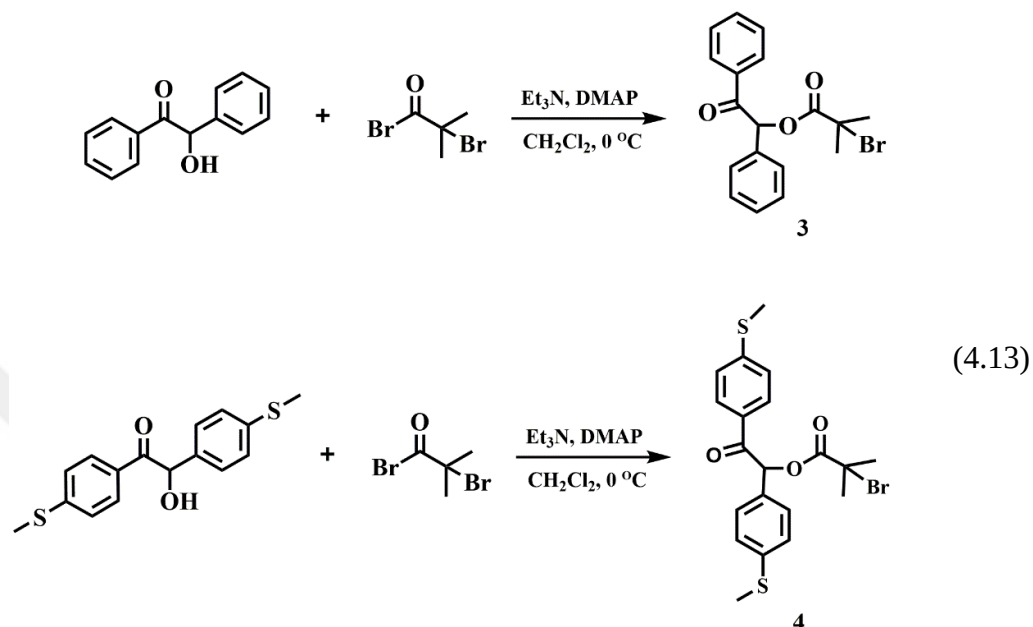
Figure 4.26 : Overlay TD-GPC traces of α -fluoro-PS + α -allyl-PS (pink), (fluoro-PS)_m-polyDVB-(allyl-PS)_m multiarm star polymer (black), (propyl-PS)_m-polyDVB-(allyl-PS)_m multiarm star polymer (green) and hetero-functionalized (propyl-PS)_m-polyDVB-(cysteine-PS)_m multiarm star polymer (blue).

4.3 Synthesis of Multiarm Star Polymer as Novel Polymeric Photoinitiator for Free Radical Polymerization

The initial objective of this work was to design polymeric photoinitiators, with benzoin and its derivative (MTB) containing alkyl bromide(s) so as to produce photo-functionalized polymers. For this aim, benzoin and MTB functional PS (benzoin-PS and MTB-PS) were prepared by ATRP of St and used as macroinitiators in a cross-linking reaction with DVB to yield multiarm star homopolymers with benzoin and MTB periphery, respectively. Obtained (benzoin-PS)_m-polyDVB and (MTB-PS)_p-polyDVB multiarm star polymers were used as polymeric photoinitiators. Photokinetics of 1,6-hexanediol diacrylate (HDDA) with (benzoin-PS)_m-polyDVB and (MTB-PS)_p-polyDVB multiarm star polymers were studied by Photo-DSC. These

polymeric photoinitiators were used in free radical photopolymerization of MMA in air atmosphere.

In the first step, initiators were prepared by the esterification reactions of α -bromoisobutryl bromide with benzoin and 2-hydroxy-1,2-bis(4-(methylsulfanyl)phenyl)-ethanone (MTB), respectively, as shown in Scheme 4.13.



Along with aromatic protons between 7.94 and 7.32 ppm, from ^1H NMR spectrum (Figure 4.27), methine protons adjacent to the phenyl ring and methyl protons next to Br were detected at 6.85 ppm and 2.02 ppm, respectively. These results confirmed that **3** was successfully obtained.

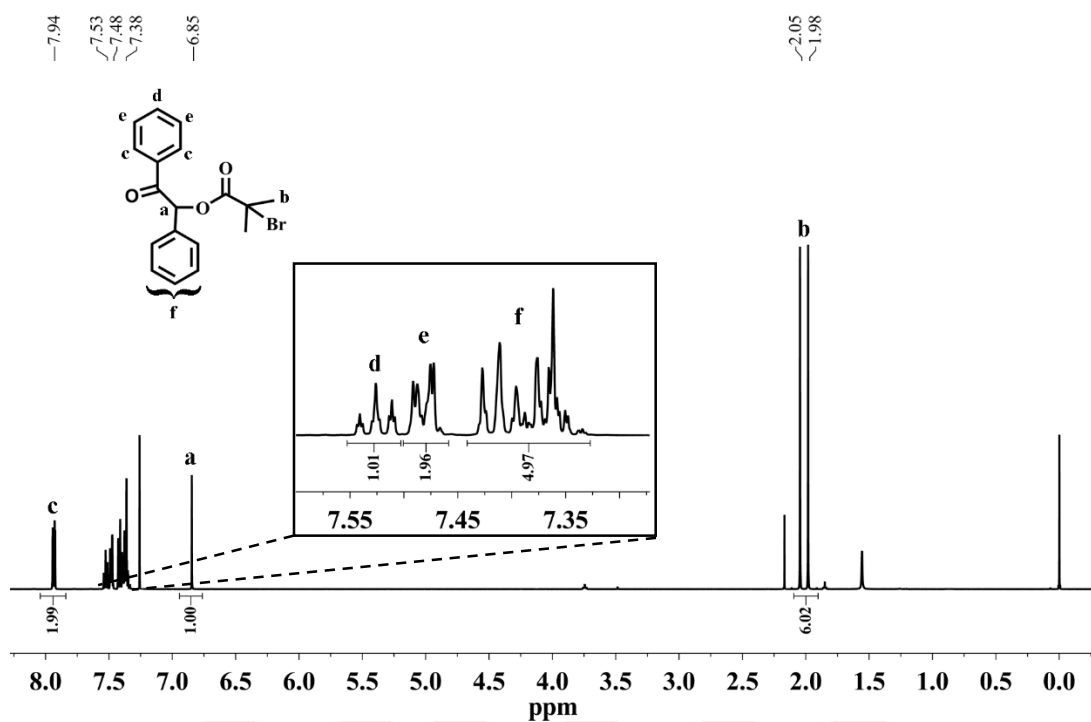
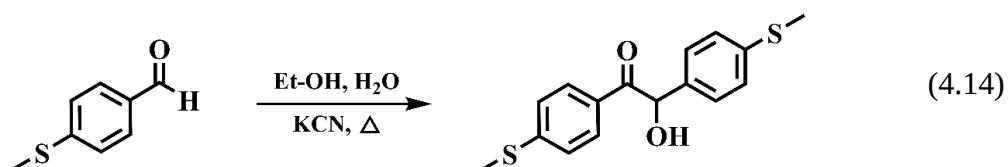


Figure 4.27 : ^1H NMR spectrum of 2-oxo-1,2-diphenylethyl 2-bromo-2-methylpropanoate (**3**) in CDCl_3 .

2-Hydroxy-1,2-bis(4-(methylsulfanyl-phenyl)-ethanone (MTB) was synthesized by YTU by Prof. Dr. Nergis Arsu group (Scheme 4.14) and characterized by ^1H NMR (Figure 4.28).



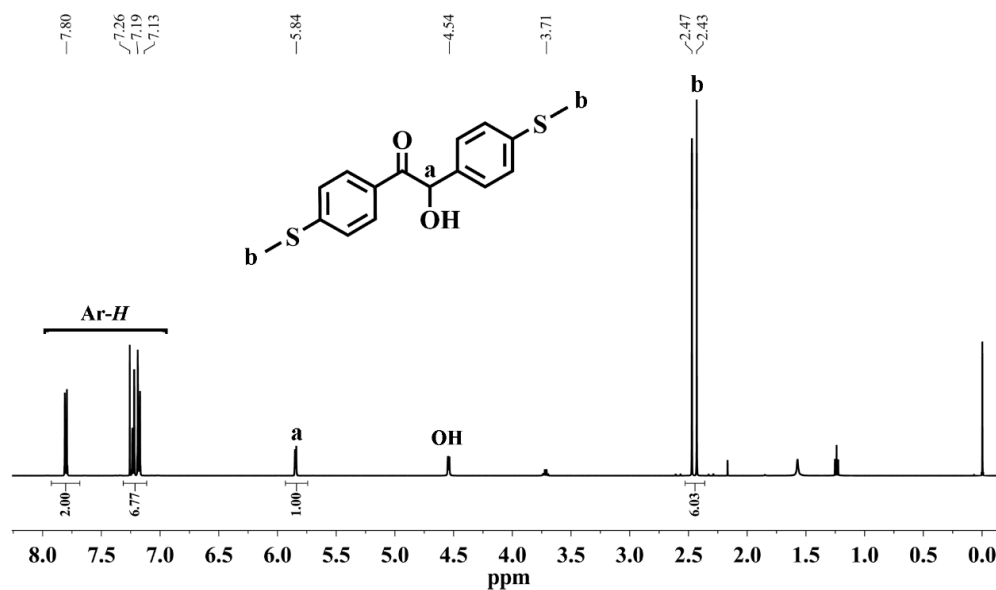


Figure 4.28 : ^1H NMR spectrum of 2-Hydroxy-1,2-bis(4-(methylsulfanyl-phenyl)-ethanone (MTB) in CDCl_3 .

After esterification reaction of MTB, again, the structure of **4** was confirmed by ^1H NMR spectrum (Figure 4.29), a shift from 5.84 ppm to 6.76 ppm of methine protons linked to phenyl ring due to esterification reaction and 2.00 ppm of methyl protons next to Br clearly indicated that **4** was achieved.

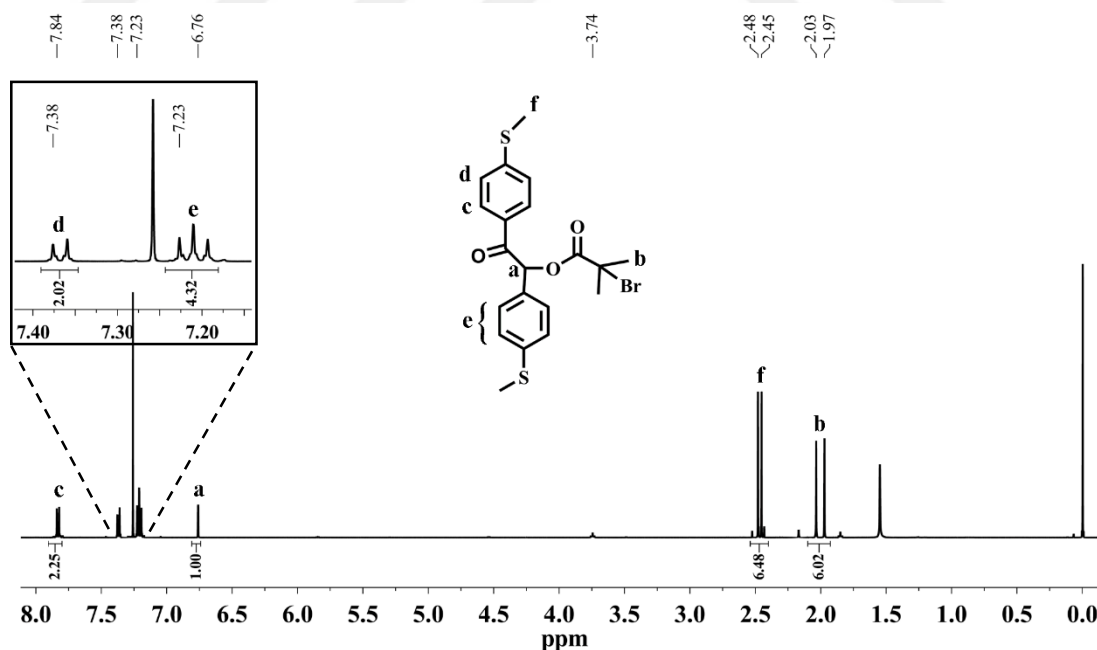
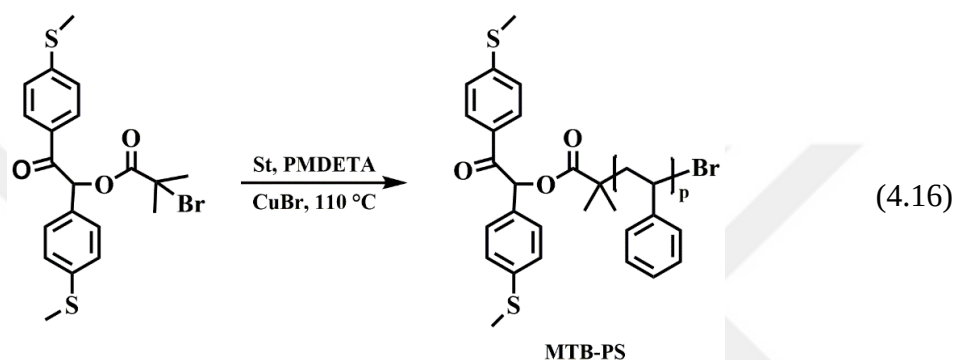
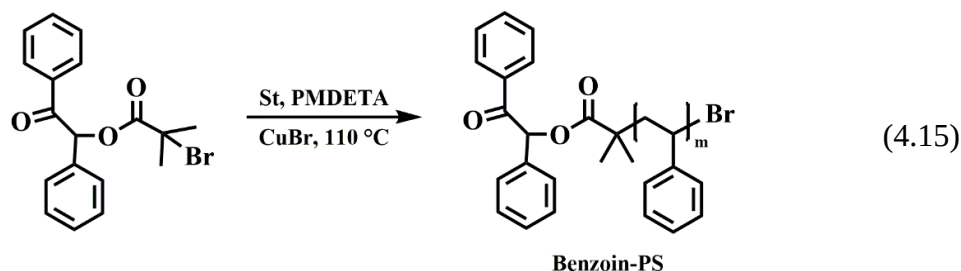


Figure 4.29 : ^1H NMR spectrum of 1,2-bis(4-(methylthio)phenyl)-2-oxoethyl 2-bromo-2-methylpropanoate (**4**) in CDCl_3 .

Next, benzoin-PS (Scheme 4.15) and MTB-PS (Scheme 4.16) were obtained by ATRP of St using **3** and **4** as initiators, respectively. All polymerization conditions and results of the benzoin and MTB functional PS polymers were tabulated in Table 4.4.



Number-average molecular weight calculated by GPC ($M_{n, \text{GPC}}$) of benzoin-PS and MTB-PS were in good agreement with the theoretical one ($M_{n, \text{theo}}$) indicating that no loss of functionality during polymerization. $M_{n, \text{NMR}}$ of benzoin-PS was calculated by comparing of the integrals of the aromatic protons of PS at 7.32-6.23 ppm and that of two protons of benzoin end group at 5.88 ppm (Figure 4.30). Besides, $M_{n, \text{NMR}}$ of MTB-PS was calculated by comparing of the integrals of the aromatic protons of PS at 7.28-6.26 ppm and that of two protons of aromatic H of phenyl groups of MTB at 7.69 ppm, due to overlapped MTB end group (Figure 4.31). Furthermore, the molecular weight of benzoin-PS ($M_{n, \text{UV}} = 5430$) and MTB-PS ($M_{n, \text{UV}} = 6400$) was calculated by employing UV-spectroscopy. From Table 4.4, each polymer showed good agreement between $M_{n, \text{theo}}$, $M_{n, \text{NMR}}$ and $M_{n, \text{GPC}}$ values.

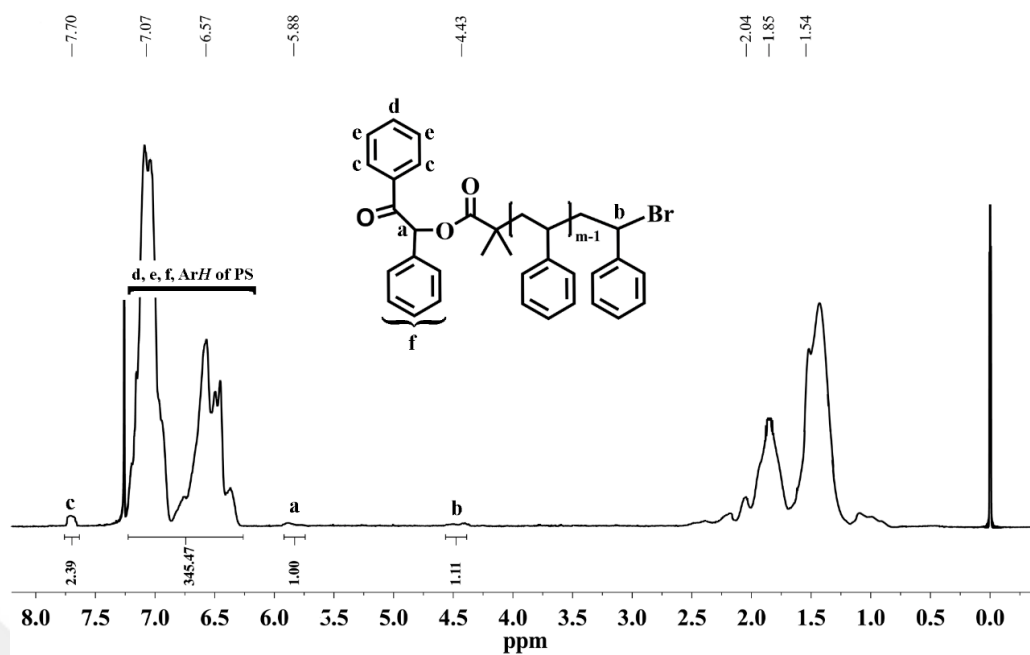


Figure 4.30 : ¹H NMR spectrum of benzoin end-functionalized PS (benzoin-PS) in CDCl₃.

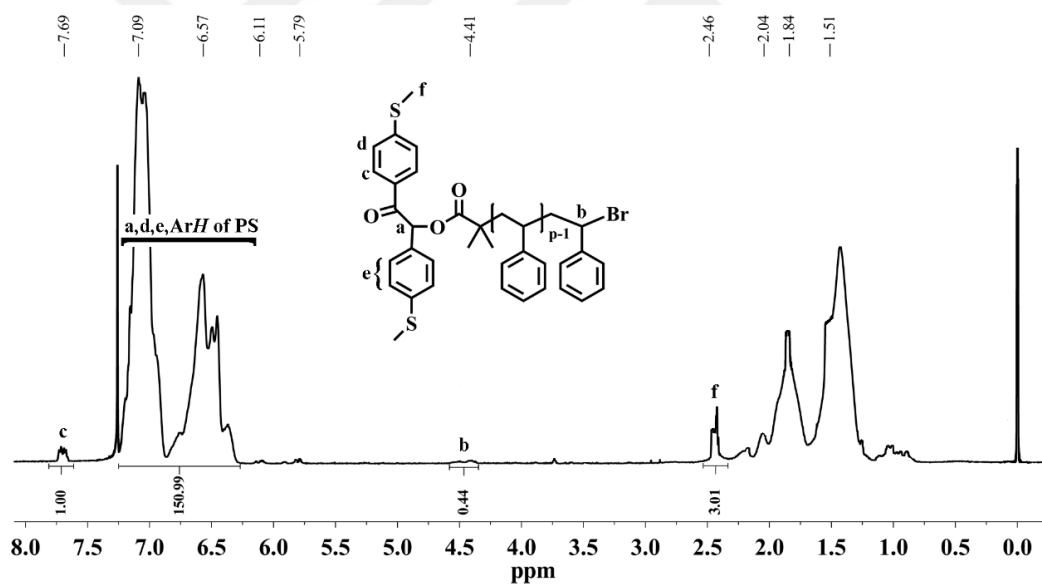


Figure 4.31 : ¹H NMR spectrum of MTB end-functionalized PS (MTB-PS) in CDCl₃.

Table 4.4 : The reaction conditions and results of linear polymers used in the synthesis of benzoin and MTB functional multiarm star polymers.

Polymer	Ini.	Time (min)	Conv. ^b (%)	$M_{n, GPC}^c$ (g/mol)	M_w/M_n	$M_{n, theo}^d$ (g/mol)	$M_{n, NMR}$ (g/mol)	$M_{n, UV}$ (g/mol)
Benzoin-PS^a	3	30	24	5600	1.10	5350	5550	5430 ^e
MTB-PS^a	4	30	25	6000	1.09	5650	5850	6400 ^f

^a $[M]_0:[I]_0:[CuBr]:[PMDETA] = 200:1:1:1$; polymerizations were carried out at 110 °C.

^b Determined by gravimetrically.

