DENDRITIC-LINEAR COPOLYMERS VIA DIELS-ALDER CYCLOADDITION

by

Murat Tonga

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APPROVED BY :

Assist. Prof. Amitav Sanyal (Thesis Supervisor)	…….
Prof. İlknur Doğan	…….
Prof. Ümit Tunca	…….

DATE OF APPROVAL:

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ABSTRACT

DENDRITIC-LINEAR COPOLYMERS VIA DIELS-ALDER CYCLOADDITION

Dendronized polymers are growing as an area in the synthesis of macromolecular architectures. Widespread interest and applications of such structural designs necessitates development of novel synthetic methods. In order to synthesize dendronized polymers, three different ways, macromonomer, graft-to and graft-from, are well-known methods. The graft-to method was chosen for this study.

Work involves three parts: Dendronized polymers via only Diels-Alder reaction, orthogonal click-click dendronization of polymers and bis-dendritic polyethylene (PE) via ROMP and click chemistry.

A styrene based polymer appended with anthracene groups for the first study and both anthracene and azido as reactive side chains for the second study were synthesized. First through third generation polyester dendrons containing furan protected maleimide groups at their focal point and polyaryl dendrons containing acetylene at their focal point were synthesized. Polyester dendrons were combined to the polymer containing only anthracene via Diels-Alder reaction and some special studies were done related to these. Secondly, polymers containing both anthracene groups and azide groups as orthogonal reactive side chains were coupled with two different dendrons via Cu(I) catalyzed Huisgen reaction and Diels-Alder reaction.

Azide containing PE was synthesized with special chain transfer agent (CTA) via ROMP. Polyaryl dendrons containing acetylene at their focal point were combined to this polymer via Cu(I) catalyzed Huisgen click reaction resulting in a bis-dendritic polymer.

ÖZET

DIELS-ALDER KİMYASI İLE DÜZ POLİMERLERE DENDRON TAKILMASI

Dendron takılmış polimerler büyük moleküler yapıların sentezinde bir alan olarak büyümektedir. Böyle yapısal dizaynlardaki geniş ilgi ve uygulamalar yeni sentetik metodların geliştirilmesini zorunluluk haline getirmiştir. Dendron takılmış polimerler sentezinde makromonomer, graft-to ve graft-from en bilinen metotlardır. Bu çalışmada graft-to metodu kullanılmıştır.

Çalışma üç kısımdan oluşmaktadır: Sadece Diels-Alder reaksiyonuyla polimere dendron takılması, ortogonal duble klik kimyasıyla polimere dendron takılması ve ROMP ve klik kimyası ile polietilene iki uçtan dendron takılması.

İlk çalışma için reaktif yan zincirinde sadece antrasin ve ikinci çalışma için hem antrasin hem de azido grup olan polimerler sentezlendi. Odak noktasında furanla korunmuş maleimid bulunan poliester dendronun ve odak noktasında asetilen bulunan poliaromatik dendronun üç jenerasyonu sentezlendi. Poliester dendron Diels-Alder reaksiyonu ile sadece antrasin içeren polimere bağlandı ve bununla ilgili bazı özel çalışmalar yapıldı. İkinci olarak, azido ve antrasin gibi ortogonal reaktif yan zincirler sahip polimerlere iki farklı dendron Diels-Alder ve bakır katalistli Huisgen reaksiyonu ile bağlandı.

Özel zincir transfer ajanı kullanarak ROMP yöntemiyle azido içeren polietilen sentezlendi. Bakır katalistli Huisgen reaksiyonuyla odak noktasında asetilen içeren poliaromatik dendron bu polimere bağlanarak iki ucu dendrimer olan bir polimeri meydana getirdi.

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LIST OF ABBREVIATIONS

AIBN	Azobisisobutironitrile
ATRP	Atom Transfer Radical Polymerization
BHT	Butylated hydroxyltoluene
$CDCl_3$	Deutorated chloroform
CH_2Cl_2	Dichloromethane
CMS	Chloromethylstyrene
CTA	Chain Transfer Agent
DA	Diels-Alder
DCC	Dicyclohexylcarbodiimide
DMAP	N,N Dimethylaminopyridine
DMF	N,N-dimethylformamide
DMSO	Dimethyl sulfoxide
DP	Degree of Polymerization
EtOAc	Ethylacetate
FTIR	Fourier Transform Infrared
GPC	Gel Permeation Chromatography
G1	Generation 1
NMP	Nitroxide Mediated Polymerization
PAD	Polyaryl Dendron
PAMAM	Polyamidoamine
PDI	Polydispersity index
PED	Polyester Dendron
PMDETA	N,N,N-pentamethyldiethylenetriamine
RAFT	Reversible Addition Fragmentation Chain Transfer
ROMP	Ring Opening Metathesis Polymerization
St	Styrene
THF	Tetrahydrofuran

1. INTRODUCTION

1.1. Dendrimers

Dendrimers are highly uniform, regularly branched, globular nanostructures [1]. They have monodisperse and highly well defined architectures. They are composed of three components: a core, branching units and surface groups (Figure 1.1) [2]. Generation number and three major components control size, shape and reactivity.