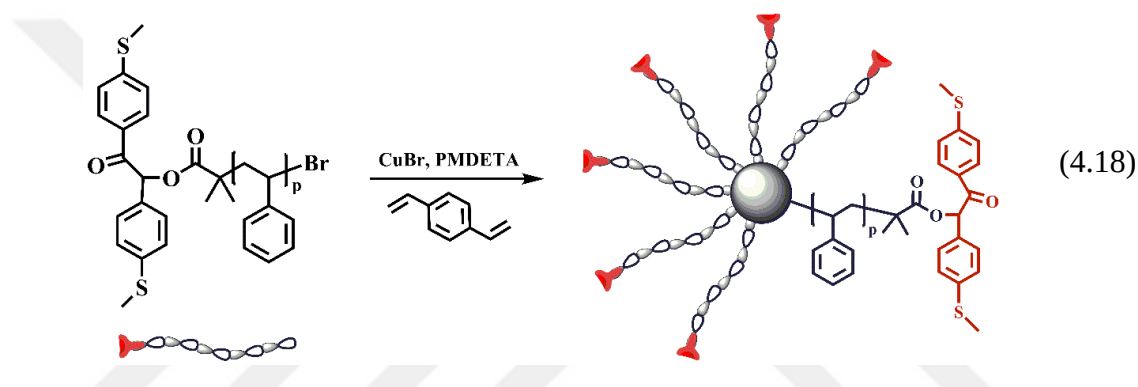
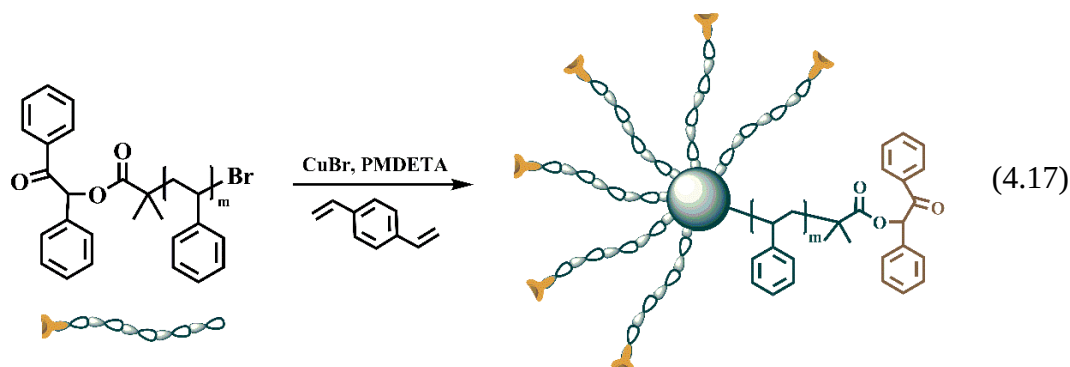
^c Determined by conventional GPC calibrated relative to linear PS standards in THF at 30 °C.

^d $M_{n, theo} = ([M]_0/[I]_0) \times \text{conversion \%} \times \text{molecular weight (MW) of monomer} + \text{MW of initiator}$.

^e Calculated by assuming that molar extinction coefficient (ϵ) of benzoin end group in the obtained polymer was the same as that of **3** ($\epsilon = 18600$ at 249 nm in CH_2Cl_2).

^f Calculated by assuming that molar extinction coefficient (ϵ) of MTB end group in the obtained polymer was the same as that of **4** ($\epsilon = 20670$ at 318 nm in CH_2Cl_2).

The multiarm (Benzoin-PS)_m-polyDVB and (MTB-PS)_p-polyDVB star polymers were obtained by ATRP of DVB in the presence of benzoin-PS (scheme 4.17) and MTB-PS (scheme 4.18) as macroinitiators and CuBr/PMDETA as catalyst at 110 °C.



The star formations were followed by GC and GPC, and terminated after 20 h at 90 % of DVB conversion for (Benzoin-PS)_m-polyDVB and 22 h at 91 % of DVB conversion for (MTB-PS)_p-polyDVB multiarm star polymer. Figure 4.32 shows conventional GPC curves of the homo PS polymers and the purified multiarm star polymers. It was observed that the peak corresponding to the star polymers were shifted to the higher molecular weight regions of the chromatogram. These results clearly indicated that the formation of the multiarm star polymers were achieved. For the purification of multiarm star polymers, they were dissolved in THF and reprecipitated into methanol/diethyl ether mixture (1/2 v/v) to remove unreacted homo PS polymers. The effectiveness of the purification procedure were confirmed by a complete disappearance of benzoin-PS (Figure 4.32a) peak and MTB-PS (Figure 4.32b) peak in an overlaid GPC chromatogram of purified sample in Figure 4.32.

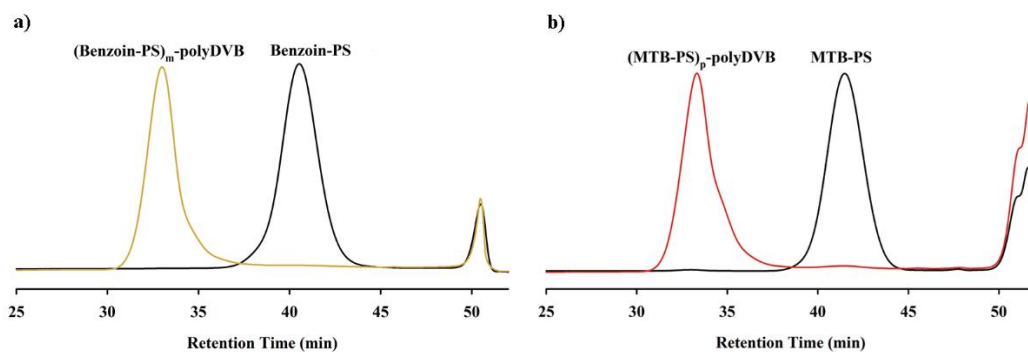


Figure 4.32 : GPC traces of a) benzoin-PS and (benzoin-PS)_m-polyDVB, b) MTB-PS and (MTB-PS)_p-polyDVB in THF at 30 °C.

¹H NMR spectrum showed significant α-chain end functionalities after star formation for both multiarm (benzoin-PS)_m-polyDVB (Figure 4.33) and (MTB-PS)_p-polyDVB star polymers (Figure 4.34).

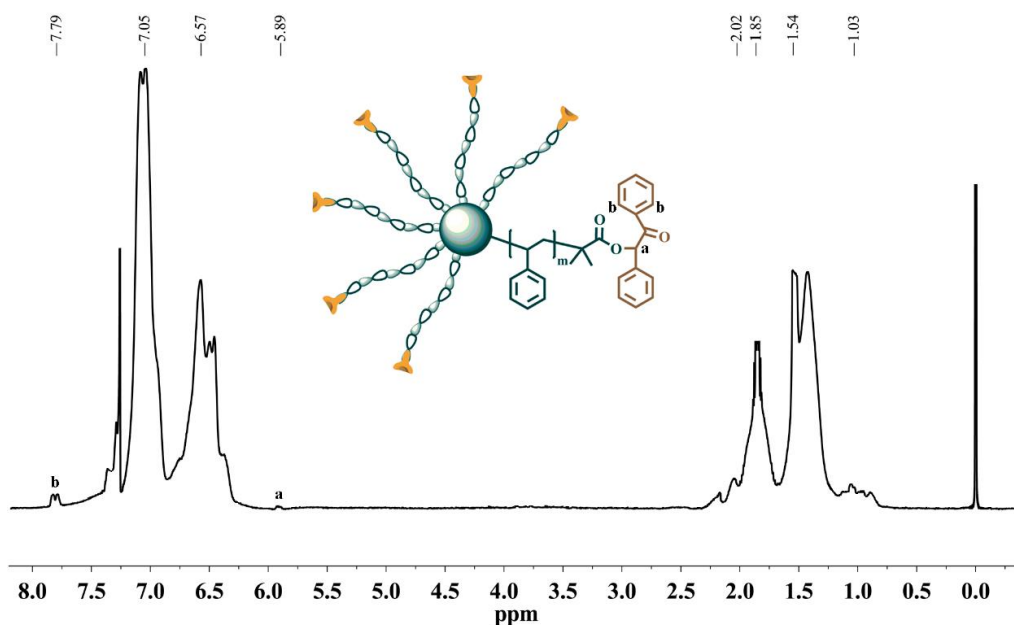


Figure 4.33 : ¹H NMR spectrum of multiarm (benzoin-PS)_m-polyDVB star polymer in CDCl₃.

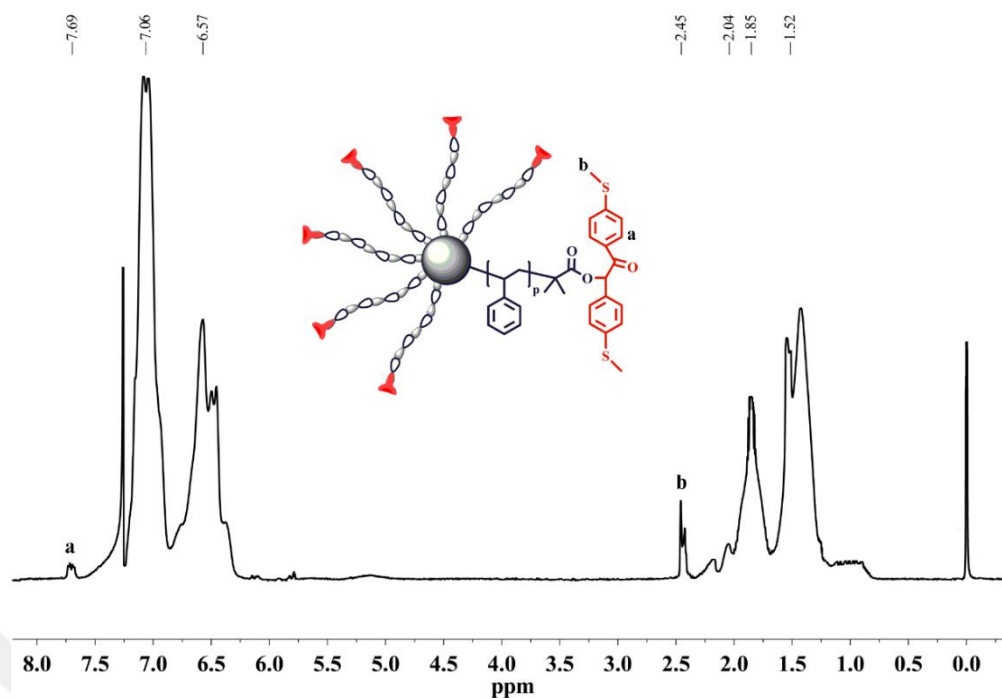


Figure 4.34 : ^1H NMR spectrum of multiarm $(\text{MTB-PS})_p\text{-polyDVB}$ star polymer in CDCl_3 .

TD-GPC traces showed monomodal distributions and weight-average molecular weights ($M_{w,\text{TD-DPC}} = 415000$) and narrow polydispersity ($M_w/M_n = 1.21$) values for $(\text{benzoin-PS})_m\text{-polyDVB}$ and ($M_{w,\text{TD-DPC}} = 305000$) and narrow polydispersity ($M_w/M_n = 1.32$) values for $(\text{MTB-PS})_p\text{-polyDVB}$ were obtained from TD-GPC in THF at 35°C , after introducing $dn/dc = 0.185 \text{ mL/g}$ of linear PS standard to the Omni-Sec software (Table 4.5). Moreover, $R_h = 10.15 \text{ nm}$ and $[\eta] = 0.170$ for $(\text{benzoin-PS})_m\text{-polyDVB}$ and $R_h = 8.78 \text{ nm}$ and $[\eta] = 0.155$ for $(\text{MTB-PS})_p\text{-polyDVB}$ were measured by viscometer detectors in TD-GPC. Consequently, f was calculated to be 46 for $(\text{benzoin-PS})_m\text{-polyDVB}$ and 32 for $(\text{MTB-PS})_p\text{-polyDVB}$, by using equations 4.1, respectively [259].

Table 4.5 : TD-GPC characterization of benzoin and MTB functional multiarm star polymers.

Polymers	TD-GPC ^a					
	M_w/M_n	M_w	$[\eta]$ (dL/g)	R_h (nm)	dn/dc (mL/g)	f^c
(Benzoin-PS)_m-polyDVB^b	1.21	415000	0.170	10.15	0.185	46(38) ^d
(MTB-PS)_p-polyDVB^b	1.32	305000	0.155	8.78	0.185	32(32) ^d

^a Calculated from triple detection GPC (TD-GPC) in THF at 35 °C.

^b [DVB]₀/15 = [benzoin-PS]₀ or [MTB-PS]₀ = [CuBr]₀ = [PMDETA]₀ = 0.020 M in anisole at 110 °C.

^c Calculated according to equation 4.1.

^d Calculated according to equations 4.2 and 4.3.

Obtained multiarm (Benzoin-PS)_m-polyDVB and (MTB-PS)_p-polyDVB star polymers were used as polymeric photoinitiators for the polymerization of mono and multifunctional acrylates. Moreover, photophysical and photochemical properties of these polymeric photoinitiators were investigated by Prof. Dr. Nergis Arsu research group at Yildiz Technical University and photoinitiation mechanism was determined by using laser flash photolysis technique.

The photolysis of multiarm (Benzoin-PS)_m-polyDVB (1.13×10^{-6} M) and (MTB-PS)_p-polyDVB star polymers (2.17×10^{-6} M) in CH₂Cl₂ were followed by detecting spectral changes upon irradiation by medium pressure spot mercury light system. The changes of UV absorption value versus wavelength as a function of irradiation time were recorded. After 450 sec of irradiation, photodecomposition of (MTB-PS)_p-polyDVB star polymer was fully completed whereas photodecomposition of (Benzoin-PS)_m-polyDVB star polymer was fully completed after 480 sec irradiation. These results show that MTB units can absorb the light effectively than benzoin units (Figure 4.35).

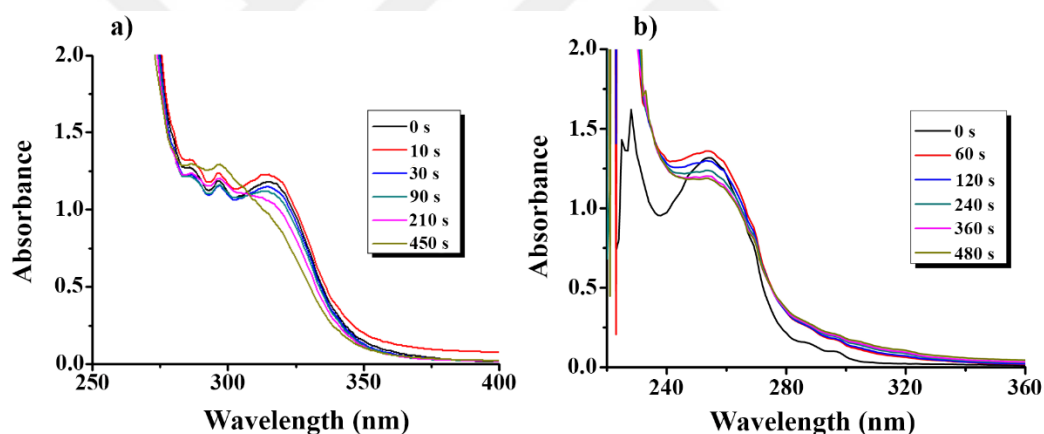
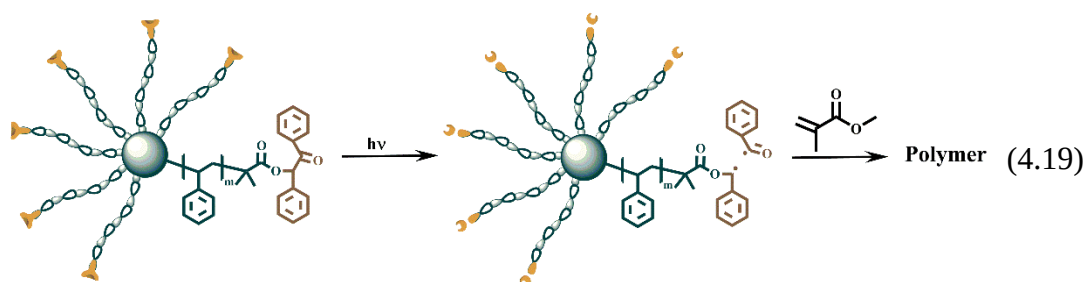
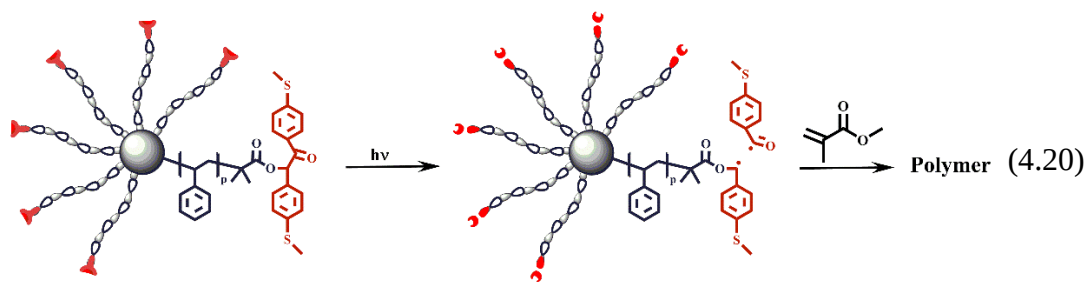


Figure 4.35 : Photolysis of a) multiarm (MTB-PS)_p-polyDVB star polymer (2.17×10^{-6} M) and b) (Benzoin-PS)_m-polyDVB star polymer (1.13×10^{-6} M) in CH₂Cl₂.

Photopolymerization studies of these multiarm star polymers, (Benzoin-PS)_m-polyDVB (scheme 4.19) and (MTB-PS)_p-polyDVB (scheme 4.20), were performed for methyl methacrylate (MMA).





For this aim, monomer, (benzoin-PS)_m-polyDVB star polymer (O.D: 0.5) and benzoin (O.D: 0.5) were dissolved in CHCl₃ and irradiated for 60 min in a photoreactor. Same polymerizations using (MTB-PS)_p-polyDVB star polymer were performed under identical experimental conditions and all results were given in Table 4.6.

Table 4.6 : Photopolymerization of MMA (4.68 mol.L⁻¹) with all photoinitiators at the same O.D.

Photoinitiator	O.D.	Conversion %
(Benzoin-PS) _m -polyDVB	0.5 (288 nm)	4.9
Benzoin	0.5 (288 nm)	3.3
MTB	0.5 (367 nm)	5.9
(MTB-PS) _p -polyDVB	0.5 (367 nm)	8.3

As can be seen from the polymerization results in Table 4.6, despite the optical densities was the same, star polymers have higher conversion values compared to those of their linear counterparts because they have benzoin or MTB units on each arms. (MTB-PS)_p-polyDVB star polymer has the highest conversion % values and secondly MTB has 5.9 % conversion after polymeric photoinitiator.

Photopolymerization of HDDA monomer investigated by using photodifferential scanning calorimeter (photo-DSC) with both (Benzoin-PS)_m-polyDVB and (MTB-PS)_p-polyDVB star polymers for monitor their performance as photoinitiators. Photopolymerization reactions were occurred at different photoinitiator concentrations (0.5% (w/w) and 1% (w/w)) and different light intensities (20 mW/cm² and 40 mW/cm²) at 25 °C and in inert atmosphere (Nitrogen flow: 50 mL/min).

As can be seen from Figure 4.36, it was found that 1% (w/w) photoinitiator concentration works better than 0.5% (w/w) photoinitiator concentration both at 20 mW/cm² light intensity (Figure 4.36a) and 40 mW/cm² light intensity (Figure 4.36b).

Also, it was found that (MTB-PS)_p-polyDVB star polymer (1% w/w and 20 mW/cm² light intensity) has approximately 45% conversion value, when the light intensity was doubled conversion values of acrylate increased and this showed that (MTB-PS)_p-polyDVB star polymer absorbed the light effectively.

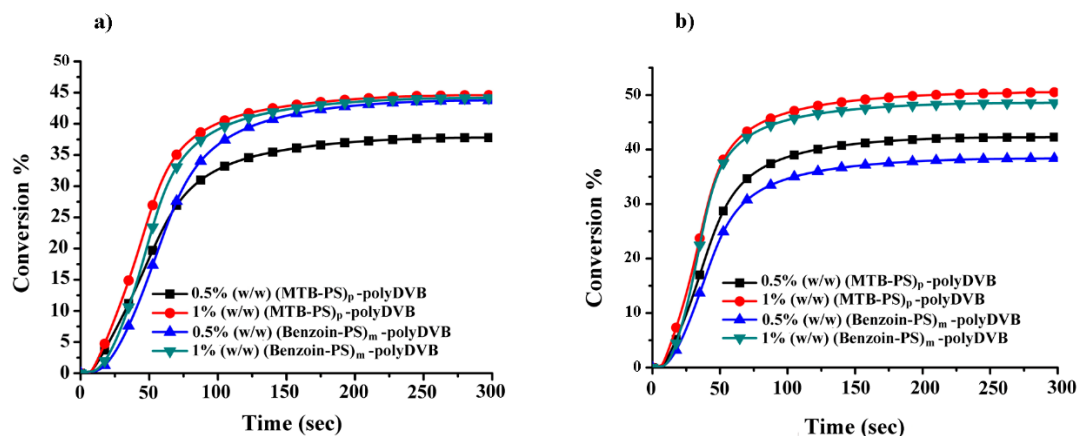


Figure 4.36 : Photo-DSC conversion graphs for polymerization of HDDA using (Benzoin-PS)_m-polyDVB star polymer (0.5% w/w and 1% w/w) and (MTB-PS)_p-polyDVB star polymer (0.5% w/w and 1% w/w) at a) 20 mW/cm² light intensity and b) 40 mW/cm² light intensity.

When we looked at the polymerization rate (Figure 4.37) and heat flow (Figure 4.38) graphs, it can be clearly seen that rate and heat flow values reached higher values for both concentrations as a result of increasing the light intensity.

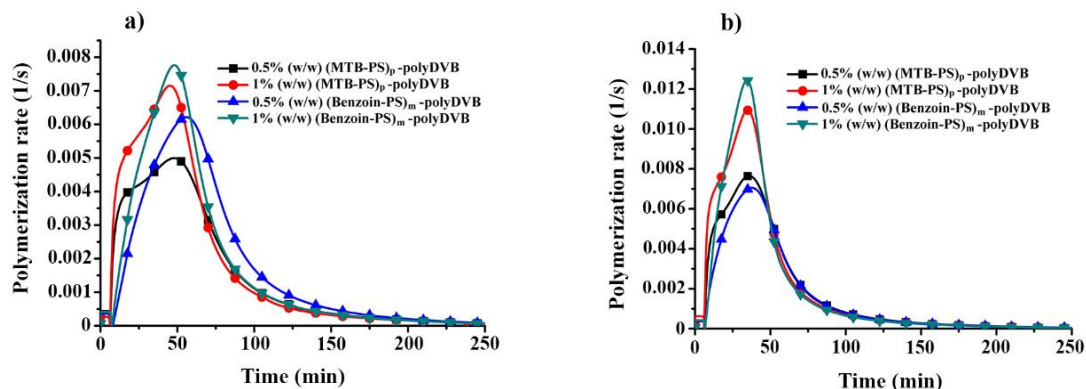


Figure 4.37 : Photo-DSC reaction rates graphs for polymerization of HDDA using (Benzoin-PS)_m-polyDVB star polymer (0.5% w/w and 1% w/w) and (MTB-PS)_p-polyDVB star polymer (0.5% w/w and 1% w/w) at a) 20 mW/cm² light intensity and b) 40 mW/cm² light intensity.

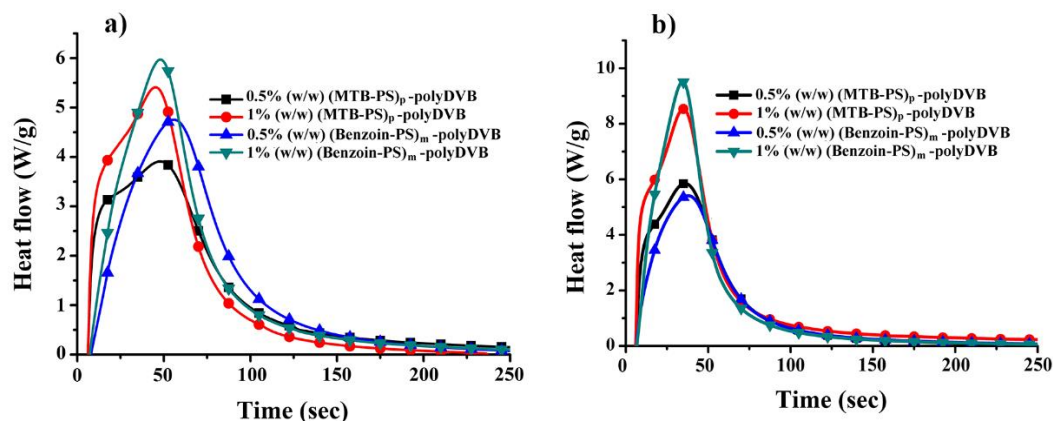


Figure 4.38 : Photo-DSC heat flow graphs for polymerization of HDDA using (Benzoin-PS)_m-polyDVB star polymer (0.5% w/w and 1% w/w) and (MTB-PS)_p-polyDVB star polymer (0.5% w/w and 1% w/w) at a) 20 mW/cm² light intensity and b) 40 mW/cm² light intensity.

4.4 Synthesis of Multiarm Star Block Copolymer Based on “Host-Guest” Inclusion Complexation

In this study, we turned our attention to “host-guest” interactions for obtain multiarm star block copolymers. For this purpose, β -cyclodextrin compound and adamantane were chosen as host and guest molecules, respectively.

Firstly, multiarm star homopolymer with adamantane functionality as reactive periphery groups was prepared by a cross-linking reaction of DVB using adamantane end functionalized PS (ada-PS) as a macroinitiator. Thus, obtained (ada-PS)_n-polyDVB multiarm star polymer was reacted with β -cyclodextrin end functionalized PEG (β -CD-PEG) resulting in the (CD-PEG)_p-(ada-PS)_n-polyDVB multiarm star block copolymer via “host-guest” inclusion complexation.

Firstly, linear adamantane functional initiator (**5**) was obtained through an esterification reaction of 1-adamantanemethanol via α -bromoisobutryl bromide as described before (Scheme 4.19).

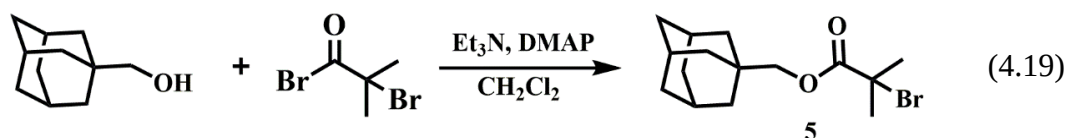


Figure 4.39 shows the ¹H NMR spectrum of initiator **5** in CDCl₃ that could be clearly confirmed via signal assignments. After esterification reaction methylene protons next

to ester unit was shifted to 3.77 ppm, methyl protons next to Br was assigned at 1.96 ppm and characteristic adamantane signals (b-d) appear unchanged at 2.1-1.5 ppm.

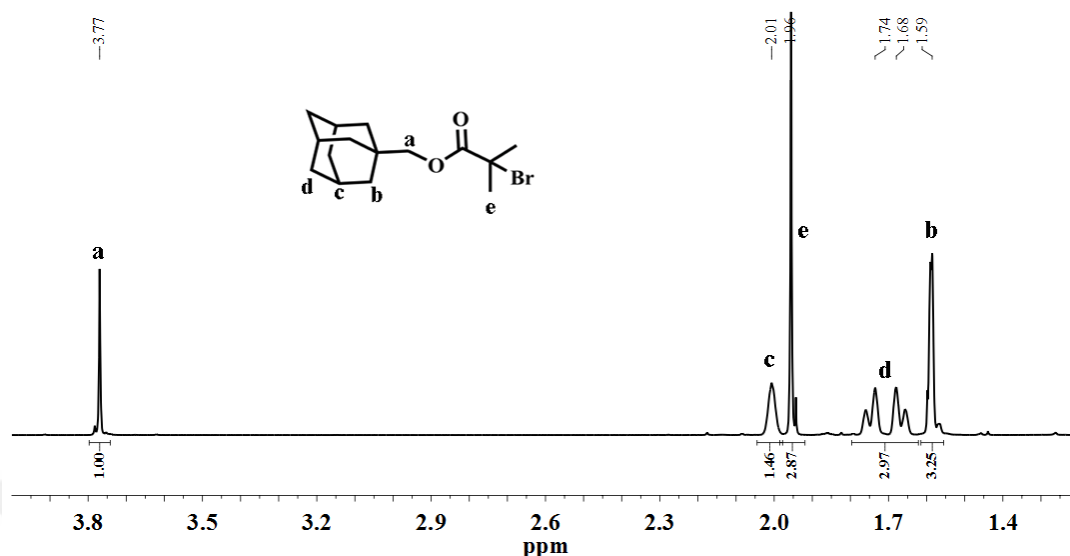
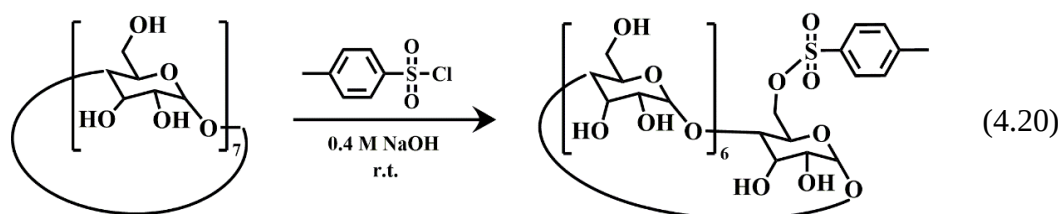


Figure 4.39 : ^1H NMR spectrum of 1-adamantane methyl-2-bromo isobutyrate (5) in CDCl_3 .

The preparation of $\beta\text{-CD-OTs}$ and $\beta\text{-CD-N}_3$ was well described by Ritter [260], so the same route was adopted to synthesize $\beta\text{-CD-N}_3$. Monosubstitution of $\beta\text{-CD}$ was carried out by the reaction of *p*-toluenesulfonyl chloride (TsCl) in aqueous NaOH at room temperature (Scheme 4.20).



Since $\beta\text{-CD}$ could react with only one TsCl in alkaline solution, monofunctionalization was proven by ^1H NMR and ESI-MS. In the ^1H NMR spectrum of $\beta\text{-CD-OTs}$ two peaks at 7.42 and 7.75 ppm are assigned to the phenyl protons. The ratio of these two peaks and the peaks corresponding to 2,3-positioned hydroxyl groups of the $\beta\text{-CD}$ ring approaches to 1:1:7, suggesting that only one TsCl is reacted with the 6-positioned hydroxyl group of the $\beta\text{-CD}$ ring (Figure 4.40).

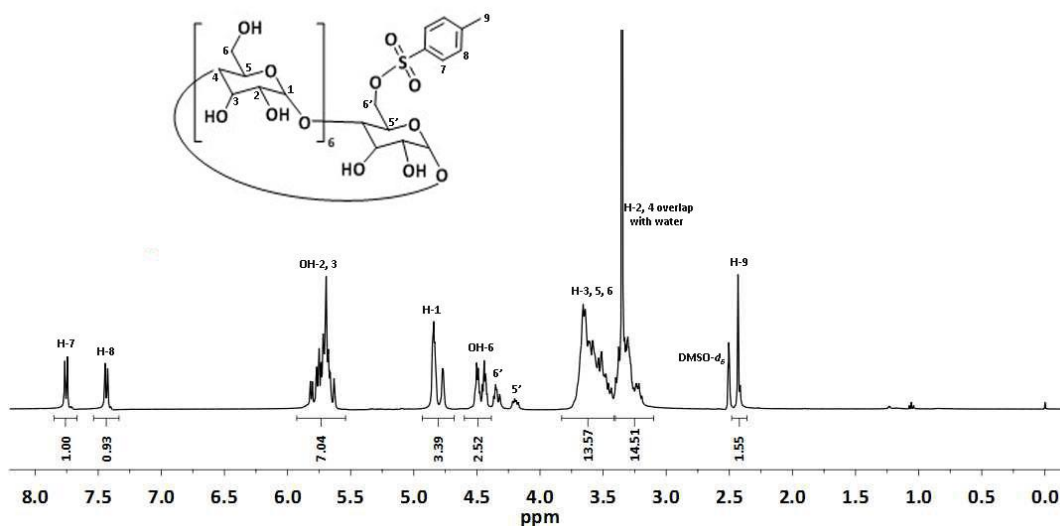


Figure 4.40 : ^1H NMR spectrum of β -CD-OTs in $\text{DMSO-}d_6$ at room temperature.

In the ESI-MS spectrum, exact molecular weight of β -CD-OTs was obtained with sodium ion $[\text{M} + \text{Na}]^+$ and proved the mono-tosylation reaction was succeed (Figure 4.41).

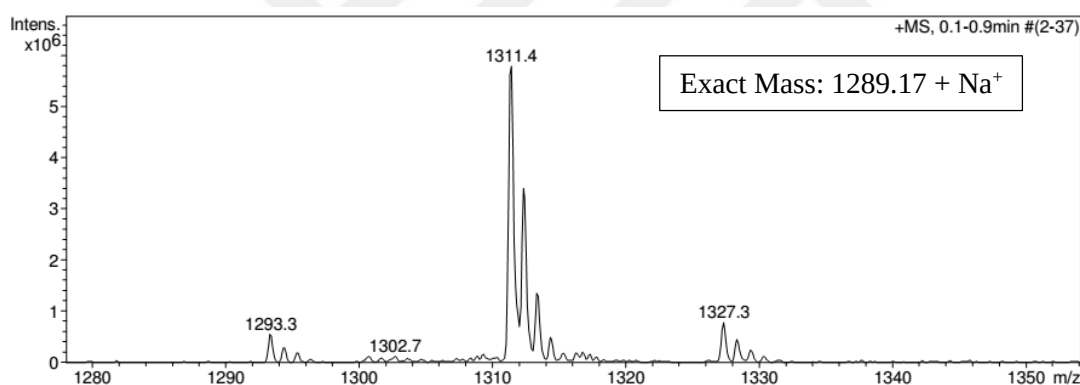
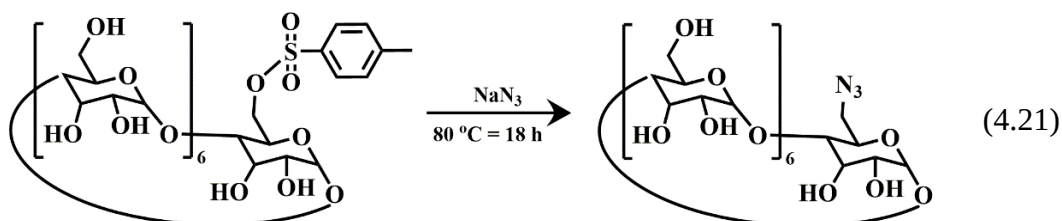


Figure 4.41 : ESI-MS spectrum of β -CD-OTs in methanol.

In further reaction, β -CD- N_3 was prepared by the azidation of β -CD-OTs with NaN_3 in water at 80°C (Scheme 4.21).



In the ^1H NMR spectrum of β -CD- N_3 the characteristic phenyl protons in β -CD-OTs was disappeared, which verifies the complete replacement of toluenesulfonyl group by azide group (Figure 4.42).

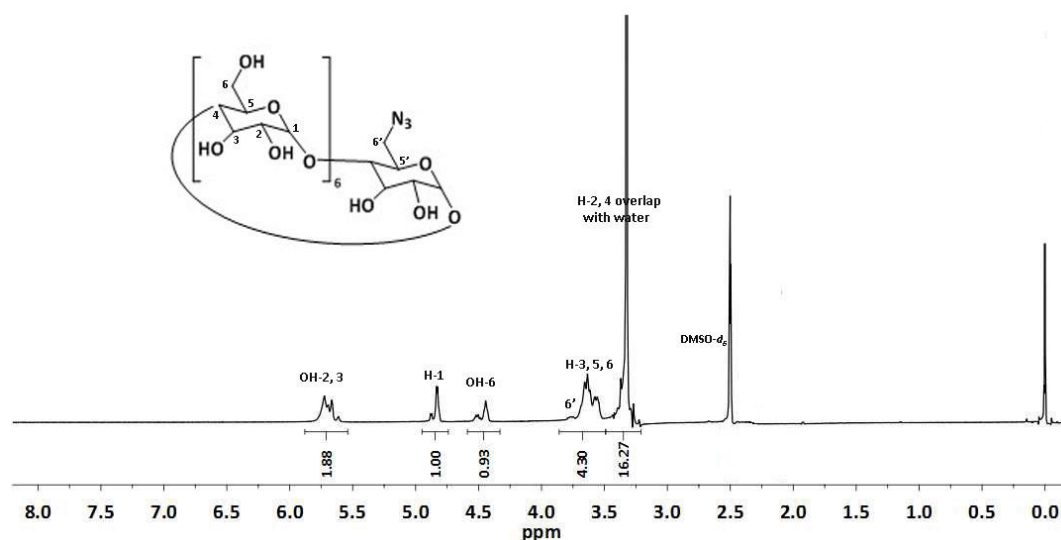


Figure 4.42 : ^1H NMR spectrum of $\beta\text{-CD-N}_3$ in $\text{DMSO-}d_6$ at room temperature.

The ESI-MS m/z spectrum showed dominant ions at m/z 1182.3, which were consistent with the expected protonated molecular ions, $(1160+\text{Na}^+)$. Hence the measured molecular weight was in good agreement with the theoretical value (Figure 4.43).

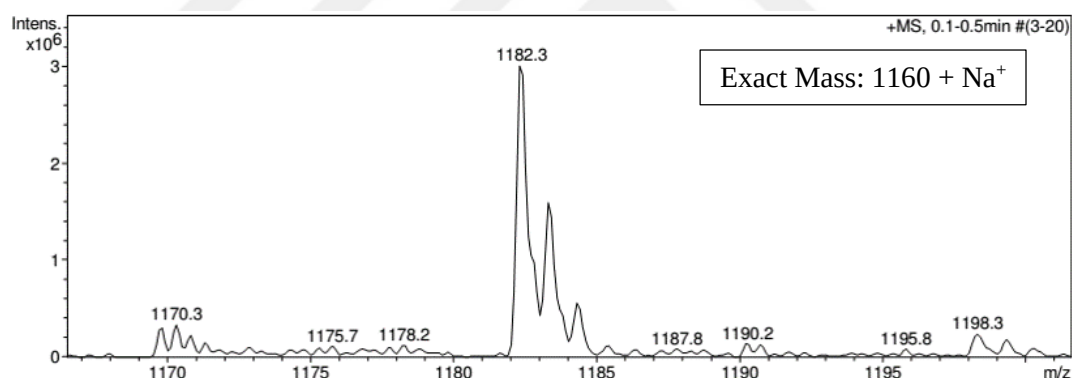
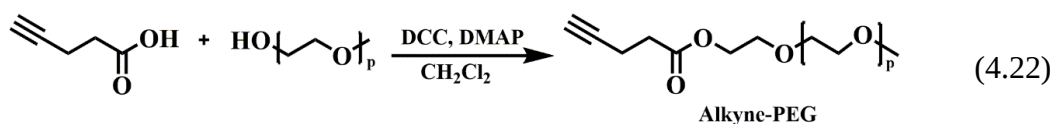


Figure 4.43 : ESI-MS spectrum of $\beta\text{-CD-N}_3$ in methanol.

Alkyne-PEG was obtained from a reaction of Me-PEG with 4-pentynoic acid at room temperature as depicted in Scheme 4.22.



^1H NMR spectrum revealed the structure of alkyne-PEG (Figure 4.44), displaying characteristic peaks such as a triplet ($\text{CH}\equiv\text{C}-$) at 1.9 ppm and a multiplet ($\text{CH}\equiv\text{CCH}_2\text{CH}_2\text{C}=\text{O}$) at 2.5 ppm. $M_{n,\text{NMR}}$ of alkyne-PEG was calculated from a ratio of peak areas of PEG repeating unit at 3.64 ppm and $\text{CH}\equiv\text{CCH}_2\text{CH}_2\text{C}=\text{O}$ end group

at 2.5 ppm. $M_{n,NMR}$ = 5180 of the polymer was consistent with those of $M_{n,theo}$ = 5100 and $M_{n,GPC}$ = 5000.

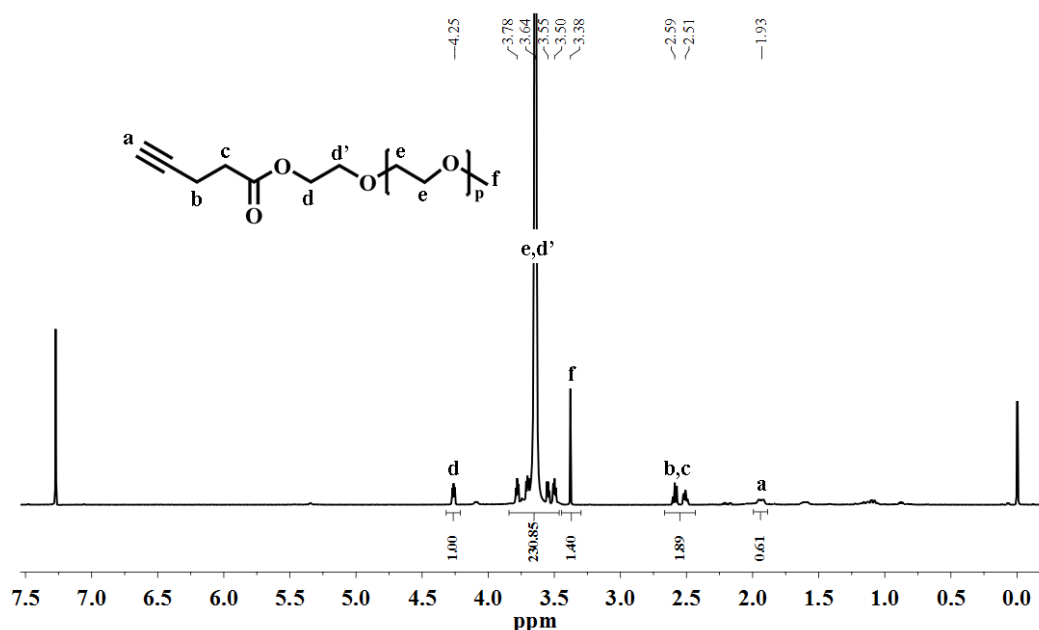


Figure 4.44 : ^1H NMR spectrum of alkyne-PEG in CDCl_3 .

The click reaction of alkyne-PEG with excess of $\beta\text{-CD-N}_3$ afforded $\beta\text{-CD-PEG}$ (Scheme 4.23). $\beta\text{-CD-PEG}$ was soluble in CHCl_3 , whereas $\beta\text{-CD-N}_3$ was not. Therefore, $\beta\text{-CD-PEG}$ dissolved in water could be purified by repeating extraction with CHCl_3 .

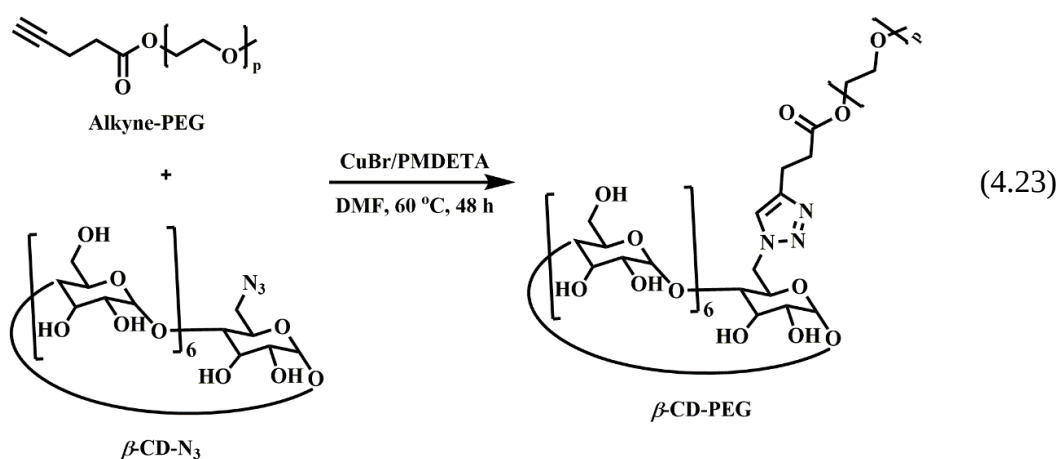


Figure 4.45 gives the ^1H NMR spectrum of $\beta\text{-CD-PEG}$. The signals at about 8.0 ppm are assigned to the proton of 1,2,3-triazole ring, and the 1:12.2 integration ratio of these peaks to 2,3-positioned hydroxyl groups of $\beta\text{-CD}$ at 5.69 ppm indicates the formation of $\beta\text{-CD-PEG}$ with high (87 %) click efficiency.