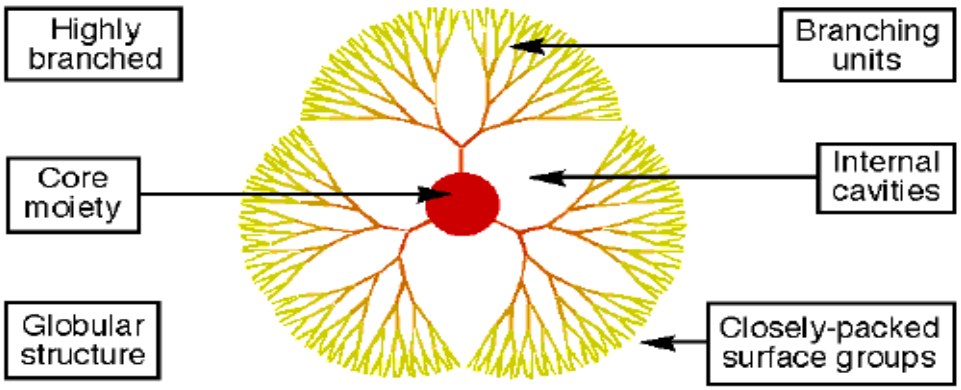


Figure 1.1. General structure of dendrimers

A core may be small molecules, nanoparticles, other dendrimers and polymer. Branching units are robust, covalent structures and connect core to surface groups. Surface groups may be cationic, anionic, neutral, hydrophobic/hydrophilic, biocompatible and target-directing groups. Also, internal cavities are useful rooms for molecular cargo. Dendrimers are generally synthesized using either ‘divergent’ or ‘convergent’ method (Figure 1.2) [2].

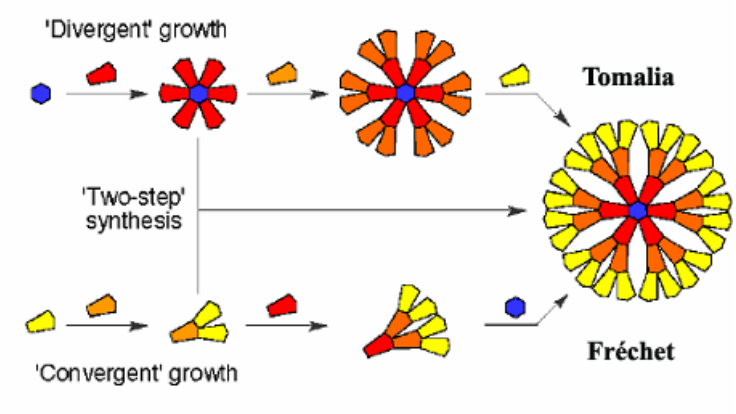


Figure 1.2. Synthesis of dendrimers via divergent and convergent method

In the *divergent methods*, dendrimers grow outwards from a core. Starting from a reactive core, a generation is grown, and then the new periphery of the molecule is activated for reaction with more monomers. The process is repeated for several generations. Tomalia and co-workers synthesized poly (amidoamine), shortly PAMAM, via this method in Figure 1.3 [1]. The divergent method is useful for production of large amount of dendrimers. Side reactions and incomplete growth steps leading to structure defects are main problems while building a dendrimer with the divergent method. To overcome this, large excess of reagents is required, but this causes difficulties in purification.

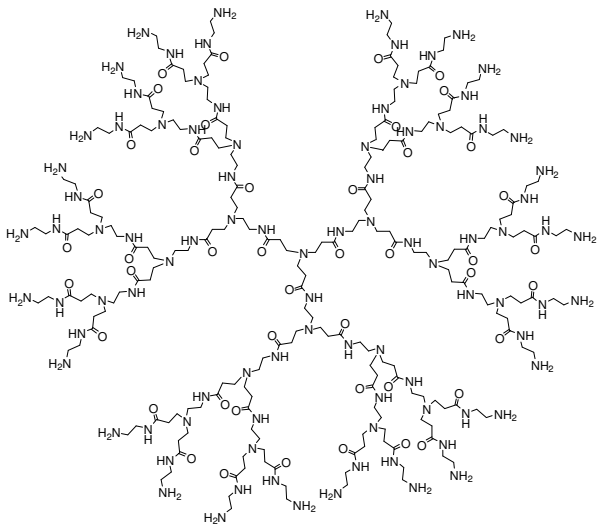


Figure 1.3. 3rd generation poly(amidoamine) dendrimer via divergent method

In the *convergent methods*, dendrimer is built from end groups and grows to inward with coupling reactions. After enough couplings, growing branched arms called as 'dendron' are connected to a multifunctional core. Fréchet and Hawker developed this method and synthesized a poly (aryl ether) dendron (Figure 1.4) [3]. The convergent method has numerous benefits. It is easy to purify the desired products and the possibility of defects is minimized. It provides subtle engineering in dendritic structure. This methodology suffers from low yield in the synthesis of huge structures. Also, another problem is steric hindrance that can be confronted in the higher generations of dendrimer at their focal point [4].