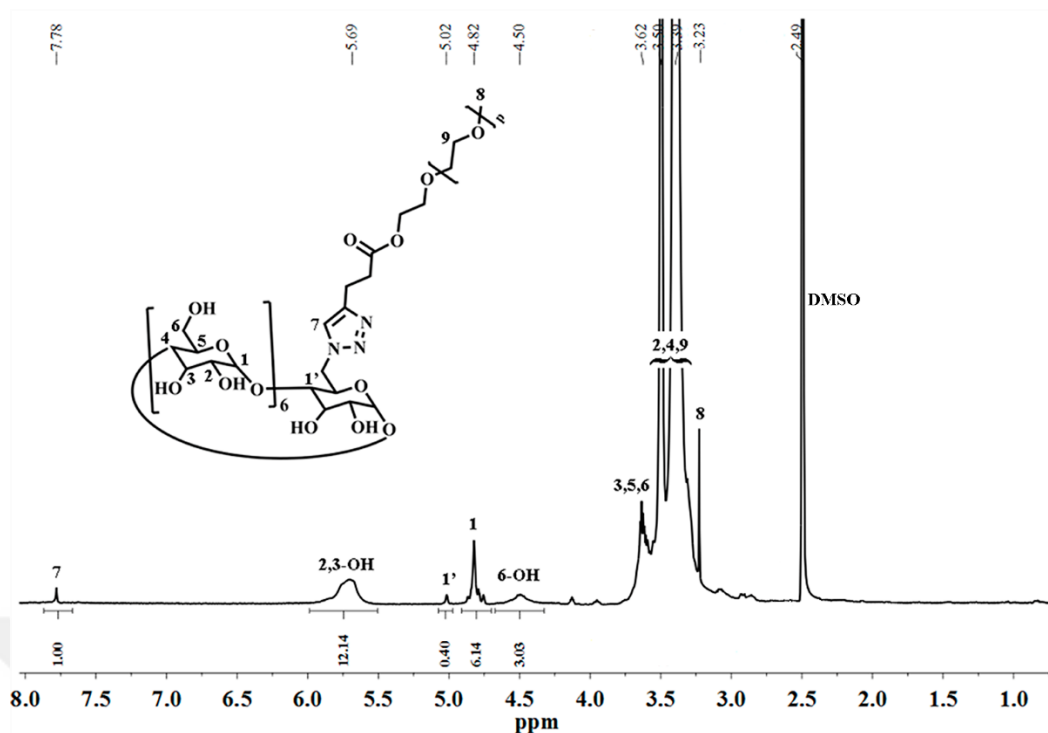


Figure 4.45 : ^1H NMR spectrum of β -CD-PEG in $\text{DMSO-}d_6$ at room temperature.

Comparing the FT-IR spectrum of β -CD-PEG with the β -CD- N_3 , the characteristic azide band of β -CD- N_3 at 2107 cm^{-1} disappears, as illustrated in Figure 4.46. The FT-IR results further validate the successful click reaction, as well as the complete removal of the excess β -CD- N_3 . Moreover, absorption peak characteristic of CD can be clearly observed, as evidenced by the presence of a strong C-O-C stretching vibration at 1030 cm^{-1} .

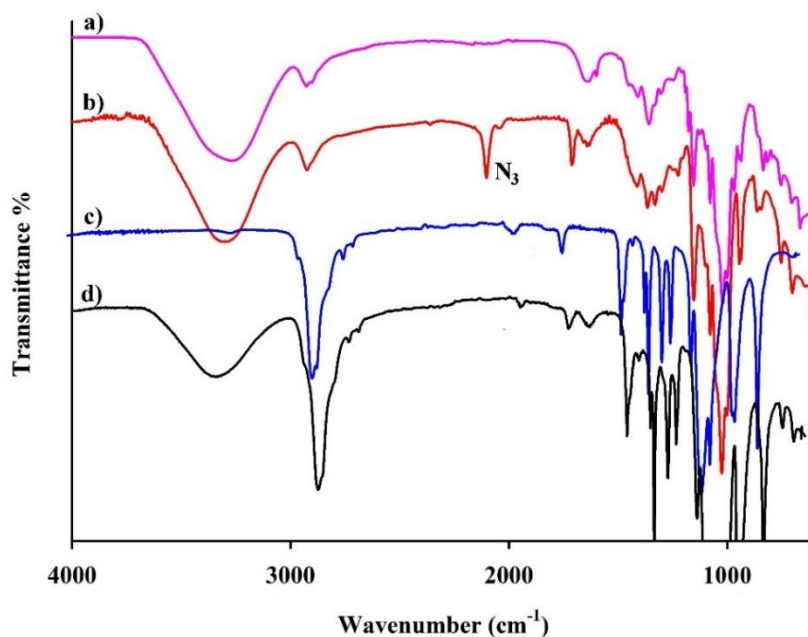


Figure 4.46 : FT-IR spectra of β -CD-OTs (pink) (a), β -CD- N_3 (red) (b), Alkyne-PEG (blue) (c) and obtained compound β -CD-PEG (black) (d).

Figure 4.47 shows the evolution of GPC traces of β -CD-PEG, Alkyne-PEG and β -CD- N_3 in DMF, due to poor solubility of β -CD- N_3 in THF. A shift for β -CD-PEG is clearly observed with respect to those of precursors.

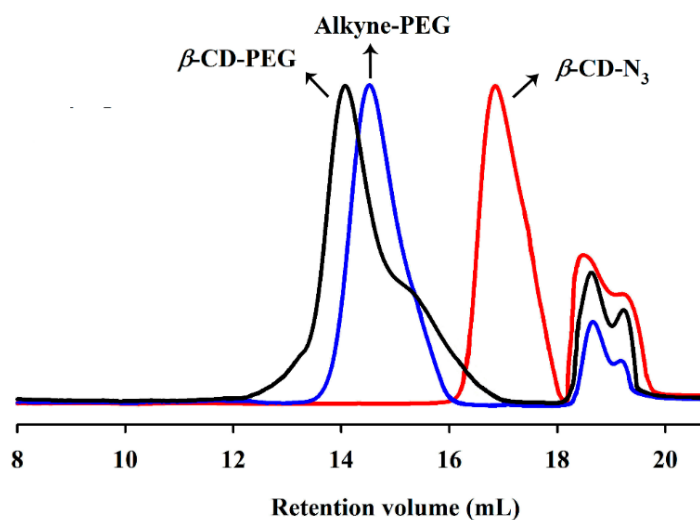
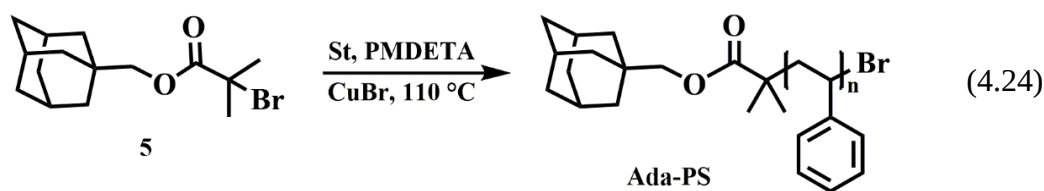


Figure 4.47 : Evolution of GPC traces of β -CD-PEG, Alkyne-PEG and β -CD- N_3 using RI detector in DMF at 60 °C.

For the preparation of $(\text{ada-PS})_n$ -polyDVB multiarm star polymer bearing adamantane functionality at the periphery, initially linear ada-PS was obtained via ATRP of St concurrently initiated by using **5** in the presence of CuBr/PMDETA at 110 °C for 40 min (Scheme 4.24).



The $M_{n,\text{theo}}$ (3570 g/mol) value is in excellent agreement with that obtained by GPC ($M_{n,\text{GPC}} = 3600$ g/mol relative to PS standards), and the PDI is low ($M_w/M_n = 1.10$). Moreover, The NMR number-average molecular weight ($M_{n,\text{NMR}} = 4060$ g/mol) of this polymer was calculated by comparing the integrations of the signals corresponding to the aromatic protons of St present on each repeating unit at 7.5–6.3 ppm and end-group proton of PS (4.45 ppm), while being included MW of **5** (315 g/mol) (Figure 4.48).

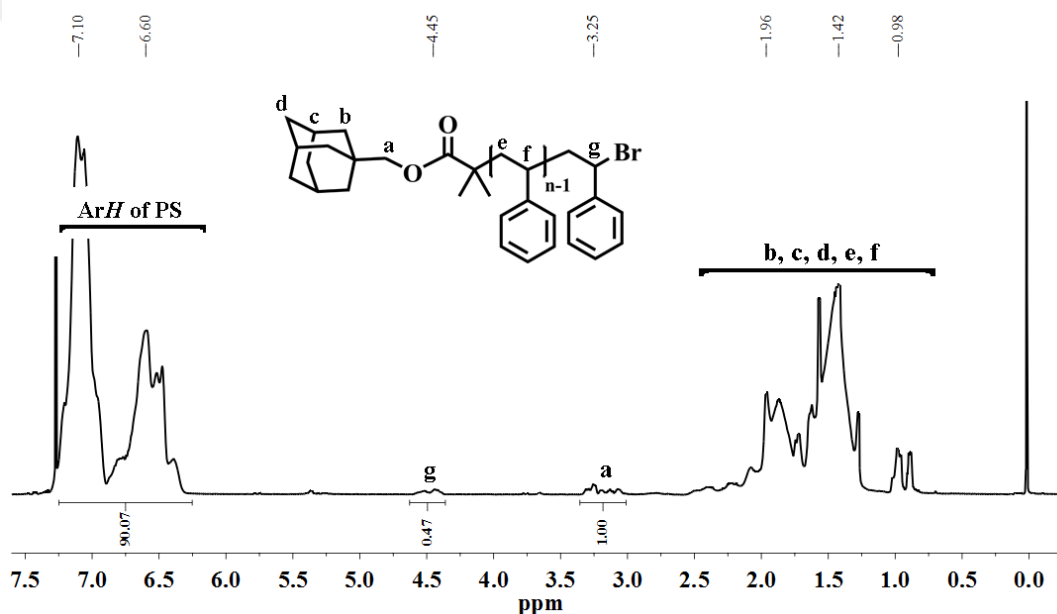


Figure 4.48 : ^1H NMR spectrum of adamantane end-functional PS (ada-PS) in CDCl_3 .

All polymerization conditions and results of the linear precursors used in the synthesis of multiarm star polymer and multiarm star block copolymers were tabulated in Table 4.7.

Table 4.7 : The conditions and results of linear polymers used in the synthesis of multiarm star and multiarm star block copolymer.

Polymer	In i.	Time (min)	Conv. ^b (%)	$M_{n, GPC}^c$ (g/mol)	M_w/M_n	$M_{n, theo}^d$ (g/mol)	$M_{n, NMR}$ (g/mol)
Ada-PS ^a	5	40	15	3600	1.10	3440 ^d	4065
Alkyne-PEG ^f	-	-	-	5000	1.06	5100 ^g	5180
β -CD-PEG	-	-	-	4750	1.06	6340 ^h	6130

^a $[M]_0:[I]_0:[CuBr]:[PMDETA] = 200:1:1:1$; polymerization was carried out at 110 °C.

^b Determined by gravimetrically.

^c Determined by conventional GPC calibrated relative to linear PS standards in THF at 30 °C.

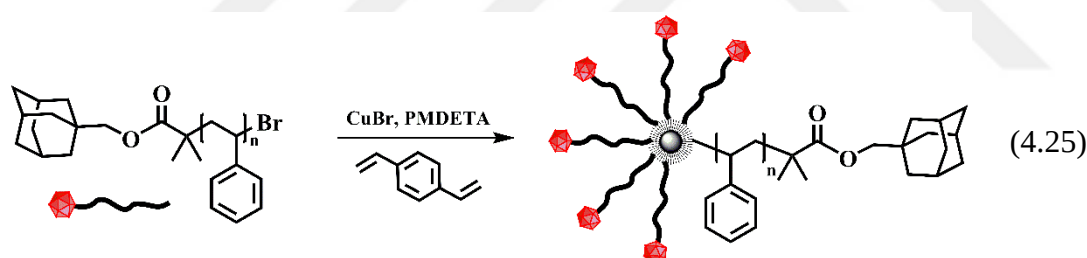
^d $M_{n, theo} = ([M]_0/[I]_0) \times \text{conversion \%} \times \text{molecular weight (MW) of monomer} + \text{MW of initiator}$.

^f Obtained by an esterification reaction between 4-pentynoic acid and Me-PEG (5000).

^g $M_{n, theo} = M_n$ of Me-PEG (5000) + MW of 4-pentynoic acid.

^h $M_{n, theo} = \text{sum of } M_{n, NMR} \text{ and ESI-MS values of the precursor polymers}$.

The (ada-PS)_n-polyDVB multiarm star polymer was obtained by ATRP of DVB in the presence of ada-PS as a macroinitiator and CuBr/PMDETA as catalyst at 110 °C (Scheme 4.25).



The progress of star formation was followed by GC and GPC while taking samples at time intervals and terminated after 18 h at 85 % of DVB conversion. (Ada-PS)_n-polyDVB multiarm star polymer was purified by two dissolution-precipitation cycles from THF into methanol/diethyl ether mixture (1/3, v/v) to remove unreacted linear ada-PS. The relevant chromatograms and the purified multiarm star polymer are overlaid in Figure 4.49. Moreover, TD-GPC results showed monomodal distributions and weight-average molecular weight ($M_{w, TD-DPC} = 74300$) and narrow polydispersity ($M_w/M_n = 1.09$) value for (ada-PS)_n-polyDVB multiarm star polymer was obtained after introducing $dn/dc = 0.185$ mL/g of linear PS standard to the Omni-Sec software (Table 4.8). Also, the number of arms (f) per molecule of the multiarm star polymer was calculated to be 13 by using equation 4.1 and found to be consistent with that obtained from equations 4.2 and 4.3.

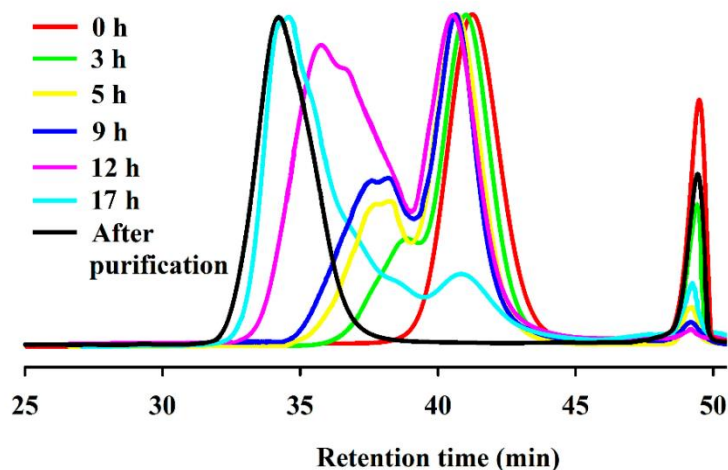


Figure 4.49 : Evolution of GPC traces of (ada-PS)_n-polyDVB multiarm star polymer using RI detector in THF at 30 °C. ([DVB]₀/15 = [Ada-PS]₀ = [CuBr]₀ = [PMDTA]₀ = 0.020 M in anisole at 110 °C).

Figure 4.50 shows the ¹H NMR spectrum of (ada-PS)_n-polyDVB multiarm star polymer recorded in CDCl₃. It was detected that end-group proton of PS (4.45 ppm) completely disappeared as a result of star formation. The characteristic signal of methylene proton adjacent to adamantane (3.26 ppm) were identified again in the multiarm star spectrum.

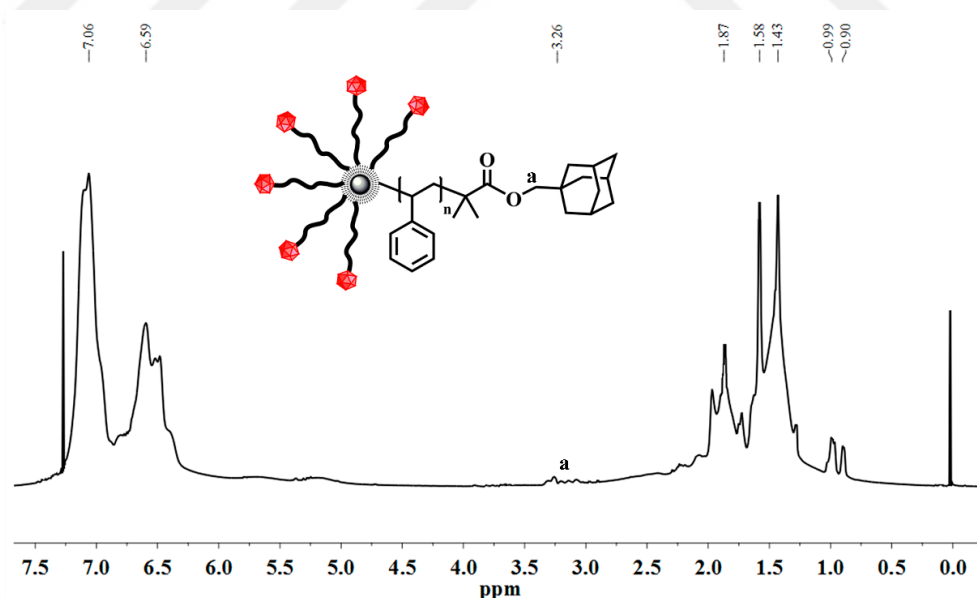
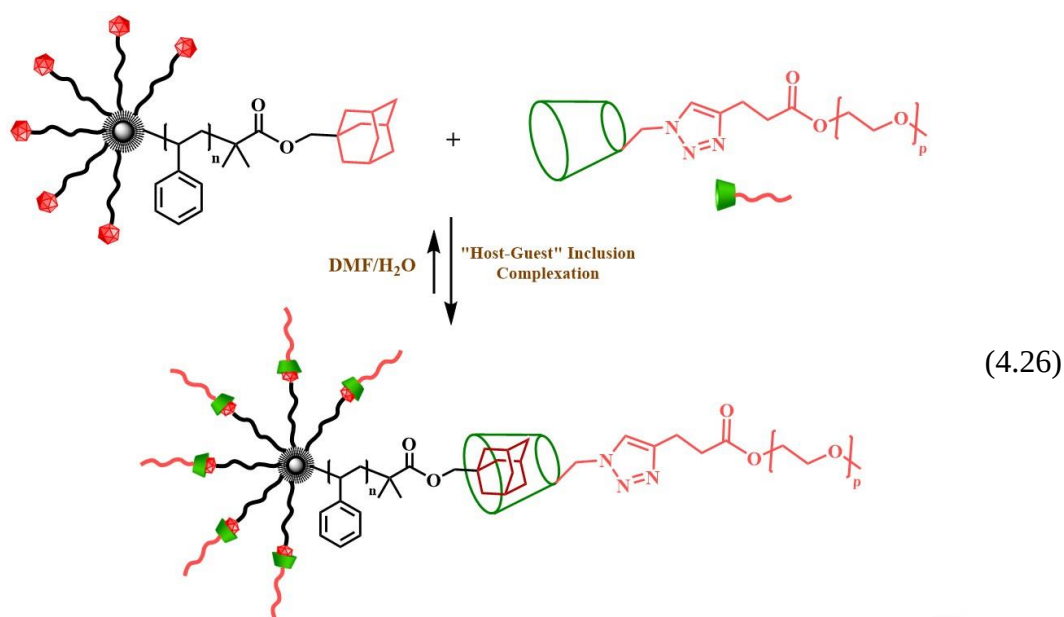


Figure 4.50 : ¹H NMR spectrum of (ada-PS)_n-polyDVB multiarm star polymer in CDCl₃.

The supramolecular (CD-PEG)_p-(ada-PS)_n-polyDVB multiarm star block copolymer was prepared via “host–guest interaction” between β-CD and ada as presented in Scheme 4.26.



In brief, the (ada-PS)_n-polyDVB multiarm star polymer and β-CD-PEG (equimolar per arm) were dissolved in DMF and one solution was added to other solution drop by drop. Subsequently, the resulting solution was dialyzed against a deionized DMF:water mixture at room temperature with increasing water content over time (Figure 4.51). Excess water content resulted the turbid polymer solution and subsequently formed a white precipitate. Finally, the solution was freeze-dried to yield the supramolecular (CD-PEG)_p-(ada-PS)_n-polyDVB multiarm star block copolymer.

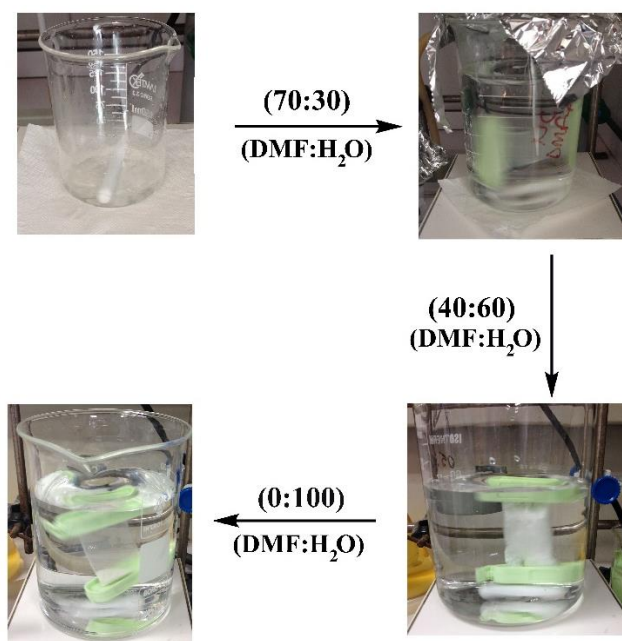


Figure 4.51 : Preparation of supramolecular (CD-PEG)_p-(ada-PS)_n-polyDVB multiarm star block copolymer with gradually decreased DMF amount in mixture.

Figure 4.52 presents the ^1H NMR spectrum of the supramolecular $(\text{CD-PEG})_p\text{-(ada-PS)}_n\text{-polyDVB}$ multiarm star block copolymer, the characteristic peaks of the two polymeric blocks (PEG and PS) can be well observed.

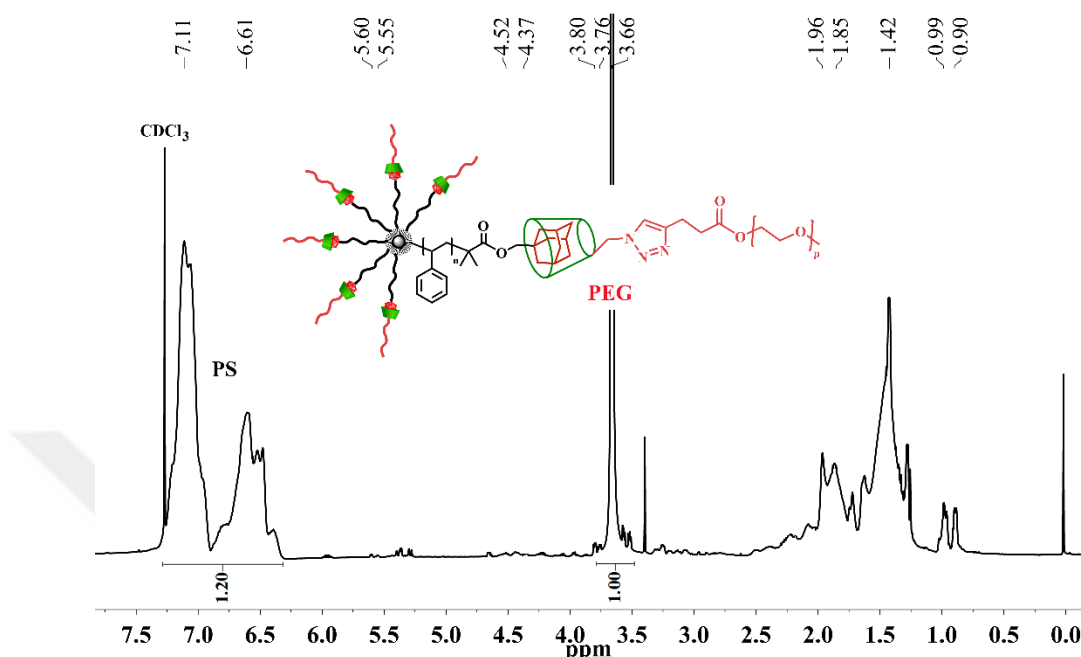


Figure 4.52 : ^1H NMR spectrum of supramolecular $(\text{CD-PEG})_p\text{-(ada-PS)}_n\text{-polyDVB}$ multiarm star block copolymer in CDCl_3 .

To study the structure of the inclusion complex of $\beta\text{-CD-PEG}$ with $(\text{ada-PS})_n\text{-polyDVB}$ multiarm star polymer, the ROESY NMR measurement was carried out. Figure 4.53 shows the ROESY NMR spectrum of the 1:1 mixture of $\beta\text{-CD-PEG}$ and $(\text{ada-PS})_n\text{-polyDVB}$ multiarm star polymer. Cross-peaks from dipolar interaction between the signals at 2.5–3.5 ppm assigned to the inner protons (the 3-, 5-, and 6-H protons) located in the cavities of $\beta\text{-CD}$ and the signals at 1.0–1.5 ppm ascribed to ada moieties are clearly observed, strongly indicating that ada moieties have been deeply embedded in the cavities of $\beta\text{-CD}$, and the supramolecular multiarm star block copolymer has been successfully synthesized via host–guest interactions.

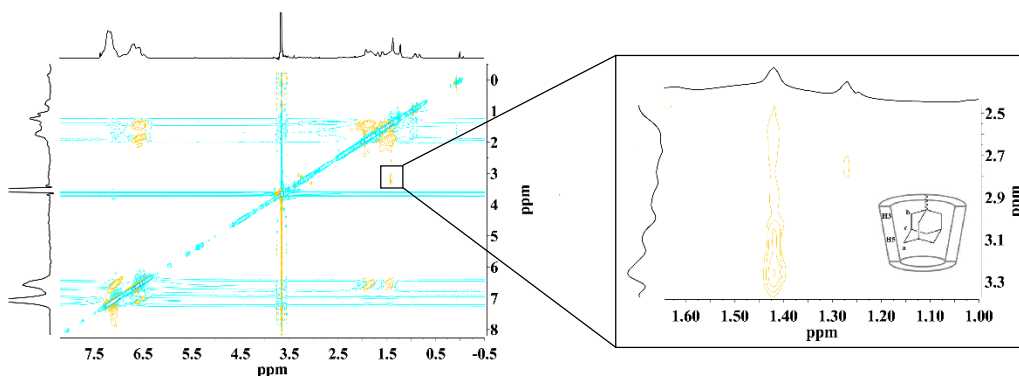


Figure 4.53 : ROESY NMR spectrum of the supramolecular $(\text{CD-PEG})_p\text{-(ada-PS)}_n\text{-polyDVB}$ multiarm star block copolymer in CDCl_3 at 25°C (magnified in the right side).

The integration ratios of PS and PEG blocks in supramolecular $(\text{CD-PEG})_p\text{-(ada-PS)}_n\text{-polyDVB}$ multiarm star block copolymer were determined by ^1H NMR spectrum and introduced in equation 4.4, as described in literature and the dn/dc value of supramolecular $(\text{CD-PEG})_p\text{-(ada-PS)}_n\text{-polyDVB}$ multiarm star block copolymer was calculated to 0.153 mL/g . In order to determine the absolute molecular weight of the supramolecular $(\text{CD-PEG})_p\text{-(ada-PS)}_n\text{-polyDVB}$ multiarm star block copolymer, the obtained dn/dc is then introduced into the Omni-Sec software of TD-GPC. As can be seen in Table 4.8, after “host-guest” inclusion complexation, the hydrodynamic radius (R_h) was increased from 4.89 nm to 5.59 nm . DLS is another versatile tool to investigate the complex formation in solution. After “host-guest” inclusion complexation, the hydrodynamic diameter (D_h) increased from the 7.40 nm to 9.69 nm (Figure 4.54). All these analysis supported the supramolecular multiarm star block copolymer formation. To the best of our knowledge, it is the first time such multiarm star block copolymer have been obtained using this “host-guest” interaction.

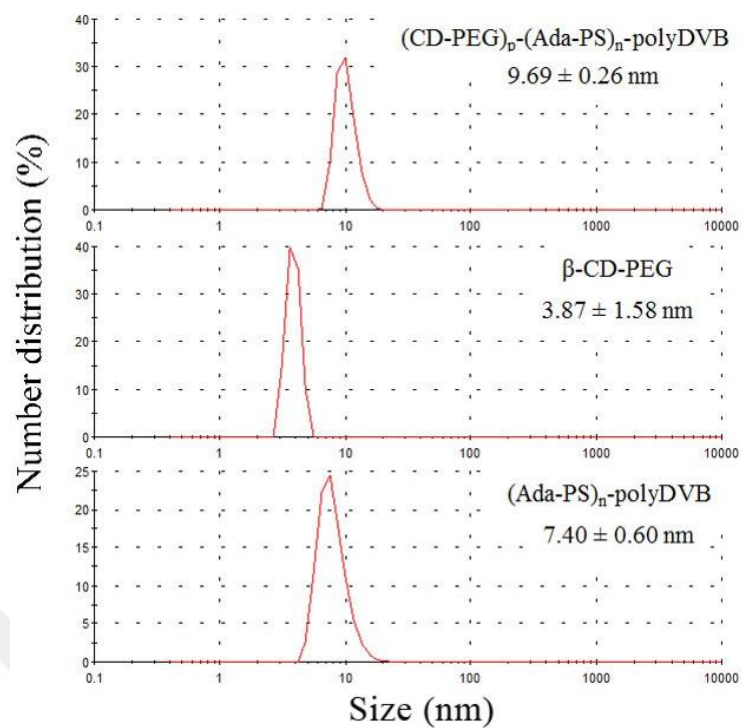


Figure 4.54 : Comparison of the number average particle size distribution of (Ada-PS)_n-polyDVB multiarm star polymer obtained from DLS measurements at room temperature.

Table 4.8 : TD-GPC characterization of Ada functional multiarm star polymer before and after “host-guest” interaction.

Polymers	TD-GPC ^a						
	M_n (g/mol)	M_w (g/mol)	M_w/M_n	$[\eta]$ (dL/g)	R_h (nm)	dn/dc (mL/g)	f^c
(Ada-PS)_n-polyDVB^b	68340	74300	1.09	0.105	4.89	0.185	13(15) ^d
(CD-PEG)_p-(Ada-PS)_n-polyDVB	95400	107300	1.13	0.120	5.59	0.153 ^e	-

^a Calculated from triple detection GPC (TD-GPC) in THF at 35 °C.

^b [DVB]₀/15 = [ada-PS]₀ = [CuBr]₀ = [PMDETA]₀ = 0.020 M in anisole at 110 °C;

^c Calculated according to equation 4.1.

^d Calculated according to equations 4.2 and 4.3.

^e Calculated according to equation 4.4

5. CONCLUSION

Functional polymers hold increasing priority in complex macromolecular architectures. The combination of various structural conformations and high local densities of functional groups makes star polymers unique candidates for a diverse range of applications, including surface engineering, novel responsive materials, and drug delivery. Here in this thesis, we have designed periphery functional multiarm star polymers with “arm-first” approach.

In the first part of the thesis, one versatile nucleophilic substitution reaction, labile *para*-fluoro groups of pentafluorophenyl (C_6F_5) ring, was investigated as a click concept for the synthesis of periphery functionalized multiarm star polymers. From this point of view, pentafluorophenyl functionalized (fluoro-PS)_n-polyDVB multiarm star polymer was synthesized using pentafluorophenyl functionalized PS (α -fluoro-PS) as a macroinitiator and DVB as a crosslinker. The obtained multiarm star polymer with pentafluorophenyl moiety at the periphery was then used for nucleophilic substitution reaction with *N*-acetyl-L-cysteine methyl ester or PEG₅₅₀-OH for post-functionalization. Both reactions were successfully synthesized and (cysteine-PS)_n-polyDVB multiarm star polymer and (PEG)_m-(PS)_n-polyDVB multiarm star block copolymer were obtained.

In the second part, the first study was extended and heterofunctionalized multiarm star polymers were synthesized via exploiting orthogonal double click reactions. Equal moles of fluoro and allyl functional initiators were used in ATRP of St affording the mixture of macroinitiators, which was subsequently reacted with DVB in order to obtain (fluoro-PS)_m-polyDVB-(allyl-PS)_m multiarm star polymer. The thiol-*para*-fluoro and thiol-ene click reactions were sequentially employed to this star polymer to prepare heterofunctionalized (propyl-PS)_m-polyDVB-(cysteine-PS)_m multiarm star polymer. It is noteworthy to say that nucleophilic substitution reaction of labile *para*-fluoro groups of pentafluorophenyl (C_6F_5) ring is a versatile and efficient route for the preparation of wide range of macromolecules. Ultimately, their widespread

acceptance as a “click” reaction in polymer synthesis is justified by their seemingly unlimited potential to create well-defined macromolecules.

In the third part, we turned our attention to polymeric photoinitiators. We have already know that benzoin and derivatives have long been known to be efficient photoinitiators for free radical polymerization of vinyl monomers and have found wide application in the polymer industry. In this study, we synthesized benzoin and MTB functional novel multiarm star polymers, called (benzoin-PS)_m-polyDVB and (MTB-PS)_p-polyDVB. Obtained multiarm star polymers were used as polymeric photoinitiators and their photokinetic properties were studied by Photo-DSC and were used in free radical photopolymerization of MMA in air atmosphere. The polymeric photoinitiators showed higher photoinitiating activity compared to those of monomeric ones. This confirms the expectation that the use of polymeric photoinitiators is advantageous compared to the corresponding monomeric ones in terms of photoinitiating activity.

In the last part of the thesis, we combined controlled polymerization techniques with supramolecular interactions. The β -cyclodextrin–adamantane (β -CD–Ada) “host–guest” inclusion complexation has been studied as supramolecular interaction on the formation of multiarm star block copolymer. (Ada-PS)_n-polyDVB multiarm star polymer was synthesized by a crosslinking reaction of DVB with adamantane functionalized PS (ada-PS) as a macroinitiator. A β -CD end functionalized PEG (β -CD-PEG) was obtained by a two-step procedure: alkyne-functionalized PEG was first generated by esterification reaction of commercially available Me-PEG and subsequently converted in a host system by CuAAC with azide-functionalized β -CD (β -CD-N₃). Subsequent self-assembly of (Ada-PS)_n-polyDVB multiarm star polymer as a guest molecule and β -CD-PEG as a host molecule in aqueous media afforded the supramolecular (CD-PEG)_p-(ada-PS)_n-polyDVB multiarm star block copolymer. The occurrence of “host–guest” inclusion complexation was unambiguously proved by ¹H NMR, 2D ROESY NMR and by TD-GPC.

REFERENCES

- [1] **Gao, H. and Matyjaszewski, K.** (2007). Low-Polydispersity Star Polymers with Core Functionality by Cross-Linking Macromonomers Using Functional ATRP Initiators, *Macromolecules*, 40 (3), 399-401.
- [2] **Gao, H. and Matyjaszewski, K.** (2008). Synthesis of Star Polymers by A New “Core-First” Method: Sequential Polymerization of Cross-Linker and Monomer, *Macromolecules*, 41 (4), 1118-1125.
- [3] **Hadjichristidis, N.** (1999). Synthesis of miktoarm star (?-star) polymers, *Journal of Polymer Science Part A: Polymer Chemistry*, 37 (7), 857-871.
- [4] **Hadjichristidis, N., Pitsikalis, M., Pispas, S. and Iatrou, H.** (2001). Polymers with Complex Architecture by Living Anionic Polymerization, *Chemical Reviews*, 101 (12), 3747-3792.
- [5] **Hadjichristidis, N., Iatrou, H., Pitsikalis, M. and Mays, J.** (2006). Macromolecular architectures by living and controlled/living polymerizations, *Progress in Polymer Science*, 31 (12), 1068-1132.
- [6] **Gao, H. and Matyjaszewski, K.** (2009). Synthesis of functional polymers with controlled architecture by CRP of monomers in the presence of cross-linkers: From stars to gels, *Progress in Polymer Science*, 34 (4), 317-350.
- [7] **Ito, S., Goseki, R., Manners, I., Ishizone, T. and Hirao, A.** (2015). Successive Synthesis of Multiarmed and Multicomponent Star-Branched Polymers by New Iterative Methodology Based on Linking Reaction between Block Copolymer In-Chain Anion and α -Phenylacrylate-Functionalized Polymer, *Macromol Chem Phys*, 216 (14), 1523-1533.
- [8] **Blencowe, A., Tan, J. F., Goh, T. K. and Qiao, G. G.** (2009). Core cross-linked star polymers via controlled radical polymerisation, *Polymer*, 50 (1), 5-32.
- [9] **Gao, H. and Matyjaszewski, K.** (2008). Synthesis of Low-Polydispersity Miktoarm Star Copolymers via a Simple “Arm-First” Method: Macromonomers as Arm Precursors, *Macromolecules*, 41 (12), 4250-4257.
- [10] **Gungor, E., Bilir, C., Hizal, G. and Tunca, U.** (2010). Multiarm star polymers with POSS at the periphery, *Journal of Polymer Science Part A: Polymer Chemistry*, 48 (21), 4835-4841.
- [11] **Sumerlin, B. S. and Vogt, A. P.** (2010). Macromolecular Engineering through Click Chemistry and Other Efficient Transformations, *Macromolecules*, 43 (1), 1-13.

- [12] **Gok, O., Yigit, S., Merve Kose, M., Sanyal, R. and Sanyal, A.** (2013). Dendron-polymer conjugates via the diels-alder “click” reaction of novel anthracene-based dendrons, *Journal of Polymer Science Part A: Polymer Chemistry*, 51 (15), 3191-3201.
- [13] **Akeroyd, N. and Klumperman, B.** (2011). The combination of living radical polymerization and click chemistry for the synthesis of advanced macromolecular architectures, *European Polymer Journal*, 47 (6), 1207-1231.
- [14] **Kempe, K., Krieg, A., Becer, C. R. and Schubert, U. S.** (2012). "Clicking" on/with polymers: a rapidly expanding field for the straightforward preparation of novel macromolecular architectures, *Chemical Society reviews*, 41 (1), 176-191.
- [15] **Doganci, E., Tasdelen, M. A. and Yilmaz, F.** (2015). Synthesis of Miktoarm Star-Shaped Polymers with POSS Core via a Combination of CuAAC Click Chemistry, ATRP, and ROP Techniques, *Macromol Chem Phys*, 216 (17), 1823-1830.
- [16] **Durmaz, H., Sanyal, A., Hizal, G. and Tunca, U.** (2012). Double click reaction strategies for polymer conjugation and post-functionalization of polymers, *Polym Chem-Uk*, 3 (4), 825.
- [17] **Kade, M. J., Burke, D. J. and Hawker, C. J.** (2010). The power of thiol-ene chemistry, *Journal of Polymer Science Part A: Polymer Chemistry*, 48 (4), 743-750.
- [18] **Hoyle, C. E., Lowe, A. B. and Bowman, C. N.** (2010). Thiol-click chemistry: a multifaceted toolbox for small molecule and polymer synthesis, *Chemical Society reviews*, 39 (4), 1355-1387.
- [19] **Grazu, V., Abian, O., Mateo, C., Batista-Viera, F., Fernandez-Lafuente, R. and Guisan, J. M.** (2003). Novel bifunctional epoxy/thiol-reactive support to immobilize thiol containing proteins by the epoxy chemistry, *Biomacromolecules*, 4 (6), 1495-1501.
- [20] **Gunay, U. S., Demirel, E., Hizal, G., Tunca, U. and Durmaz, H.** (2015). Ring-opening reactions of backbone epoxidized polyoxanorbornene, *Reactive and Functional Polymers*, 94, 35-42.
- [21] **Xu, J., Tao, L., Boyer, C., Lowe, A. B. and Davis, T. P.** (2010). Combining Thio-Bromo “Click” Chemistry and RAFT Polymerization: A Powerful Tool for Preparing Functionalized Multiblock and Hyperbranched Polymers, *Macromolecules*, 43 (1), 20-24.
- [22] **Noy, J.-M., Koldevitz, M. and Roth, P. J.** (2015). Thiol-reactive functional poly(meth)acrylates: multicomponent monomer synthesis, RAFT (co)polymerization and highly efficient thiol-para-fluoro postpolymerization modification, *Polym. Chem.*, 6 (3), 436-447.
- [23] **Bartels, J. W., Cheng, C., Powell, K. T., Xu, J. and Wooley, K. L.** (2007). Hyperbranched Fluoropolymers and their Hybridization into Complex Amphiphilic Crosslinked Copolymer Networks, *Macromol Chem Phys*, 208 (15), 1676-1687.

- [24] **Hoogenboom, R.** (2010). Thiol-yne chemistry: a powerful tool for creating highly functional materials, *Angewandte Chemie*, 49 (20), 3415-3417.
- [25] **Meng, Y., Tsai, M., Schmidt, G. R. and Anthamatten, M.** (2015). Gradient-index materials based on thiol-ene networks, *ACS Appl Mater Interfaces*, 7 (16), 8601-8605.
- [26] **Fraser, A. K., Ki, C. S. and Lin, C.-C.** (2014). PEG-Based Microgels Formed by Visible-Light-Mediated Thiol-Ene Photo-Click Reactions, *Macromol Chem Phys*, 215 (6), 507-515.
- [27] **Uygun, M., Tasdelen, M. A. and Yagci, Y.** (2010). Influence of Type of Initiation on Thiol-ene-Click Chemistry, *Macromol Chem Phys*, 211 (1), 103-110.
- [28] **Samaroo, D., Vinodu, M., Chen, X. and Drain, C. M.** (2007). meso-Tetra(pentafluorophenyl)porphyrin as an efficient platform for combinatorial synthesis and the selection of new photodynamic therapeutics using a cancer cell line, *Journal of combinatorial chemistry*, 9 (6), 998-1011.
- [29] **ten Brummelhuis, N. and Weck, M.** (2012). Orthogonal Multifunctionalization of Random and Alternating Copolymers, *Acs Macro Lett*, 1 (10), 1216-1218.
- [30] **Becer, C. R., Kokado, K., Weber, C., Can, A., Chujo, Y. and Schubert, U. S.** (2010). Metal-free synthesis of responsive polymers: Cloud point tuning by controlled “click” reaction, *Journal of Polymer Science Part A: Polymer Chemistry*, 48 (6), 1278-1286.
- [31] **Chen, J., Dumas, L., Duchet-Rumeau, J., Fleury, E., Charlot, A. and Portinha, D.** (2012). Tuning h-bond capability of hydroxylated-poly(2,3,4,5,6-pentafluorostyrene) grafted copolymers prepared by chemoselective and versatile thiol-para-fluoro “click-type” coupling with mercaptoalcohols, *Journal of Polymer Science Part A: Polymer Chemistry*, 50 (16), 3452-3460.
- [32] **Álvarez-Paino, M., Muñoz-Bonilla, A., Marcelo, G., Rodríguez-Hernández, J. and Fernández-García, M.** (2012). Synthesis and lectin recognition studies of glycosylated polystyrene microspheres functionalized via thiol-para-fluorine “click” reaction, *Polym Chem-Uk*, 3 (12), 3282.
- [33] **Becer, C. R., Babiuch, K., Pilz, D., Hornig, S., Heinze, T., Gottschaldt, M. and Schubert, U. S.** (2009). Clicking Pentafluorostyrene Copolymers: Synthesis, Nanoprecipitation, and Glycosylation, *Macromolecules*, 42 (7), 2387-2394.
- [34] **Tunca, U.** (2014). Orthogonal multiple click reactions in synthetic polymer chemistry, *Journal of Polymer Science Part A: Polymer Chemistry*, 52 (22), 3147-3165.
- [35] **Golas, P. L. and Matyjaszewski, K.** (2010). Marrying click chemistry with polymerization: expanding the scope of polymeric materials, *Chemical Society reviews*, 39 (4), 1338-1354.
- [36] **Corrales, T., Catalina, F., Peinado, C., Allen, N. S., Rufs, A. M., Bueno, C. and Encinas, M. V.** (2002). Photochemical study and photoinitiation

activity of macroinitiators based on thioxanthone, *Polymer*, 43 (17), 4591-4597.