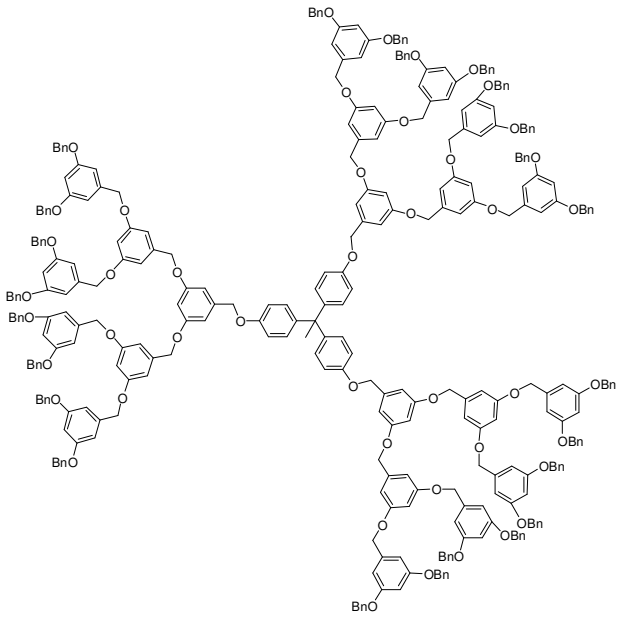


Figure 1.4. Poly (aryl ether) dendron attached to a multifunctional group via convergent method

1.2. Controlled Polymerization Methods

Controlled polymerization has attracted much attention due to enabling complete conversion with controlled molecular weight, low polydispersity (PDI) and tailored architecture [5]. Several strategies have been built up such as atom transfer radical polymerization (ATRP), nitroxide mediated free radical polymerization (NMP), and reversible addition-fragmentation chain transfer (RAFT).

1.2.1. Reversible Addition-Fragmentation Chain Transfer Polymerization (RAFT)

Reversible addition-fragmentation chain transfer (RAFT) is the one of the most versatile polymerization technique for synthesis of different well-defined macromolecular structures (block copolymers, star polymer, graft polymer and dendronized polymers [6], [7, 8]) with low PDI. RAFT polymerization is well suited to a wide range of monomers containing functional groups like acid, amine, hydroxyl, epoxy and amide [9, 10].

The principle of RAFT polymerization depends on introduction of a small amount of dithio derivative (Figure 1.5) [11].

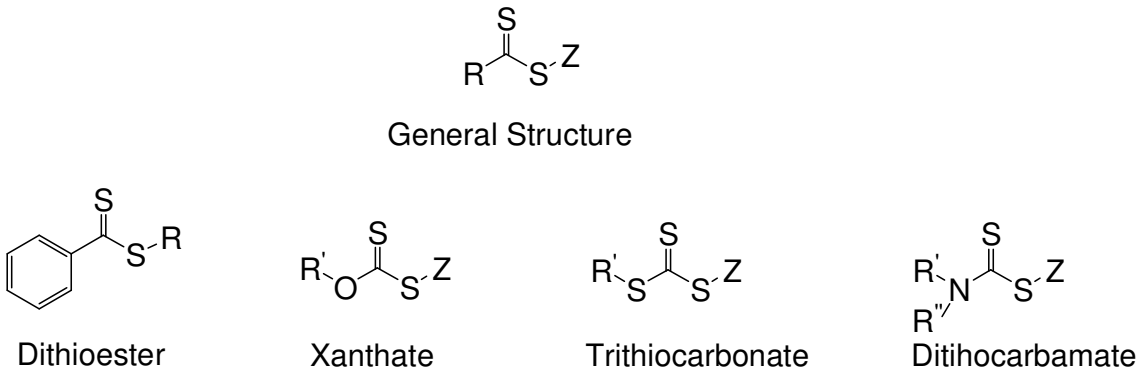


Figure 1.5. Common chain transfer agents

The mechanism of RAFT is drawn in Figure 1.6 [11]. In the initiation step, decomposition of initiator initiates polymerization resulting in growing polymer chain P^*_n. This growing polymer chain adds to C=S bond of the chain transfer agent. The fragmentation of the intermediate takes place reversibly either the initial growing chain or free reinitiating group R^* and a macro chain transfer agent. R^* reinitiate polymerization by reacting with monomer forming a new polymer chain P^*_m or react back with the macro chain transfer agent. The equilibrium is set up following the initial CTA has been consumed and the macro CTA is the only species found in the reaction medium. This equilibrium is thought the main equilibrium, and a quick switch of active and dormant chains direct the polymerization by resulting in the narrow molecular weight distribution [11].

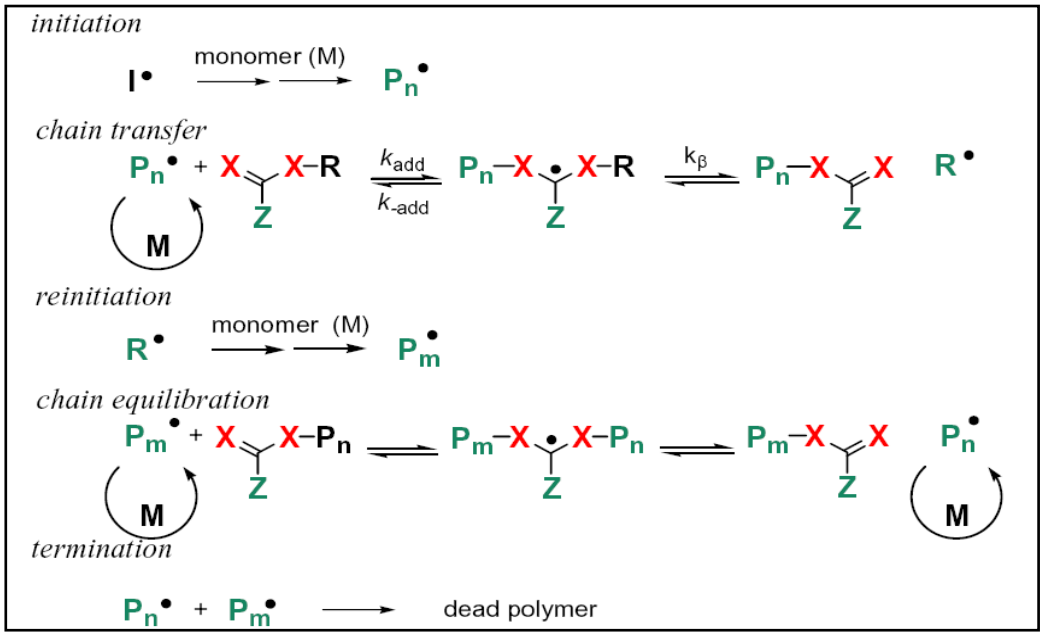


Figure 1.6. The mechanism of RAFT

The Z group strongly has effect on the stability of the thiocarbonyl-thioradical intermediate. Strong stabilizing groups help the formation of the intermediate leading to higher activity towards radical addition. Fine adjustments of the stability of intermediate facilitate the reinitiating group to free. Phenyl Z groups are appropriate for most monomers. The most important requirement of R group is that it has to be a good leaving group compared to the growing polymer chain and a good reinitiating species toward to the monomer used [11].

1.2.2. Ring Opening Metathesis Polymerization (ROMP)

The ring opening metathesis polymerization (ROMP) is a chain growth polymerization method where a cyclic olefin such as cyclobutene, cyclooctene and norbornene is converted to an unsaturated polyalkene with the driving force which is release of ring strain [12]. Advanced materials such as block copolymers, comb polymers, Janus-type polymers, liquid crystalline polymers and dendronized polymers can be synthesized via ROMP [13, 14].

The mechanism of polymerization is depicted in Figure 1.7 and based on olefin metathesis, a metal-mediated carbon-carbon double bond exchange process [15].

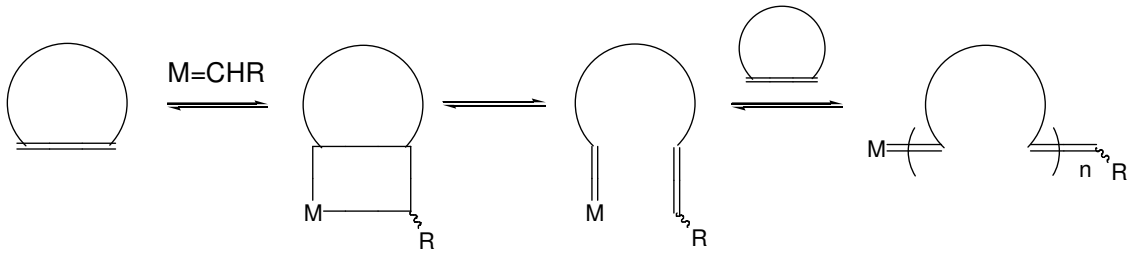
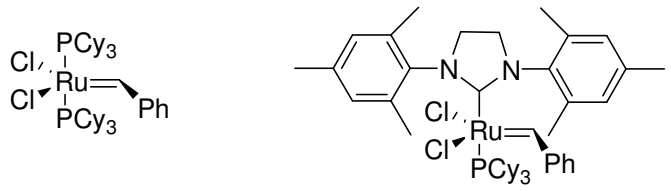


Figure 1.7. The mechanism of ROMP

Catalysts used in ROMP are usually based on titanium, tungsten, molybdenum, or ruthenium [14]. Of these transition metals, ruthenium is among the most commonly used metals for catalysts for olefin methathesis reactions since they have the highest functional group tolerance, and the lowest sensitivity towards moisture and oxygen [12, 16]. Figure 1.8 depicts two of the commercially available ruthenium catalysts developed by Grubbs *et al* [12].



Grubbs 1st Generation

Grubbs 2nd Generation

Figure 1.8. Grubbs' 1st and 2nd generation catalyst

1.3. Dendronized Polymers

Dendronized polymers are subdivison of comb polymers where the comb's teeth are substituted by dendrons [17, 18]. Depending of the lots of different reasons such as type of dendron, attachment density along the backbone, end group functionality and degree of polymerization these kinds of polymers show special properties [19, 20]. Appended large

dendrons to the backbone transform random coil conformation of backbone to extended conformation (Figure 1.9) [17, 18].

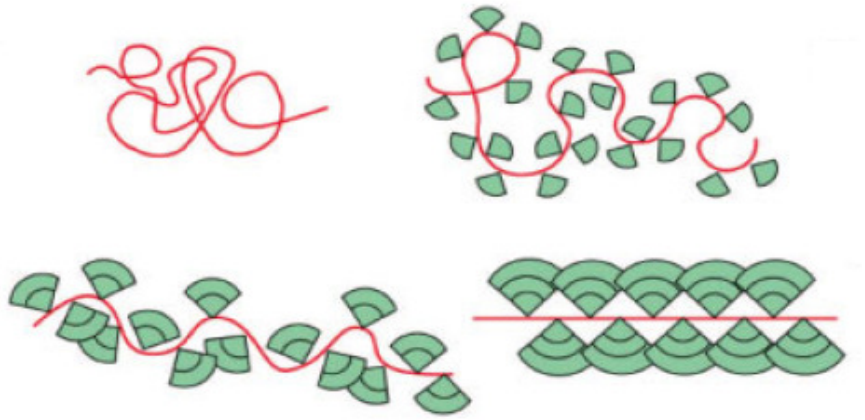


Figure 1.9. Different conformations of dendronized polymers

Dendron polymer conjugates are rapidly becoming common macromolecular building blocks in both biopharmaceutical and materials research. Dendronized polymers have been studied for different applications such as the synthesis of hierarchically structured materials, catalysis, applications in the biosciences and optoelectronic [21, 22, 23].