- [37] **Karaca Balta, D., Karahan, Ö., Avci, D. and Arsu, N.** (2015). Synthesis, photophysical and photochemical studies of benzophenone based novel monomeric and polymeric photoinitiators, *Progress in Organic Coatings*, 78, 200-207.
- [38] **Carlini, C., Angiolini, L., Caretti, D. and Corelli, E.** (1996). Recent advances on photosensitive polymers: Polymeric photoinitiators, *Polym Advan Technol*, 7 (5-6), 379-384.
- [39] **Ma, X. and Zhao, Y.** (2015). Biomedical Applications of Supramolecular Systems Based on Host-Guest Interactions, *Chem Rev*, 115 (15), 7794-7839.
- [40] **Szwarc, M.** (1956). 'Living' Polymers, *Nature*, 178 (4543), 1168-1169.
- [41] **Matyjaszewski, K.** (1995). Introduction to living polymeriz. Living and/or controlled polymerization, *Journal of Physical Organic Chemistry*, 8 (4), 197-207.
- [42] **Litvinenko, G. and Müller, A. H. E.** (1997). General Kinetic Analysis and Comparison of Molecular Weight Distributions for Various Mechanisms of Activity Exchange in Living Polymerizations, *Macromolecules*, 30 (5), 1253-1266.
- [43] **Quirk, R. P. and Lee, B.** (1992). Experimental Criteria for Living Polymerizations, *Polymer International*, 27 (4), 359-367.
- [44] **Percec, V. and Tirrell, D. A.** (2000). Living or controlled?, *Journal of Polymer Science Part A: Polymer Chemistry*, 38 (10), 1705-1705.
- [45] **Johnson, C., Moad, G., Solomon, D., Spurling, T. and Vearring, D.** (1990). The Application of Supercomputers in Modeling Chemical Reaction Kinetics: Kinetic Simulation of 'Quasi-Living' Radical Polymerization, *Aust J Chem*, 43 (7), 1215-1230.
- [46] **Kamigaito, M., Ando, T. and Sawamoto, M.** (2001). Metal-Catalyzed Living Radical Polymerization, *Chemical Reviews*, 101 (12), 3689-3746.
- [47] **Matyjaszewski, K. and Xia, J.** (2001). Atom Transfer Radical Polymerization, *Chemical Reviews*, 101 (9), 2921-2990.
- [48] **Wang, J.-S. and Matyjaszewski, K.** (1995). Controlled/"living" radical polymerization. atom transfer radical polymerization in the presence of transition-metal complexes, *J Am Chem Soc*, 117 (20), 5614-5615.
- [49] **Hawker, C. J., Bosman, A. W. and Harth, E.** (2001). New Polymer Synthesis by Nitroxide Mediated Living Radical Polymerizations, *Chemical Reviews*, 101 (12), 3661-3688.
- [50] **Georges, M. K., Veregin, R. P. N., Kazmaier, P. M. and Hamer, G. K.** (1993). Narrow molecular weight resins by a free-radical polymerization process, *Macromolecules*, 26 (11), 2987-2988.
- [51] **Chiefari, J., Chong, Y. K., Ercole, F., Krstina, J., Jeffery, J., Le, T. P. T., Mayadunne, R. T. A., Meijs, G. F., Moad, C. L., Moad, G., Rizzardo, E. and Thang, S. H.** (1998). Living Free-Radical

Polymerization by Reversible Addition–Fragmentation Chain Transfer: The RAFT Process, *Macromolecules*, 31 (16), 5559-5562.

- [52] **Rizzardo, E., Chiefari, J., Mayadunne, R., Moad, G. and Thang, S.** (2001). Tailored polymer architectures by reversible addition-fragmentation chain transfer, *Macromolecular Symposia*, 174 (1), 209-212.
- [53] **Fischer, H.** (2001). The Persistent Radical Effect: A Principle for Selective Radical Reactions and Living Radical Polymerizations, *Chemical Reviews*, 101 (12), 3581-3610.
- [54] **Arslan, H., Yeşilyurt, N. and Hazer, B.** (2007). The synthesis of poly(3-hydroxybutyrate)-g-poly(methylmethacrylate) brush type graft copolymers by atom transfer radical polymerization method, *J Appl Polym Sci*, 106 (3), 1742-1750.
- [55] **Arslan, H., Yeşilyurt, N. and Hazer, B.** (2008). Brush Type Copolymers of Poly(3-hydroxybutyrate) and Poly(3-hydroxyoctanoate) with Same Vinyl Monomers via “Grafting From” Technique by Using Atom Transfer Radical Polymerization Method, *Macromolecular Symposia*, 269 (1), 23-33.
- [56] **Boyes, S. G., Granville, A. M., Baum, M., Akgun, B., Mirous, B. K. and Brittain, W. J.** (2004). Polymer brushes—surface immobilized polymers, *Surface Science*, 570 (1–2), 1-12.
- [57] **Cai, Y., Hartenstein, M. and Müller, A. H. E.** (2004). Synthesis of Amphiphilic Graft Copolymers of n-Butyl Acrylate and Acrylic Acid by Atom Transfer Radical Copolymerization of Macromonomers, *Macromolecules*, 37 (20), 7484-7490.
- [58] **Chung, I. S. and Matyjaszewski, K.** (2003). Synthesis of Degradable Poly(methyl methacrylate) via ATRP: Atom Transfer Radical Ring-Opening Copolymerization of 5-Methylene-2-phenyl-1,3-dioxolan-4-one and Methyl Methacrylate, *Macromolecules*, 36 (9), 2995-2998.
- [59] **Lipscomb, C. E. and Mahanthappa, M. K.** (2009). Poly(vinyl ester) Block Copolymers Synthesized by Reversible Addition–Fragmentation Chain Transfer Polymerizations, *Macromolecules*, 42 (13), 4571-4579.
- [60] **Sarbu, T., Lin, K.-Y., Spanswick, J., Gil, R. R., Siegwart, D. J. and Matyjaszewski, K.** (2004). Synthesis of Hydroxy-Telechelic Poly(methyl acrylate) and Polystyrene by Atom Transfer Radical Coupling, *Macromolecules*, 37 (26), 9694-9700.
- [61] **Zhang, M., Breiner, T., Mori, H. and Müller, A. H. E.** (2003). Amphiphilic cylindrical brushes with poly(acrylic acid) core and poly(n-butyl acrylate) shell and narrow length distribution, *Polymer*, 44 (5), 1449-1458.
- [62] **Matyjaszewski, K.** (1999). Transition metal catalysis in controlled radical polymerization: atom transfer radical polymerization, *Chemistry-A European Journal*, 5 (11), 3095-3102.
- [63] **Patten, T. E. and Matyjaszewski, K.** (1998). Atom Transfer Radical Polymerization and the Synthesis of Polymeric Materials, *Advanced Materials*, 10 (12), 901-915.

- [64] **Patten, T. E. and Matyjaszewski, K.** (1999). Copper(I)-Catalyzed Atom Transfer Radical Polymerization, *Accounts of Chemical Research*, 32 (10), 895-903.
- [65] **Goto, A. and Fukuda, T.** (1999). Determination of the activation rate constants of alkyl halide initiators for atom transfer radical polymerization, *Macromol Rapid Comm*, 20 (12), 633-636.
- [66] **Matyjaszewski, K.** (1997). Mechanistic and Synthetic Aspects of Atom Transfer Radical Polymerization, *Journal of Macromolecular Science, Part A*, 34 (10), 1785-1801.
- [67] **Patten, T. E., Xia, J., Abernathy, T. and Matyjaszewski, K.** (1996). Polymers with Very Low Polydispersities from Atom Transfer Radical Polymerization, *Science*, 272 (5263), 866-868.
- [68] **Matyjaszewski, K., Coca, S., Gaynor, S. G., Wei, M. and Woodworth, B. E.** (1998). Controlled Radical Polymerization in the Presence of Oxygen, *Macromolecules*, 31 (17), 5967-5969.
- [69] **Beers, K. L., Matyjaszewski, K. and Woodworth, B.** (2001). Controlled/Living Radical Polymerization in the Undergraduate Laboratories. 1. Using ATRP to Prepare Block and Statistical Copolymers of n-Butyl Acrylate and Styrene, *Journal of Chemical Education*, 78 (4), 544.
- [70] **Matyjaszewski, K., Beers, K. L., Metzner, Z. and Woodworth, B.** (2001). Controlled/Living Radical Polymerization in the Undergraduate Laboratories. 2. Using ATRP in Limited Amounts of Air to Prepare Block and Statistical Copolymers of n-Butyl Acrylate and Styrene, *Journal of Chemical Education*, 78 (4), 547.
- [71] **Kickelbick, G., Paik, H.-j. and Matyjaszewski, K.** (1999). Immobilization of the Copper Catalyst in Atom Transfer Radical Polymerization, *Macromolecules*, 32 (9), 2941-2947.
- [72] **Haddleton, D. M., Duncalf, D. J., Kukulj, D. and Radigue, A. P.** (1999). 3-Aminopropyl Silica Supported Living Radical Polymerization of Methyl Methacrylate: Dichlorotris(triphenylphosphine)ruthenium(II) Mediated Atom Transfer Polymerization, *Macromolecules*, 32 (15), 4769-4775.
- [73] **M. Haddleton, D., Kukulj, D. and P. Radigue, A.** (1999). Atom transfer polymerisation of methyl methacrylate mediated by solid supported copper catalysts, *Chem Commun*, (1), 99-100.
- [74] **Sonmez, H. B. and Bicak, N.** (2002). Quaternization of poly(4-vinyl pyridine) beads with 2-chloroacetamide for selective mercury extraction, *Reactive and Functional Polymers*, 51 (1), 55-60.
- [75] **Mishra, M. and Yagci, Y.** (2009). Handbook of Vinyl Polymers: *CRC Press: Boca Raton, FL, USA*,
- [76] **Singha, N. K. and Klumperman, B.** (2000). Atom-transfer radical polymerization of methyl methacrylate (MMA) using CuSCN as the catalyst, *Macromol Rapid Comm*, 21 (16), 1116-1120.

- [77] **Kotani, Y., Kamigaito, M. and Sawamoto, M.** (1999). Re(V)-Mediated Living Radical Polymerization of Styrene: $1\text{ReO}_2\text{I}(\text{PPh}_3)_2/\text{R-I}$ Initiating Systems, *Macromolecules*, 32 (8), 2420-2424.
- [78] **Simal, F., Demonceau, A. and Noels, A. F.** (1999). Highly Efficient Ruthenium-Based Catalytic Systems for the Controlled Free-Radical Polymerization of Vinyl Monomers, *Angewandte Chemie International Edition*, 38 (4), 538-540.
- [79] **Percec, V., Barboiu, B., Neumann, A., Ronda, J. C. and Zhao, M.** (1996). Metal-Catalyzed "Living" Radical Polymerization of Styrene Initiated with Arenesulfonyl Chlorides. From Heterogeneous to Homogeneous Catalysis, *Macromolecules*, 29 (10), 3665-3668.
- [80] **Tang, H., Radosz, M. and Shen, Y.** (2009). Atom transfer radical polymerization and copolymerization of vinyl acetate catalyzed by copper halide/terpyridine, *AIChE Journal*, 55 (3), 737-746.
- [81] **O'Reilly, R. K., Gibson, V. C., White, A. J. P. and Williams, D. J.** (2004). Five-coordinate iron(II) complexes bearing tridentate nitrogen donor ligands as catalysts for atom transfer radical polymerisation, *Polyhedron*, 23 (17), 2921-2928.
- [82] **Uchiike, C., Ouchi, M., Ando, T., Kamigaito, M. and Sawamoto, M.** (2008). Evolution of iron catalysts for effective living radical polymerization: P-N chelate ligand for enhancement of catalytic performances, *Journal of Polymer Science Part A: Polymer Chemistry*, 46 (20), 6819-6827.
- [83] **Uegaki, H., Kotani, Y., Kamigaito, M. and Sawamoto, M.** (1997). Nickel-Mediated Living Radical Polymerization of Methyl Methacrylate, *Macromolecules*, 30 (8), 2249-2253.
- [84] **Riva, R., Schmeits, S., Jérôme, C., Jérôme, R. and Lecomte, P.** (2007). Combination of Ring-Opening Polymerization and "Click Chemistry": Toward Functionalization and Grafting of Poly(ϵ -caprolactone), *Macromolecules*, 40 (4), 796-803.
- [85] **Matyjaszewski, K.** (1998). Mechanistic Aspects of Atom Transfer Radical Polymerization, 685, 258-283.
- [86] **Wakioka, M., Baek, K.-Y., Ando, T., Kamigaito, M. and Sawamoto, M.** (2002). Possibility of Living Radical Polymerization of Vinyl Acetate Catalyzed by Iron(I) Complex, *Macromolecules*, 35 (2), 330-333.
- [87] **Haddleton, D. M., Jasieczek, C. B., Hannon, M. J. and Shooter, A. J.** (1997). Atom Transfer Radical Polymerization of Methyl Methacrylate Initiated by Alkyl Bromide and 2-Pyridinecarbaldehyde Imine Copper(I) Complexes, *Macromolecules*, 30 (7), 2190-2193.
- [88] **Beers, K. L., Gaynor, S. G., Matyjaszewski, K., Sheiko, S. S. and Möller, M.** (1998). The Synthesis of Densely Grafted Copolymers by Atom Transfer Radical Polymerization, *Macromolecules*, 31 (26), 9413-9415.
- [89] **Zhang, X. and Matyjaszewski, K.** (1999). Synthesis of Functional Polystyrenes by Atom Transfer Radical Polymerization Using Protected and Unprotected Carboxylic Acid Initiators, *Macromolecules*, 32 (22), 7349-7353.

- [90] **Matyjaszewski, K., Mu Jo, S., Paik, H.-j. and Gaynor, S. G.** (1997). Synthesis of Well-Defined Polyacrylonitrile by Atom Transfer Radical Polymerization, *Macromolecules*, 30 (20), 6398-6400.
- [91] **Matyjaszewski, K., Gaynor, S. G., Qiu, J., Beers, K., Coca, S., Davis, K., Muhlebach, A., Xia, J. and Zhang, X.** (2000). The Preparation of Well-Defined Water Soluble-Swellable (Co)Polymers by Atom Transfer Radical Polymerization, *Associative Polymers in Aqueous Media: American Chemical Society*, Vol. 765, pp 52-71
- [92] **Odian, G.** (2004). Introduction, Principles of Polymerization: *John Wiley & Sons, Inc.*, pp 1-38
- [93] **Hawker, C. J. and Hedrick, J. L.** (1995). Accurate Control of Chain Ends by a Novel "Living" Free-Radical Polymerization Process, *Macromolecules*, 28 (8), 2993-2995.
- [94] **Gromada, J. and Matyjaszewski, K.** (2001). Simultaneous Reverse and Normal Initiation in Atom Transfer Radical Polymerization, *Macromolecules*, 34 (22), 7664-7671.
- [95] **Mueller, L. and Matyjaszewski, K.** (2010). Reducing Copper Concentration in Polymers Prepared via Atom Transfer Radical Polymerization, *Macromolecular Reaction Engineering*, 4 (3-4), 180-185.
- [96] **Pintauer, T. and Matyjaszewski, K.** (2008). Atom transfer radical addition and polymerization reactions catalyzed by ppm amounts of copper complexes, *Chemical Society reviews*, 37 (6), 1087-1097.
- [97] **Plichta, A., Li, W. and Matyjaszewski, K.** (2009). ICAR ATRP of Styrene and Methyl Methacrylate with Ru(Cp*)Cl(PPh₃)₂, *Macromolecules*, 42 (7), 2330-2332.
- [98] **Jakubowski, W., Min, K. and Matyjaszewski, K.** (2006). Activators Regenerated by Electron Transfer for Atom Transfer Radical Polymerization of Styrene, *Macromolecules*, 39 (1), 39-45.
- [99] **Min, K., Gao, H. and Matyjaszewski, K.** (2005). Preparation of Homopolymers and Block Copolymers in Miniemulsion by ATRP Using Activators Generated by Electron Transfer (AGET), *J Am Chem Soc*, 127 (11), 3825-3830.
- [100] **Min, K., Jakubowski, W. and Matyjaszewski, K.** (2006). AGET ATRP in the Presence of Air in Miniemulsion and in Bulk, *Macromol Rapid Comm*, 27 (8), 594-598.
- [101] **Nguyen, N. H. and Percec, V.** (2010). Dramatic acceleration of SET-LRP of methyl acrylate during catalysis with activated Cu(0) wire, *Journal of Polymer Science Part A: Polymer Chemistry*, 48 (22), 5109-5119.
- [102] **Percec, V., Guliashvili, T., Ladislaw, J. S., Wistrand, A., Stjerndahl, A., Sienkowska, M. J., Monteiro, M. J. and Sahoo, S.** (2006). Ultrafast synthesis of ultrahigh molar mass polymers by metal-catalyzed living radical polymerization of acrylates, methacrylates, and vinyl chloride mediated by SET at 25 degrees C, *J Am Chem Soc*, 128 (43), 14156-14165.

- [103] **Min, K., Gao, H. and Matyjaszewski, K.** (2007). Use of Ascorbic Acid as Reducing Agent for Synthesis of Well-Defined Polymers by ARGET ATRP, *Macromolecules*, 40 (6), 1789-1791.
- [104] **Gnanou, Y. and Hizal, G. r.** (2004). Effect of phenol and derivatives on atom transfer radical polymerization in the presence of air, *Journal of Polymer Science Part A: Polymer Chemistry*, 42 (2), 351-359.
- [105] **Mert, H., Tunca, U. and Hizal, G.** (2006). Thiophenol derivatives as a reducing agent for in situ generation of Cu(I) species via electron transfer reaction in copper-catalyzed living/controlled radical polymerization of styrene, *Journal of Polymer Science Part A: Polymer Chemistry*, 44 (20), 5923-5932.
- [106] **Dag, A., Mert, H., Dervaux, B., Du Prez, F. E., Tunca, U. and Hizal, G.** (2007). Fructose as a reducing agent for in situ generation of Cu(I) species via an electron-transfer reaction in copper-catalyzed living/controlled radical polymerization of styrene, *Designed Monomers and Polymers*, 10 (5), 425-438.
- [107] **Otsu, T. and Yoshida, M.** (1982). Role of initiator-transfer agent-terminator (iniferter) in radical polymerizations: Polymer design by organic disulfides as iniferters, *Die Makromolekulare Chemie, Rapid Communications*, 3 (2), 127-132.
- [108] **Devonport, W., Michalak, L., Malmström, E., Mate, M., Kurdi, B., Hawker, C. J., Barclay, G. G. and Sinta, R.** (1997). "Living" Free-Radical Polymerizations in the Absence of Initiators: Controlled Autopolymerization, *Macromolecules*, 30 (7), 1929-1934.
- [109] **Skene, W. G., Scaiano, J. C., Listigovers, N. A., Kzmaier, P. M. and Georges, M. K.** (2000). Rate Constants for the Trapping of Various Carbon-Centered Radicals by Nitroxides: Unimolecular Initiators for Living Free Radical Polymerization, *Macromolecules*, 33 (14), 5065-5072.
- [110] **Moad, G., Rizzardo, E. and Solomon, D. H.** (1982). Selectivity of the reaction of free radicals with styrene, *Macromolecules*, 15 (3), 909-914.
- [111] **Moad, G., Rizzardo, E. and Thang, S. H.** (2005). Living Radical Polymerization by the RAFT Process, *Aust J Chem*, 58 (6), 379-410.
- [112] **Destarac, M., Taton, D., Zard, S. Z., Saleh, T. and Six, Y.** (2003). On the Importance of Xanthate Substituents in the MADIX Process, *Advances in Controlled/Living Radical Polymerization: American Chemical Society*, Vol. 854, pp 536-550
- [113] **Moad, G., Rizzardo, E. and Thang, S. H.** (2006). Living Radical Polymerization by the RAFT Process—A First Update, *Aust J Chem*, 59 (10), 669-692.
- [114] **Moad, G., Rizzardo, E. and Thang, S. H.** (2009). Living Radical Polymerization by the RAFT Process – A Second Update, *Aust J Chem*, 62 (11), 1402-1472.

- [115] **Rizzardo, E., Moad, G. and Thang, S. H.** (2008). RAFT Polymerization in Bulk Monomer or in (Organic) Solution, *Handbook of RAFT Polymerization: Wiley-VCH Verlag GmbH & Co. KGaA*, pp 189-234
- [116] **Moad, G., Chiefari, J., Chong, Y. K., Krstina, J., Mayadunne, R. T. A., Postma, A., Rizzardo, E. and Thang, S. H.** (2000). Living free radical polymerization with reversible addition – fragmentation chain transfer (the life of RAFT), *Polymer International*, 49 (9), 993-1001.
- [117] **Dong, Z.-m., Liu, X.-h., Tang, X.-l. and Li, Y.-s.** (2009). Synthesis of Hyperbranched Polymers with Pendent Norbornene Functionalities via RAFT Polymerization of a Novel Asymmetrical Divinyl Monomer, *Macromolecules*, 42 (13), 4596-4603.
- [118] **Liu, J., Liu, H., Jia, Z., Bulmus, V. and Davis, T. P.** (2008). An approach to biodegradable star polymeric architectures using disulfide coupling, *Chem Commun*, (48), 6582-6584.
- [119] **Quinn, J. F., Chaplin, R. P. and Davis, T. P.** (2002). Facile synthesis of comb, star, and graft polymers via reversible addition-fragmentation chain transfer (RAFT) polymerization, *Journal of Polymer Science Part A: Polymer Chemistry*, 40 (17), 2956-2966.
- [120] **Xu, J., Tao, L., Liu, J., Bulmus, V. and Davis, T. P.** (2009). Synthesis of Functionalized and Biodegradable Hyperbranched Polymers from Novel AB₂ Macromonomers Prepared by RAFT Polymerization, *Macromolecules*, 42 (18), 6893-6901.
- [121] **Kolb, H. C., Finn, M. G. and Sharpless, K. B.** (2001). Click Chemistry: Diverse Chemical Function from a Few Good Reactions, *Angewandte Chemie International Edition*, 40 (11), 2004-2021.
- [122] **Huisgen, R.** (1963). 1,3-Dipolare Cycloadditionen Rückschau und Ausblick, *Angewandte Chemie*, 75 (13), 604-637.
- [123] **Tornøe, C. W., Christensen, C. and Meldal, M.** (2002). Peptidotriazoles on Solid Phase: [1,2,3]-Triazoles by Regiospecific Copper(I)-Catalyzed 1,3-Dipolar Cycloadditions of Terminal Alkynes to Azides, *The Journal of Organic Chemistry*, 67 (9), 3057-3064.
- [124] **Huisgen, R.** (1963). 1,3-Dipolar Cycloadditions. Past and Future, *Angewandte Chemie International Edition in English*, 2 (10), 565-598.
- [125] **Pachón, L. D., van Maarseveen, J. H. and Rothenberg, G.** (2005). Click Chemistry: Copper Clusters Catalyse the Cycloaddition of Azides with Terminal Alkynes, *Advanced Synthesis & Catalysis*, 347 (6), 811-815.
- [126] **Appukkuttan, P., Dehaen, W., Fokin, V. V. and Van der Eycken, E.** (2004). A Microwave-Assisted Click Chemistry Synthesis of 1,4-Disubstituted 1,2,3-Triazoles via a Copper(I)-Catalyzed Three-Component Reaction, *Organic letters*, 6 (23), 4223-4225.
- [127] **Wu, P., Feldman, A. K., Nugent, A. K., Hawker, C. J., Scheel, A., Voit, B., Pyun, J., Frechet, J. M., Sharpless, K. B. and Fokin, V. V.** (2004). Efficiency and fidelity in a click-chemistry route to triazole dendrimers by the copper(i)-catalyzed ligation of azides and alkynes, *Angewandte Chemie*, 43 (30), 3928-3932.