Growing interest in these materials necessitates development of novel effective methodologies to synthesize them in an efficient and preferably in a modular manner. In order to synthesize dendronized polymers, three main routes are employed; namely, 'macromonomer method', 'graft-to' method, and the 'graft from' method. Macromonomer method involves polymerization of a dendron containing monomer (Figure 1.10) [17]. The advantage of this approach is that it guarantees that in a dendronized homopolymer all side chains contain the well defined dendron synthesized prior to the polymerization. The general limitation being, due to steric hindrance, monomers containing higher generation dendrons cannot be easily polymerized to high degree of polymerization (DP). Polymerizations under very high monomer concentration carried out to address these concerns provide dendronized polymers with high DP [24].

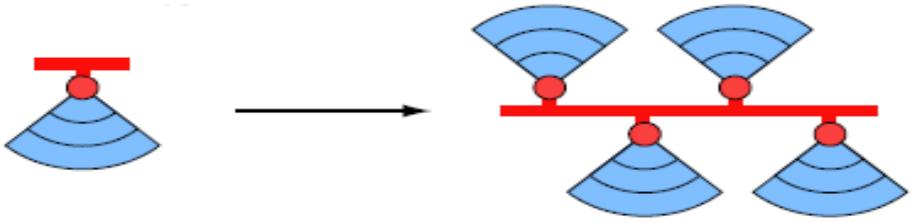


Figure 1.10. General scheme of macromonomer method

The monomers were studied via several polymerization methods such as radical polymerization (Figure 1.11) [25, 26, 27], insertion polymerization [28], ring opening-metathesis polymerization (ROMP) [29, 30, 31], Suzuki polycondensation [32], Heck coupling [33] and Stille coupling [34].

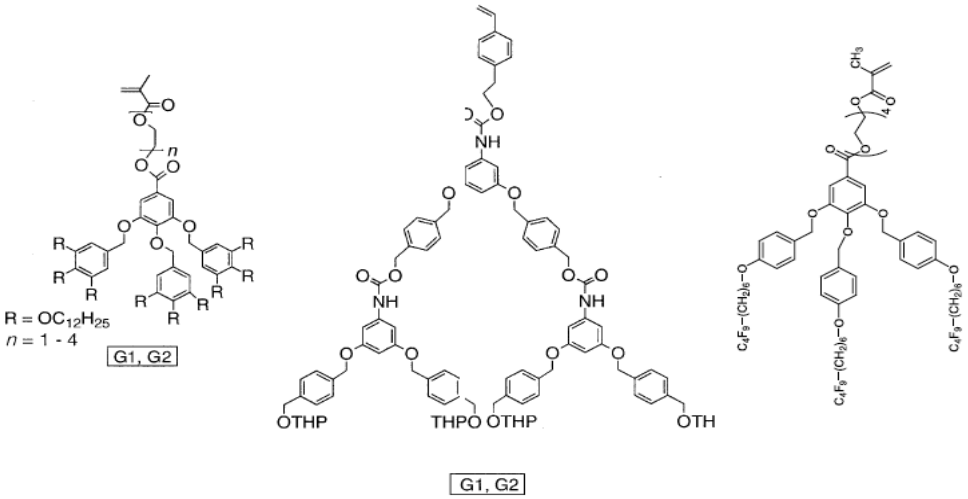


Figure 1.11. Structures of macromonomers used to obtain dendronized polymers by radical polymerization

On the other hand, the ‘graft from’ and ‘graft to’ methodologies involve the synthesis of the parent polymer chain prior to dendron growth or dendron attachment, respectively. ‘Graft-from’ method is carried out by increasing the dendron generation from polymer backbone after the attachment of G1 dendron onto polymer backbone (Figure 1.12) [17]. This methodology employs the ‘divergent route’ dendron synthesis on the polymer backbone. However, this method suffers from defect in structures and it is difficult to get rid off these defects species from the desired products since they are similar both

structurally and size. That is why the characterization of the products with ^{1}H-NMR, IR Spectroscopy or other methods is hard. Figure 1.13 [35] and Figure 1.14 [36] shows examples of dendronized polymer by graft-from strategy.