- [128] **Diels, O. and Alder, K.** (1928). Synthesen in der hydroaromatischen Reihe, *Justus Liebigs Annalen der Chemie*, 460 (1), 98-122.
- [129] **Hizal, G., Tunca, U. and Sanyal, A.** (2011). Discrete macromolecular constructs via the Diels-Alder “Click” reaction, *Journal of Polymer Science Part A: Polymer Chemistry*, n/a-n/a.
- [130] **Fringuelli, F., Taticchi, A.** (1990). Dienes in the Diels-Alder Reaction: *John Wiley: New York*,
- [131] **Alder, K. and Stein, G.** (1937). Investigations over the course of the Diene Synthesis, *Angewandte Chemie*, 50 (28), 510-519.
- [132] **Woodward, R. B. and Hoffmann, R.** (1965). Stereochemistry of Electrocyclic Reactions, *J Am Chem Soc*, 87 (2), 395-397.
- [133] **Houk, K. N. and Strozier, R. W.** (1973). Lewis acid catalysis of Diels-Alder reactions, *J Am Chem Soc*, 95 (12), 4094-4096.
- [134] **Cativiela, C., Garcia, J. I., Mayoral, J. A. and Salvatella, L.** (1994). Solvent effects on endo/exo- and regio-selectivities of Diels-Alder reactions of carbonyl-containing dienophiles, *Journal of the Chemical Society, Perkin Transactions 2*, (4), 847-851.
- [135] **Dondoni, A.** (2008). The emergence of thiol-ene coupling as a click process for materials and bioorganic chemistry, *Angewandte Chemie*, 47 (47), 8995-8997.
- [136] **Posner, T.** (1905). Beiträge zur Kenntniss der ungesättigten Verbindungen. II. Ueber die Addition von Mercaptanen an ungesättigte Kohlenwasserstoffe, *Berichte der deutschen chemischen Gesellschaft*, 38 (1), 646-657.
- [137] **Mayo, F. R. and Walling, C.** (1940). The Peroxide Effect in the Addition of Reagents to Unsaturated Compounds and in Rearrangement Reactions, *Chemical Reviews*, 27 (2), 351-412.
- [138] **Griesbaum, K.** (1970). Problems and Possibilities of the Free-Radical Addition of Thiols to Unsaturated Compounds, *Angewandte Chemie International Edition in English*, 9 (4), 273-287.
- [139] **Kharasch, M. S., Read, A. T., and Mayo, F. R.** (1938). *Journal of the Society of Chemical Industry*, 57 (32), 752-754.
- [140] **Sangermano, M., Bongiovanni, R., Malucelli, G., Priola, A., Harden, A. and Rehnberg, N.** (2002). Synthesis of new fluorinated allyl ethers for the surface modification of thiol-ene ultraviolet-curable formulations, *Journal of Polymer Science Part A: Polymer Chemistry*, 40 (15), 2583-2590.
- [141] **Sangermano, M., Gross, S., Priola, A., Rizza, G. and Sada, C.** (2007). Thiol-ene Hybrid Organic/Inorganic Nanostructured Coatings Based on Thiol-Functionalized Zirconium Oxoclusters, *Macromol Chem Phys*, 208 (23), 2560-2568.
- [142] **Morgan, C. R., Magnotta, F. and Ketley, A. D.** (1977). Thiol/ene photocurable polymers, *Journal of Polymer Science: Polymer Chemistry Edition*, 15 (3), 627-645.

- [143] **Campos, L. M., Killops, K. L., Sakai, R., Paulusse, J. M. J., Damiron, D., Drockenmuller, E., Messmore, B. W. and Hawker, C. J.** (2008). Development of Thermal and Photochemical Strategies for Thiol–Ene Click Polymer Functionalization, *Macromolecules*, **41** (19), 7063–7070.
- [144] **Liu, M., van Hensbergen, J., Burford, R. P. and Lowe, A. B.** (2012). Thiol–Michael coupling chemistry: facile access to a library of functional exo-7-oxanorbornenes and their ring-opening metathesis (co)polymerization, *Polym Chem-Uk*, **3** (6), 1647–1658.
- [145] **Hoyle, C. E. and Bowman, C. N.** (2010). Thiol-ene click chemistry, *Angewandte Chemie*, **49** (9), 1540–1573.
- [146] **Mather, B. D., Viswanathan, K., Miller, K. M. and Long, T. E.** (2006). Michael addition reactions in macromolecular design for emerging technologies, *Progress in Polymer Science*, **31** (5), 487–531.
- [147] **Killops, K. L., Campos, L. M. and Hawker, C. J.** (2008). Robust, efficient, and orthogonal synthesis of dendrimers via thiol-ene "click" chemistry, *J Am Chem Soc*, **130** (15), 5062–5064.
- [148] **Chan, J. W., Yu, B., Hoyle, C. E. and Lowe, A. B.** (2008). Convergent synthesis of 3-arm star polymers from RAFT-prepared poly(N,N-diethylacrylamide) via a thiol-ene click reaction, *Chem Commun*, (40), 4959–4961.
- [149] **Singha, N. K., Gibson, M. I., Koiry, B. P., Danial, M. and Klok, H.-A.** (2011). Side-Chain Peptide-Synthetic Polymer Conjugates via Tandem “Ester-Amide/Thiol–Ene” Post-Polymerization Modification of Poly(pentafluorophenyl methacrylate) Obtained Using ATRP, *Biomacromolecules*, **12** (8), 2908–2913.
- [150] **van Hensbergen, J. A., Burford, R. P. and Lowe, A. B.** (2013). Post-functionalization of a ROMP polymer backbone via radical thiol-ene coupling chemistry, *Journal of Polymer Science Part A: Polymer Chemistry*, **51** (3), 487–492.
- [151] **Altintas, O., Josse, T., De Winter, J., Matsumoto, N. M., Gerbaux, P., Wilhelm, M. and Barner-Kowollik, C.** (2015). Ready access to end-functional polystyrenes via a combination of ARGET ATRP and thiol–ene chemistry, *Polym. Chem.*
- [152] **Lowe, A. B.** (2010). Thiol-ene “click” reactions and recent applications in polymer and materials synthesis, *Polym. Chem.*, **1** (1), 17–36.
- [153] **Koo, S. P. S., Stamenović, M. M., Prasath, R. A., Inglis, A. J., Du Prez, F. E., Barner-Kowollik, C., Van Camp, W. and Junkers, T.** (2010). Limitations of radical thiol-ene reactions for polymer–polymer conjugation, *Journal of Polymer Science Part A: Polymer Chemistry*, **48** (8), 1699–1713.
- [154] **Lowe, A. B.** (2014). Thiol–ene “click” reactions and recent applications in polymer and materials synthesis: a first update, *Polym Chem-Uk*, **5** (17), 4820.

- [155] **Barbey, R. and Perrier, S.** (2013). A Facile Route to Functional Hyperbranched Polymers by Combining Reversible Addition–Fragmentation Chain Transfer Polymerization, Thiol–Yne Chemistry, and Postpolymerization Modification Strategies, *Acs Macro Lett*, 2 (5), 366-370.
- [156] **Samaroo, D., Soll, C. E., Todaro, L. J. and Drain, C. M.** (2006). Efficient microwave-assisted synthesis of amine-substituted tetrakis(pentafluorophenyl)porphyrin, *Organic letters*, 8 (22), 4985-4988.
- [157] **Battioni, P., Brigaud, O., Desvaux, H., Mansuy, D. and Traylor, T. G.** (1991). Preparation of functionalized polyhalogenated tetraaryl-porphyrins by selective substitution of the p-Fluorines of meso-tetra-(pentafluorophenyl)porphyrins, *Tetrahedron Letters*, 32 (25), 2893-2896.
- [158] **Burdon, J. and Westwood, W. T.** (1970). Aromatic polyfluoro-compounds. Part XLIX. Nucleophilic replacement reactions of 2,3,4,5,6-pentafluorostyrene, *Journal of the Chemical Society C: Organic*, (9), 1271.
- [159] **Brooke, G. M., Chambers, R. D., Drury, C. J. and Bower, M. J.** (1993). Remarkable orientational effects in the displacement of the fluorine from heptafluoro-isoquinoline and -quinoline towards sulfur nucleophiles. Further reactions with oxygen nucleophiles, *Journal of the Chemical Society, Perkin Transactions 1*, (18), 2201-2209.
- [160] **Gan, D., Mueller, A. and Wooley, K. L.** (2003). Amphiphilic and hydrophobic surface patterns generated from hyperbranched fluoropolymer/linear polymer networks: Minimally adhesive coatings via the crosslinking of hyperbranched fluoropolymers, *Journal of Polymer Science Part A: Polymer Chemistry*, 41 (22), 3531-3540.
- [161] **Gudipati, C. S., Greenlief, C. M., Johnson, J. A., Prayongpan, P. and Wooley, K. L.** (2004). Hyperbranched fluoropolymer and linear poly(ethylene glycol) based amphiphilic crosslinked networks as efficient antifouling coatings: An insight into the surface compositions, topographies, and morphologies, *Journal of Polymer Science Part A: Polymer Chemistry*, 42 (24), 6193-6208.
- [162] **Ma, J., Cheng, C., Sun, G. and Wooley, K. L.** (2008). Well-Defined Polymers Bearing Pendent Alkene Functionalities via Selective RAFT Polymerization, *Macromolecules*, 41 (23), 9080-9089.
- [163] **Ott, C., Hoogenboom, R. and Schubert, U. S.** (2008). Post-modification of poly(pentafluorostyrene): a versatile “click” method to create well-defined multifunctional graft copolymers, *Chem Commun*, (30), 3516.
- [164] **Slavin, S., Burns, J., Haddleton, D. M. and Becer, C. R.** (2011). Synthesis of glycopolymers via click reactions, *European Polymer Journal*, 47 (4), 435-446.
- [165] **Wong, C.-H. and Zimmerman, S. C.** (2013). Orthogonality in organic, polymer, and supramolecular chemistry: from Merrifield to click chemistry, *Chem Commun*, 49 (17), 1679-1695.

- [166] **Goldmann, A. S., Glassner, M., Inglis, A. J. and Barner-Kowollik, C.** (2013). Post-functionalization of polymers via orthogonal ligation chemistry, *Macromol Rapid Commun*, 34 (10), 810-849.
- [167] **Iha, R. K., Wooley, K. L., Nystrom, A. M., Burke, D. J., Kade, M. J. and Hawker, C. J.** (2009). Applications of orthogonal "click" chemistries in the synthesis of functional soft materials, *Chem Rev*, 109 (11), 5620-5686.
- [168] **Tunca, U.** (2013). Triple Click Reaction Strategy for Macromolecular Diversity, *Macromol Rapid Comm*, 34 (1), 38-46.
- [169] **Durmaz, H., Dag, A., Altintas, O., Erdogan, T., Hizal, G. and Tunca, U.** (2007). One-Pot Synthesis of ABC Type Triblock Copolymers via in situ Click [3 + 2] and Diels–Alder [4 + 2] Reactions, *Macromolecules*, 40 (2), 191-198.
- [170] **Dag, A., Durmaz, H., Demir, E., Hizal, G. and Tunca, U.** (2008). Heterograft copolymers via double click reactions using one-pot technique, *Journal of Polymer Science Part A: Polymer Chemistry*, 46 (20), 6969-6977.
- [171] **Glassner, M., Oehlenschlaeger, K. K., Gruendling, T. and Barner-Kowollik, C.** (2011). Ambient Temperature Synthesis of Triblock Copolymers via Orthogonal Photochemically and Thermally Induced Modular Conjugation, *Macromolecules*, 44 (12), 4681-4689.
- [172] **Antoni, P., Robb, M. J., Campos, L., Montanez, M., Hult, A., Malmström, E., Malkoch, M. and Hawker, C. J.** (2010). Pushing the Limits for Thiol–Ene and CuAAC Reactions: Synthesis of a 6th Generation Dendrimer in a Single Day, *Macromolecules*, 43 (16), 6625-6631.
- [173] **Iskin, B., Yilmaz, G. and Yagci, Y.** (2011). Synthesis of ABC type miktoarm star copolymers by triple click chemistry, *Polym Chem-Uk*, 2 (12), 2865-2871.
- [174] **Uysal, B. B., Gunay, U. S., Hizal, G. and Tunca, U.** (2014). Orthogonal multifunctionalization of aliphatic polycarbonate via sequential Michael addition and radical-thiol-ene click reactions, *Journal of Polymer Science Part A: Polymer Chemistry*, 52 (11), 1581-1587.
- [175] **Braunecker, W. A. and Matyjaszewski, K.** (2007). Controlled/living radical polymerization: Features, developments, and perspectives, *Progress in Polymer Science*, 32 (1), 93-146.
- [176] **Inoue, K.** (2000). Functional dendrimers, hyperbranched and star polymers, *Progress in Polymer Science*, 25 (4), 453-571.
- [177] **Wiltshire, J. T. and Qiao, G. G.** (2007). Recent Advances in Star Polymer Design: Degradability and the Potential for Drug Delivery, *Aust J Chem*, 60 (10), 699-705.
- [178] **Hawker, C. J. and Wooley, K. L.** (2005). The Convergence of Synthetic Organic and Polymer Chemistries, *Science*, 309 (5738), 1200-1205.
- [179] **Kuckling, D. and Wycisk, A.** (2013). Stimuli-responsive star polymers, *Journal of Polymer Science Part A: Polymer Chemistry*, 51 (14), 2980-2994.

- [180] **Hirao, A., Hayashi, M., Loykulnant, S., Sugiyama, K., Ryu, S. W., Haraguchi, N., Matsuo, A. and Higashihara, T.** (2005). Precise syntheses of chain-multi-functionalized polymers, star-branched polymers, star-linear block polymers, densely branched polymers, and dendritic branched polymers based on iterative approach using functionalized 1,1-diphenylethylene derivatives, *Progress in Polymer Science*, 30 (2), 111-182.
- [181] **Gao, H.** (2012). Development of star polymers as unimolecular containers for nanomaterials, *Macromol Rapid Commun*, 33 (9), 722-734.
- [182] **Altintas, O., Vogt, A. P., Barner-Kowollik, C. and Tunca, U.** (2012). Constructing star polymers via modular ligation strategies, *Polym Chem-Uk*, 3 (1), 34-45.
- [183] **Gnanou, Y. and Taton, D.** (2001). Stars and dendrimer-like architectures by the divergent method using controlled radical polymerization, *Macromolecular Symposia*, 174 (1), 333-341.
- [184] **Shohi, H., Sawamoto, M. and Higashimura, T.** (1991). Tri-armed star polymers by living cationic polymerization. 1. Trifunctional initiators for living polymerization of isobutyl vinyl ether, *Macromolecules*, 24 (17), 4926-4931.
- [185] **Ohno, K., Wong, B. and Haddleton, D. M.** (2001). Synthesis of well-defined cyclodextrin-core star polymers, *Journal of Polymer Science Part A: Polymer Chemistry*, 39 (13), 2206-2214.
- [186] **Celik, C., Hizal, G. and Tunca, U.** (2003). Synthesis of miktoarm star and miktoarm star block copolymers via a combination of atom transfer radical polymerization and stable free-radical polymerization, *Journal of Polymer Science Part A: Polymer Chemistry*, 41 (16), 2542-2548.
- [187] **Erdogan, T., Ozyurek, Z., Hizal, G. and Tunca, U.** (2004). Facile synthesis of AB₂-type miktoarm star polymers through the combination of atom transfer radical polymerization and ring-opening polymerization, *Journal of Polymer Science Part A: Polymer Chemistry*, 42 (10), 2313-2320.
- [188] **Tao, Y., Xu, Q., Li, N., Lu, J., Wang, L. and Xia, X.** (2011). Synthesis and photoluminescent property of star polymers with carbzole pendent and a zinc porphyrin core by ATRP, *Polymer*, 52 (19), 4261-4267.
- [189] **Liu, J.-X., Yuan, C., Su, Z., Xu, T.-T., Wei, L.-H. and Ma, Z.** (2013). Three-arm star block copolymers of ϵ -caprolactone and acrylic acid: Synthesis and micellization behavior, *Journal of Polymer Science Part A: Polymer Chemistry*, 51 (9), 1969-1975.
- [190] **Li, Y., Zhang, B., Hoskins, J. N. and Grayson, S. M.** (2012). Synthesis, purification, and characterization of “perfect” star polymers via “Click” coupling, *Journal of Polymer Science Part A: Polymer Chemistry*, 50 (6), 1086-1101.
- [191] **Hawker, C. J.** (1995). Architectural Control in “Living” Free Radical Polymerizations: Preparation of Star and Graft Polymers, *Angewandte Chemie International Edition in English*, 34 (13-14), 1456-1459.

- [192] **Tunca, U., Ozyurek, Z., Erdogan, T. and Hizal, G.** (2004). Novel miktofunctional initiator for the preparation of an ABC-type miktoarm star polymer via a combination of controlled polymerization techniques, *Journal of Polymer Science Part A: Polymer Chemistry*, 42 (17), 4228-4236.
- [193] **Zhang, W., Zhang, W., Zhang, Z., Cheng, Z., Tu, Y., Qiu, Y. and Zhu, X.** (2010). Thermo-responsive fluorescent micelles from amphiphilic A3B miktoarm star copolymers prepared via a combination of SET-LRP and RAFT polymerization, *Journal of Polymer Science Part A: Polymer Chemistry*, 48 (19), 4268-4278.
- [194] **Matyjaszewski, K., Gnanou, Y. and Leibler, L.** (2007). Macromolecular Engineering, *Macromolecular Engineering: Wiley-VCH Verlag GmbH & Co. KGaA*, pp 1-6
- [195] **Zilliox, J.-G., Rempp, P. and Parrod, J.** (1968). Préparation de Macromolécules à Structure en Etoile, par Copolymerisation Anionique, *Journal of Polymer Science Part C: Polymer Symposia*, 22 (1), 145-156.
- [196] **Kanaoka, S., Sawamoto, M. and Higashimura, T.** (1991). Star-shaped polymers by living cationic polymerization. 1. Synthesis of star-shaped polymers of alkyl and vinyl ethers, *Macromolecules*, 24 (9), 2309-2313.
- [197] **Xia, J., Zhang, X. and Matyjaszewski, K.** (1999). Synthesis of Star-Shaped Polystyrene by Atom Transfer Radical Polymerization Using an "Arm First" Approach, *Macromolecules*, 32 (13), 4482-4484.
- [198] **Zhang, X., Xia, J. and Matyjaszewski, K.** (2000). End-Functional Poly(tert-butyl acrylate) Star Polymers by Controlled Radical Polymerization, *Macromolecules*, 33 (7), 2340-2345.
- [199] **Baek, K.-Y., Kamigaito, M. and Sawamoto, M.** (2001). Star-Shaped Polymers by Metal-Catalyzed Living Radical Polymerization. 1. Design of Ru(II)-Based Systems and Divinyl Linking Agents¹, *Macromolecules*, 34 (2), 215-221.
- [200] **Baek, K.-Y., Kamigaito, M. and Sawamoto, M.** (2002). Star-shaped polymers by Ru(II)-catalyzed living radical polymerization. II. Effective reaction conditions and characterization by multi-angle laser light scattering/size exclusion chromatography and small-angle X-ray scattering, *Journal of Polymer Science Part A: Polymer Chemistry*, 40 (14), 2245-2255.
- [201] **Tsoukatos, T., Pispas, S. and Hadjichristidis, N.** (2001). Star-branched polystyrenes by nitroxide living free-radical polymerization, *Journal of Polymer Science Part A: Polymer Chemistry*, 39 (2), 320-325.
- [202] **Lord, H. T., Quinn, J. F., Angus, S. D., Whittaker, M. R., Stenzel, M. H. and Davis, T. P.** (2003). Microgel stars via Reversible Addition Fragmentation Chain Transfer (RAFT) polymerisation - a facile route to macroporous membranes, honeycomb patterned thin films and inverse opal substrates, *J Mater Chem*, 13 (11), 2819-2824.