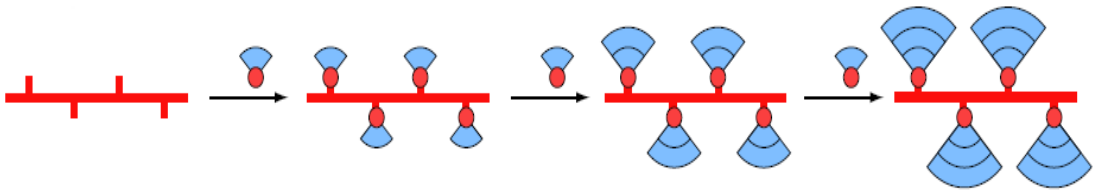


Figure 1.12. General scheme of graft-from method

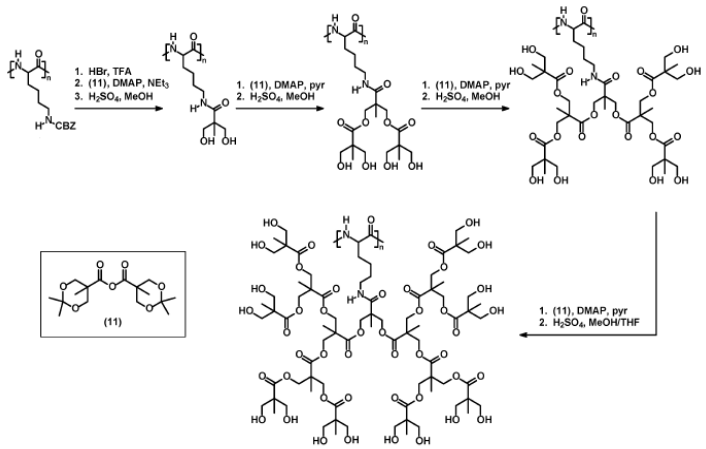


Figure 1.13. Synthesis of Poly (L-Lysine) based dendronized polymer by graft-from method

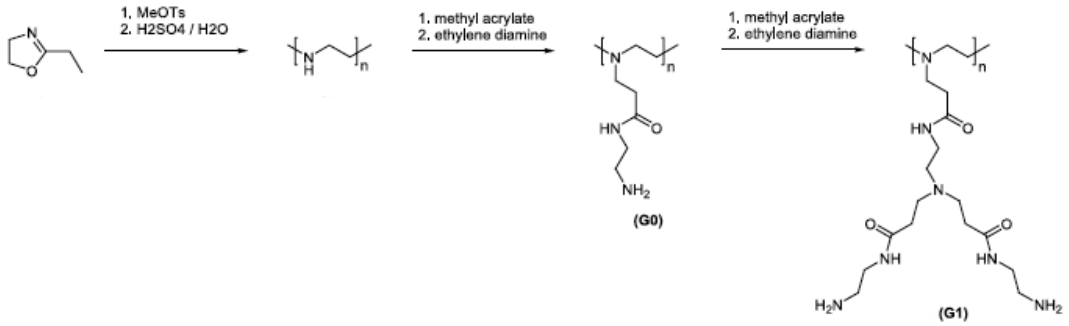


Figure 1.14. Synthesis of PAMAM based dendronized polymer by graft-from method

'Graft-to' method on the other hand makes use of a convergent method where a dendron is attached to a polymer that contains reactive functional groups as side chains for attachment (Figure 1.15) [17]. The 'graft to' method provides a modular 'plug and play' type advantage. Availability of polymers with reactive side chain functionalities provides a modular route for generating a family of polymers with the same backbone without the necessity to optimize the polymerization conditions for individual monomers. Furthermore, the concentration of the appended side chains can be easily controlled by the amount of reactive functional group.

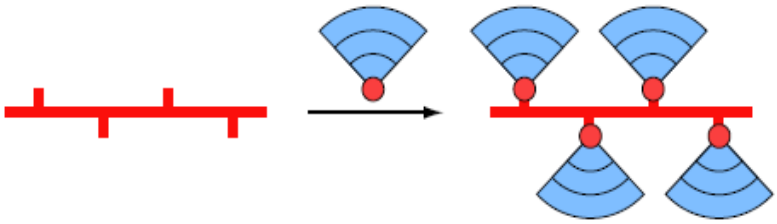


Figure 1.15. General scheme of graft-to method

Perhaps the most widely used approach utilizes polymers containing N-hydroxysuccinimide based activated ester groups that can be easily functionalized with amine containing molecules for attachment through amide bond formation. Indeed, Hawker and coworkers evaluated the efficiency of polymers containing N-hydroxysuccinimide groups as side chains to obtain dendron grafted polymers by reacting them with dendrons containing amine groups at their focal points in Figure 1.16.a [37].

Efficiency of such strategies depends upon efficient organic transformations that allow facile functionalization of the polymer backbone [38].

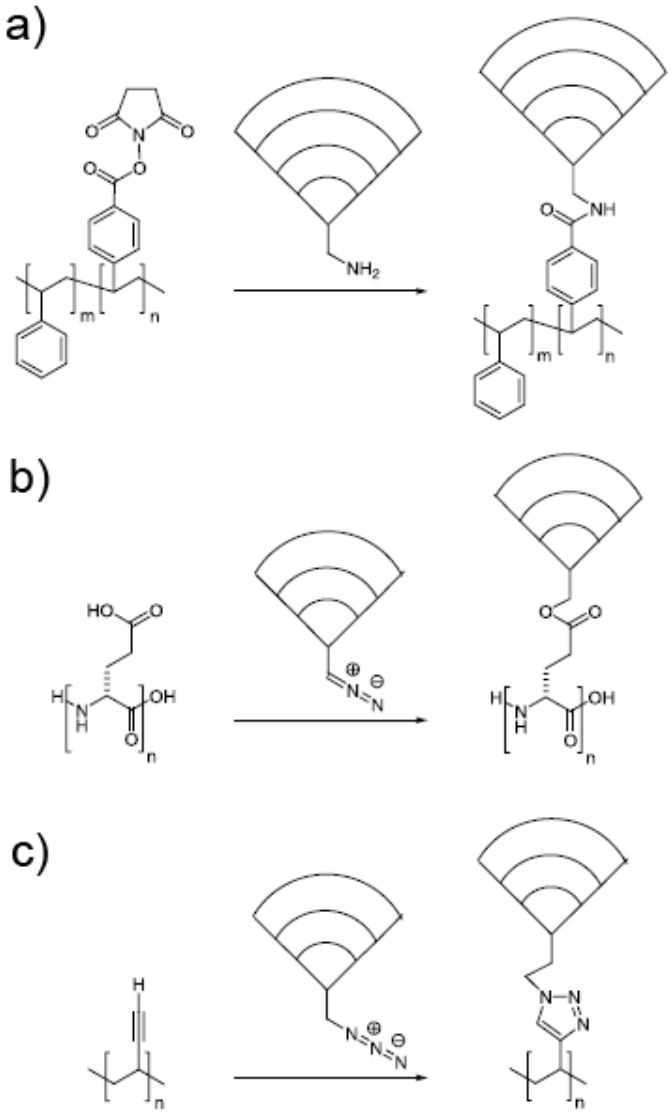


Figure 1.16. Example of dendronized polymers provided by graft-to method. a) amidation, b)esterification [39], c) copper catalyzed click reaction [40]

"Click reactions" have been utilized for achieving such efficient transformations due to their high reaction yields and mild reaction conditions. Recently, the copper catalyzed [3 + 2] Huisgen type cycloaddition reaction was utilized to obtain "dendronized polymer" with impressive effectiveness. From the toolbox of click reactions, the Diels-Alder

cycloaddition reaction has also attracted considerable interest due to its “reagent free” reaction conditions.

1.4. Click Chemistry

There are mainly 4 types of “Click” reactions which are ‘nucleophilic opening of higly strained rings’ such as epoxides, aziridines, cyclic sulfates, cyclic sulfamidates and aziridinium ions, ‘protecting group reactions’ such as acetals, ketals and their aza-analogs, most famous ones ‘cycloaddition reactions such as Diels-Alder [4+2] and Copper catalyzed Huisgen [3+2] or Huisgen 1,3 dipolar cycloadditon reactions [41].

1.4.1. Copper Catalyzed Huisgen [3+2] Cycloaddition

The most famous Click reaction is Huisgen [3+2] cycloaddition reaction. The cycloadditon reaction happens between an azide and alkyne to give a mixture of 1,4 and 1,5-disubstituted triazoles (Figure 1.17). It is a concerted reaction and generally done at high temperature.

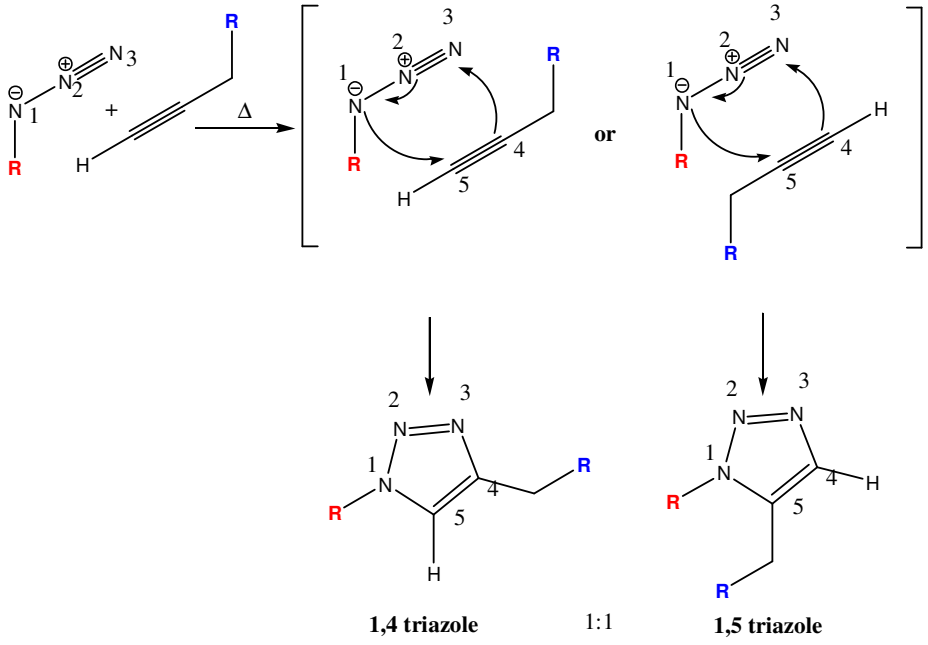
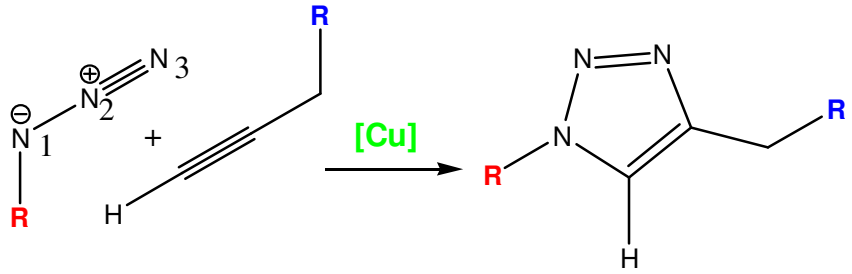


Figure 1.17. Click reaction between an azide and alkyne

In 2002 Sharpless and Fokin [42] developed the Huisgen reaction by introducing a Cu (I) catalyst that directs the region-specific result of the reaction, leading to only 1,4-disubstituted triazole (Figure 1.18).