- [203] **Barner-Kowollik, C., Davis, T. P. and Stenzel, M. H.** (2006). Synthesis of Star Polymers using RAFT Polymerization: What is Possible?, *Aust J Chem*, 59 (10), 719-727.
- [204] **Stenzel, M. H., Davis, T. P. and Barner-Kowollik, C.** (2004). Poly(vinyl alcohol) star polymers prepared via MADIX/RAFT polymerisation, *Chem Commun*, (13), 1546-1547.
- [205] **Gao, H., Tsarevsky, N. V. and Matyjaszewski, K.** (2005). Synthesis of Degradable Miktoarm Star Copolymers via Atom Transfer Radical Polymerization, *Macromolecules*, 38 (14), 5995-6004.
- [206] **Gao, H. and Matyjaszewski, K.** (2006). Synthesis of Miktoarm Star Polymers via ATRP Using the “In–Out” Method: Determination of Initiation Efficiency of Star Macroinitiators, *Macromolecules*, 39 (21), 7216-7223.
- [207] **Gao, H. and Matyjaszewski, K.** (2007). Arm-first method as a simple and general method for synthesis of miktoarm star copolymers, *J Am Chem Soc*, 129 (38), 11828-11834.
- [208] **Dag, A., Durmaz, H., Kirmizi, V., Hizal, G. and Tunca, U.** (2010). An easy way to the preparation of multi-miktoarm star block copolymers via sequential double click reactions, *Polym Chem-Uk*, 1 (5), 621.
- [209] **Durmaz, H., Dag, A., Gursay, D., Demirel, A. L., Hizal, G. and Tunca, U.** (2010). Multiarm star triblock terpolymers via sequential double click reactions, *Journal of Polymer Science Part A: Polymer Chemistry*, 48 (7), 1557-1564.
- [210] **Gao, H. and Matyjaszewski, K.** (2006). Synthesis of Star Polymers by a Combination of ATRP and the “Click” Coupling Method, *Macromolecules*, 39 (15), 4960-4965.
- [211] **Dag, A., Durmaz, H., Hizal, G. and Tunca, U.** (2008). Preparation of 3-arm star polymers (A3) via Diels–Alder click reaction, *Journal of Polymer Science Part A: Polymer Chemistry*, 46 (1), 302-313.
- [212] **Gao, H., Min, K. and Matyjaszewski, K.** (2007). Synthesis of 3-Arm Star Block Copolymers by Combination of “Core-First” and “Coupling-Onto” Methods Using ATRP and Click Reactions, *Macromol Chem Phys*, 208 (13), 1370-1378.
- [213] **Durmaz, H., Karatas, F., Tunca, U. and Hizal, G.** (2006). Preparation of ABC miktoarm star terpolymer containing poly(ethylene glycol), polystyrene, and poly(tert-butylacrylate) arms by combining diels-alder reaction, atom transfer radical, and stable free radical polymerization routes, *Journal of Polymer Science Part A: Polymer Chemistry*, 44 (1), 499-509.
- [214] **Gunay, U. S., Durmaz, H., Gungor, E., Dag, A., Hizal, G. and Tunca, U.** (2012). 3-miktoarm star terpolymers using triple click reactions: Diels-Alder, copper-catalyzed azide-alkyne cycloaddition, and nitroxide radical coupling reactions, *Journal of Polymer Science Part A: Polymer Chemistry*, 50 (4), 729-735.

- [215] **Bosman, A. W., Vestberg, R., Heumann, A., Frechet, J. M. and Hawker, C. J.** (2003). A modular approach toward functionalized three-dimensional macromolecules: from synthetic concepts to practical applications, *J Am Chem Soc*, 125 (3), 715-728.
- [216] **Baek, K.-Y., Kamigaito, M. and Sawamoto, M.** (2002). Star poly(methyl methacrylate) with end-functionalized arm chains by ruthenium-catalyzed living radical polymerization, *Journal of Polymer Science Part A: Polymer Chemistry*, 40 (12), 1972-1982.
- [217] **Ohno, S., Gao, H., Cusick, B., Kowalewski, T. and Matyjaszewski, K.** (2009). Methacryloyl and/or Hydroxyl End-Functional Star Polymers Synthesized by ATRP Using the Arm-First Method, *Macromol Chem Phys*, 210 (6), 421-430.
- [218] **Erdogan, T., Bilir, C., Erdal Unveren, E., Demirel, A. L. and Tunca, U.** (2014). Novel multiarm star block copolymer ionomers as proton conductive membranes, *Polym. Chem.*, 6 (4), 561-572.
- [219] **Sumerlin, B. S., Tsarevsky, N. V., Louche, G., Lee, R. Y. and Matyjaszewski, K.** (2005). Highly Efficient "Click" Functionalization of Poly(3-azidopropyl methacrylate) Prepared by ATRP, *Macromolecules*, 38 (18), 7540-7545.
- [220] **Dag, A., Aydin, M., Durmaz, H., Hizal, G. and Tunca, U.** (2012). Various polycarbonate graft copolymers via diels-alder click reaction, *Journal of Polymer Science Part A: Polymer Chemistry*, 50 (21), 4476-4483.
- [221] **Boyer, C., Whittaker, M. and Davis, T. P.** (2011). Synthesis and Postfunctionalization of Well-Defined Star Polymers via "Double" Click Chemistry, *J Polym Sci Pol Chem*, 49 (24), 5245-5256.
- [222] (2009). Handbook of vinyl polymers : radical polymerization, process, and technology, In: M. K. Mishra, Y. Yagci and M. K. Mishra, editors. 2nd ed. ed. Boca Raton :: CRC Press/Taylor & Francis,
- [223] **Yağci, Y. and Schnabel, W.** (1990). Light-induced synthesis of block and graft copolymers, *Progress in Polymer Science*, 15 (4), 551-601.
- [224] **Yagci, Y., Jockusch, S. and Turro, N. J.** (2010). Photoinitiated Polymerization: Advances, Challenges, and Opportunities, *Macromolecules*, 43 (15), 6245-6260.
- [225] **Angiolini, L., Caretti, D. and Salatelli, E.** (2000). Synthesis and photoinitiation activity of radical polymeric photoinitiators bearing side-chain camphorquinone moieties, *Macromol Chem Phys*, 201 (18), 2646-2653.
- [226] **Jiang, X. and Yin, J.** (2004). Polymeric Photoinitiator Containing In-Chain Thioxanthone and Coinitiator Amines, *Macromol Rapid Comm*, 25 (6), 748-752.
- [227] **Dufour, P., Oldring, P. K. T. and Allen, N. S.** (1991). Chemistry and Technology of UV & EB Formulation for Coatings, Inks & Paints: Photoinitiators for free radical and cationic polymerisation: *SITA Technology*,

- [228] **Angiolini, L., Caretti, D., Carlini, C., Corelli, E. and Salatelli, E.** (1999). Polymeric photoinitiators having benzoin methylether moieties connected to the main chain through the benzyl aromatic ring and their activity for ultraviolet-curable coatings, *Polymer*, **40** (26), 7197-7207.
- [229] **Degirmenci, M., Cianga, I. and Yagci, Y.** (2002). Synthesis of well-defined polystyrene macrophotoinitiators by atom-transfer radical polymerization, *Macromol Chem Phys*, **203** (10-11), 1279-1284.
- [230] **Xie, Y. and Huang, H.** (2016). Preparation and characterization of an amphiphilic macrophotoinitiator based on 2-hydroxyl-2-methyl-1-phenylpropanone, *J Appl Polym Sci*, **133** (36), n/a-n/a.
- [231] **Karahan, Ö., Balta, D. K., Arsu, N. and Avci, D.** (2014). Synthesis and evaluations of novel photoinitiators with side-chain benzophenone, derived from alkyl α -hydroxymethacrylates, *Journal of Photochemistry and Photobiology A: Chemistry*, **274**, 43-49.
- [232] **Temel, G., Aydogan, B., Arsu, N. and Yagci, Y.** (2009). Synthesis and Characterization of One-Component Polymeric Photoinitiator by Simultaneous Double Click Reactions and Its Use in Photoinduced Free Radical Polymerization, *Macromolecules*, **42** (16), 6098-6106.
- [233] **Wen, Y., Jiang, X., Liu, R. and Yin, J.** (2009). Amphipathic hyperbranched polymeric thioxanthone photoinitiators (AHPTXs): Synthesis, characterization and photoinitiated polymerization, *Polymer*, **50** (16), 3917-3923.
- [234] **Allonas, X., Fouassier, J.-P., Angiolini, L. and Caretti, D.** (2001). Excited-State Properties of Camphorquinone Based Monomeric and Polymeric Photoinitiators, *Helvetica Chimica Acta*, **84** (9), 2577-2588.
- [235] **Gacal, B., Akat, H., Balta, D. K., Arsu, N. and Yagci, Y.** (2008). Synthesis and Characterization of Polymeric Thioxanthone Photoinitiators via Double Click Reactions, *Macromolecules*, **41** (7), 2401-2405.
- [236] **Altintas, O., Schulze-Suenninghausen, D., Luy, B. and Barner-Kowollik, C.** (2013). Facile Preparation of Supramolecular H-Shaped (Ter)polymers via Multiple Hydrogen Bonding, *Acs Macro Lett*, **2** (3), 211-216.
- [237] **Fustin, C. A., Guillet, P., Schubert, U. S. and Gohy, J. F.** (2007). Metallo-Supramolecular Block Copolymers, *Advanced Materials*, **19** (13), 1665-1673.
- [238] **Chen, G. and Jiang, M.** (2011). Cyclodextrin-based inclusion complexation bridging supramolecular chemistry and macromolecular self-assembly, *Chemical Society reviews*, **40** (5), 2254-2266.
- [239] **Schmidt, B. V. K. J., Hetzer, M., Ritter, H. and Barner-Kowollik, C.** (2014). Complex macromolecular architecture design via cyclodextrin host/guest complexes, *Progress in Polymer Science*, **39** (1), 235-249.
- [240] **Liu, B.-w., Zhou, H., Zhou, S.-t. and Yuan, J.-y.** (2015). Macromolecules based on recognition between cyclodextrin and guest molecules: Synthesis, properties and functions, *European Polymer Journal*, **65**, 63-81.

- [241] **Stadermann, J., Komber, H., Erber, M., Däbritz, F., Ritter, H. and Voit, B.** (2011). Diblock Copolymer Formation via Self-Assembly of Cyclodextrin and Adamantyl End-Functionalized Polymers, *Macromolecules*, 44 (9), 3250-3259.
- [242] **Zeng, J., Shi, K., Zhang, Y., Sun, X. and Zhang, B.** (2008). Construction and micellization of a noncovalent double hydrophilic block copolymer, *Chem Commun*, (32), 3753-3755.
- [243] **Ang, C. Y., Tan, S. Y., Wang, X., Zhang, Q., Khan, M., Bai, L., Tamil Selvan, S., Ma, X., Zhu, L., Nguyen, K. T., Tan, N. S. and Zhao, Y.** (2014). Supramolecular nanoparticle carriers self-assembled from cyclodextrin- and adamantane-functionalized polyacrylates for tumor-targeted drug delivery, *Journal of Materials Chemistry B*, 2 (13), 1879-1890.
- [244] **Li, N., Chen, Y., Zhang, Y.-M., Yang, Y., Su, Y., Chen, J.-T. and Liu, Y.** (2014). Polysaccharide-Gold Nanocluster Supramolecular Conjugates as a Versatile Platform for the Targeted Delivery of Anticancer Drugs, *Scientific Reports*, 4, 4164.
- [245] **Cakir, N., Hizal, G. and Becer, C. R.** (2015). Supramolecular glycopolymers with thermo-responsive self-assembly and lectin binding, *Polym. Chem.*
- [246] **Bertrand, A., Stenzel, M., Fleury, E. and Bernard, J.** (2012). Host-guest driven supramolecular assembly of reversible comb-shaped polymers in aqueous solution, *Polym. Chem.*, 3 (2), 377-383.
- [247] **Zhang, Z.-X., Liu, X., Xu, F. J., Loh, X. J., Kang, E.-T., Neoh, K.-G. and Li, J.** (2008). Pseudo-Block Copolymer Based on Star-Shaped Poly(N-isopropylacrylamide) with a β -Cyclodextrin Core and Guest-Bearing PEG: Controlling Thermoresponsivity through Supramolecular Self-Assembly, *Macromolecules*, 41 (16), 5967-5970.
- [248] **Setijadi, E., Tao, L., Liu, J., Jia, Z., Boyer, C. and Davis, T. P.** (2009). Biodegradable star polymers functionalized with beta-cyclodextrin inclusion complexes, *Biomacromolecules*, 10 (9), 2699-2707.
- [249] **Schmidt, B. V. K. J., Hetzer, M., Ritter, H. and Barner-Kowollik, C.** (2013). UV Light and Temperature Responsive Supramolecular ABA Triblock Copolymers via Reversible Cyclodextrin Complexation, *Macromolecules*, 46 (3), 1054-1065.
- [250] **Schmidt, B. V. K. J., Rudolph, T., Hetzer, M., Ritter, H., Schacher, F. H. and Barner-Kowollik, C.** (2012). Supramolecular three-armed star polymers via cyclodextrin host-guest self-assembly, *Polym Chem-Uk*, 3 (11), 3139.
- [251] **Schmidt, B. V. K. J., Hetzer, M., Ritter, H. and Barner-Kowollik, C.** (2012). Miktoarm star polymers via cyclodextrin-driven supramolecular self-assembly, *Polym Chem-Uk*, 3 (11), 3064-3067.
- [252] **Schmidt, B. V. K. J. and Barner-Kowollik, C.** (2014). Supramolecular X- and H-shaped star block copolymers via cyclodextrin-driven supramolecular self-assembly, *Polym Chem-Uk*, 5 (7), 2461.

- [253] **Huan, X., Wang, D., Dong, R., Tu, C., Zhu, B., Yan, D. and Zhu, X.** (2012). Supramolecular ABC Miktoarm Star Terpolymer Based on Host–Guest Inclusion Complexation, *Macromolecules*, 45 (15), 5941-5947.
- [254] **Cakir, N., Tunca, U., Hizal, G. and Durmaz, H.** (2016). Heterofunctionalized Multiarm Star Polymers via Sequential Thiol-para-Fluoro and Thiol-Ene Double “Click” Reactions, *Macromol Chem Phys*, n/a-n/a.
- [255] **von Werne, T. and Patten, T. E.** (2001). Atom Transfer Radical Polymerization from Nanoparticles: A Tool for the Preparation of Well-Defined Hybrid Nanostructures and for Understanding the Chemistry of Controlled/“Living” Radical Polymerizations from Surfaces, *J Am Chem Soc*, 123 (31), 7497-7505.
- [256] **Esen, D. S., Arsu, N., Da Silva, J. P., Jockusch, S. and Turro, N. J.** (2013). Benzoin type photoinitiator for free radical polymerization, *Journal of Polymer Science Part A: Polymer Chemistry*, 51 (8), 1865-1871.
- [257] **Grest, G. S., Fetters, L. J., Huang, J. S. and Richter, D.** (2007). Star Polymers: Experiment, Theory, and Simulation, *Advances in Chemical Physics: John Wiley & Sons, Inc.*, pp 67-163
- [258] **Durmaz, H., Dag, A., Onen, C., Gok, O., Sanyal, A., Hizal, G. and Tunca, U.** (2010). Multiarm star polymers with peripheral dendritic PMMA arms through Diels-Alder click reaction, *Journal of Polymer Science Part A: Polymer Chemistry*, 48 (21), 4842-4846.
- [259] **Dag, A., Durmaz, H., Tunca, U. and Hizal, G.** (2009). Multiarm star block copolymers via Diels-Alder click reaction, *Journal of Polymer Science Part A: Polymer Chemistry*, 47 (1), 178-187.
- [260] **Amajjahe, S., Choi, S., Munteanu, M. and Ritter, H.** (2008). Pseudopolyanions based on poly(NIPAAM-co-beta-cyclodextrin methacrylate) and ionic liquids, *Angewandte Chemie*, 47 (18), 3435-3437.



CURRICULUM VITAE



Name Surname : Neşe ÇAKIR YİĞİT
Place and Date of Birth : Çorlu, 13.02.1987
E-Mail : nesecakirr@gmail.com

EDUCATION :

- **B.Sc.** : 2009, Trakya University, Chemistry
- **M.Sc.** : 2011, Istanbul Technical University, Polymer Science and Technology

PROFESSIONAL EXPERIENCE AND REWARDS:

- ÖYP (Teaching staff training program) Research Assistant
Yalova University, Polymer Engineering (09/2010)
- Visiting Graduate Scholar
Queen Mary University of London, School of Engineering and Materials Science,
London, UK (03/2014-09/2014)

PUBLICATIONS, PRESENTATIONS AND PATENTS ON THE THESIS:

- **Çakır N.**, Tunca Ü., Hızal, G., Durmaz H., 2016. Heterofunctionalized Multiarm Star Polymers via Sequential Thiol-para-Fluoro and Thiol-Ene Double “Click” Reactions, *Macromolecular Chemistry and Physics*, 217(5), 636-645.
- **Çakır N.**, Duygu S. E., Tunca Ü., Nergis A., Hızal, G., 2016. Multiarm Star Polymer as Novel Polymeric Photoinitiator for Free Radical Polymerization. *MACRO 2016-46th IUPAC World Polymer Congress*, July 17-21, 2016 İstanbul, Turkey.
- **Çakır N.**, Hızal, G., Tunca Ü., 2015. Multiarm Star Block Copolymers Driven by Host-Guest Inclusion Complexation. *Advanced Polymers via Macromolecular Engineering (APME 2015)*, October 18-22, 2015 Yokohama, Japan.

- **Çakır N.**, Tunca Ü., Hızal, G., 2015. Çakır N., Hızal, G., Tunca Ü., 2015. Post-functionalized multi-miktoarm star polymers via sequential para-fluoro and thiol-ene click reactions. *European Polymer Congress (EPF 2015)*, June 21-26, 2015 Dresden, Germany.
- **Çakır N.**, Duygu S. E., Tunca Ü., Nergis A., Hızal, G., 2013. Benzoin Based Multiarm Star Polymer as a Visible Photoinitiator. *Green and Sustainable Surface and Materials Chemistry*, October 23, 2013 Stockholm, Sweden.
- **Çakır N.**, Hızal, G., Tunca Ü., 2013. Post-Functionalization of Multiarm Star Polymers via Metal-Free “Click” Reaction of Aromatic Fluoro Groups. *IUPAC 10th International Conference on Advanced Polymers via Macromolecular Engineering (APME2013)*, August 18-22, 2013 Durham, UK.

OTHER PUBLICATIONS, PRESENTATIONS AND PATENTS:

- **Çakır N.**, Hızal G., Becer C. R., 2015. Supramolecular glycopolymers with thermoresponsive self-assembly and lectin binding, *Polymer Chemistry*, 6(37), 6623-6631.
- Bahadori F., Dağ A., Durmaz H., **Çakır N.**, Önyüksel H., Tunca Ü., Topçu G., Hızal G., 2014. Synthesis and Characterization of Biodegradable Amphiphilic Star and Y-Shaped Block Copolymers as Potential Carriers for Vinorelbine. *Polymers*, 6(1), 214-242.
- **Çakır N.**, Yavuzarslan M., Durmaz H., Hızal G., Tunca Ü., 2013. Heterograft Brush Copolymers via Romp and Triple Click Reaction Strategies Involving CuAAC, Diels-Alder, And Nitroxide Radical Coupling Reactions, *Journal of Polymer Science Part A: Polymer Chemistry*, 51(4), 899-907.
- Cerit N., **Çakır N.**, Dağ A., Sirkecioğlu O., Durmaz H., Hızal G., Tunca Ü., 2011. Various Brush Polymers Through Ring Opening Metathesis Polymerization and Nitroxide Radical Coupling Reaction, *Journal of Polymer Science Part A: Polymer Chemistry*, 49(13), 2850-2858.
- **Çakır N.**, Becer C. R., 2014. Sequence Controlled Polymers Containing Adamantane and β -Cyclodextrin Moieties For Single Polymer Chain Folding. *2014 Macro Group UK Young Researchers' Meeting*, July 24-25, 2014 Durham, UK.
- Baysak E., **Çakır. N.**, Hızal G., Tunca U., 2013. A Versatile Route for The Synthesis of Functional Polycarbonates Having o-Nitrobenzyl and Allyl Groups. *IUPAC 2013 44th World Chemistry Congress*, August 11-16, 2013 Istanbul, Turkey.
- Temelkaya E., **Çakır. N.**, Hızal G., Tunca U., 2013. Synthesis and Characterization of Telechelic Polytetrahydrofuran. *European Polymer Congress EPF 2013*, June 16-21, 2013 Pisa, Italy.
- Yavuzarslan M., **Çakır. N.**, Durmaz H., Hızal G., Tunca U., 2012. Synthesis of Heterograft Copolymers via Triple Click Reactions. *EUPOC 2012 Porous Polymer-Based Systems: From Design To Application*, June 3-7, 2012 Gargnano, Italy.

- **Çakır. N.**, Yavuzarslan M., Durmaz H., Hızal G., Tunca U., 2012. Synthesis of Block-Brush Copolymers via ROMP and Sequential Triple Click Reactions. *POLYCHAR 20 World Forum on Advanced Materials*, March 26-30, 2012 Dubrovnik, Croatia.
- **Çakır. N.**, Durmaz H., Hızal G., Tunca U., 2011. Easy Modification of Multiarm Star Polymers via Thiol-Yne Reaction. *9th International Conference on Advanced Polymers via Macromolecular Engineering*, September 5-8, 2011 Cappadocia, Turkey.
- **Çakır. N.**, Durmaz H., Dağ A., Hızal G., Tunca U., 2011. Synthesis of Amphiphilic Multiarm Star Block Copolymer via Diels-Alder Click Reaction. *European Polymer Congress EPF 2011*, July 1- June 26, 2011 Granada, Spain.
- **Çakır. N.**, Durmaz H., Dağ A., Hızal G., Tunca U., 2011. Synthesis of Amphiphilic Miktoarm Star Block Copolymer via Diels-Alder Click Reaction. *2nd International Symposium on Controlled/Living Polymerization: From Synthesis to Applications (CLP'11)*, April 12-16, 2011 Antalya, Turkey.
- **Çakır. N.**, Dağ A., Durmaz H., Hızal G., Tunca U., 2010. Amphiphilic Multiarm Star Block Copolymer via Diels Alder Click Reaction. *8th Hellenic Polymer Society Symposium*, October 24-29, 2010 Crete, Greece.