1,4 triazole

Figure 1.18. Copper catalyzed Huisgen reaction

The addition of copper also increased the yield and tolerated reaction at room temperature. Nowadays, this reaction is called as copper (I)-catalyzed azide-alkyne reaction. The catalyst can be directly introduced Cu (I) salt (CuI or CuBr) or generated in situ by reduction of Cu (II) salts [43, 44] and amine containing base such as 2,6-lutidine, triethylamine, pyridine and PMDETA. Commonly used Cu-systems are $CuSO_4$/ NaAsc and CuBr/PMDETA due to exclusive regiospecificity, mild reaction conditions, easy purification, high yield and functional group tolerance.

'Click' applications are widely used for well-defined macromolecules such as dendrimer synthesis, dendronized polymers and DNA functionalization. Sharpless and co-workers performed the convergent synthesis of triazole dendrimers via copper (I) catalyzed Click chemistry [45].

In another study, Fréchet and Hawker [40] synthesized dendronized linear polymers via Click chemistry (Figure 1.20). The 'graft-to' route was applied where azide containing dendrons at the focal point were attached to the pendant alkynes on the polymer of poly-(vinylacetylene) via Click chemistry.

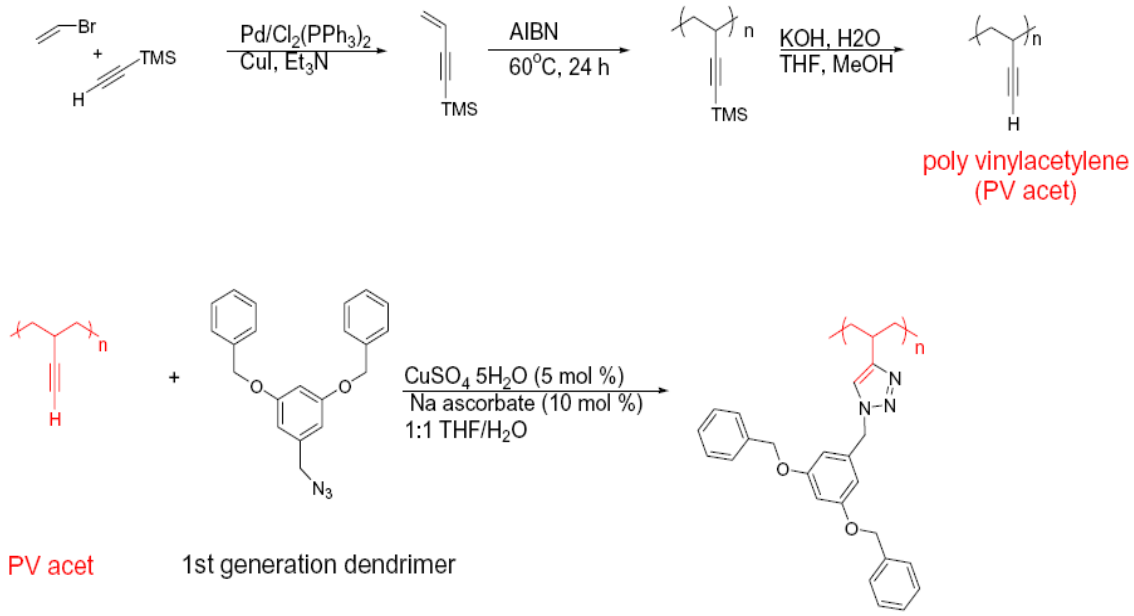


Figure 1.19. Dendronized linear polymers via click chemistry

Click chemistry have been used in biological studies: building of fluorescent oligonucleotides for DNA sequencing [46], in situ assembly of acetylcholinesterase inhibitors [47] and synthesis of HIV-1 protease inhibitor [48].

1.4.2. Diels-Alder [4+2] Cycloaddition

Diels-Alder reaction is an addition reaction between a diene and dienophile to form a six membered ring (Figure 1.21). Cyclic movement of electron pairs shows the breakage of Л bonds and the formation of 2 σ bonds and one new Л bond. Diels-Alder reaction is a concerted reaction in which the breakage of bonds and the formation of the new bonds occur at the same time. A typical Diels-Alder reaction is initiated by heat.

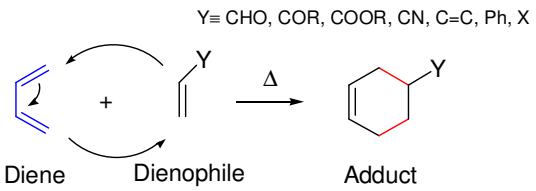


Figure 1.20. A Diels-Alder reaction

Due to reagent free conditions, Diels-Alder reaction has catched the great attention. The reaction has been used for surface functionalization, peptide-peptide coupling, synthesis of diblock and graft copolymers and total synthesis. Chaikof used the Diels-Alder and Huisgen Click reaction for immobilization of carbohydrates and proteins onto a solid surface [49]. Waldmann and co-workers developed a method for the chemoselective ligation of peptides and proteins by using Diels-Alder reaction in Figure 1.22 [50].

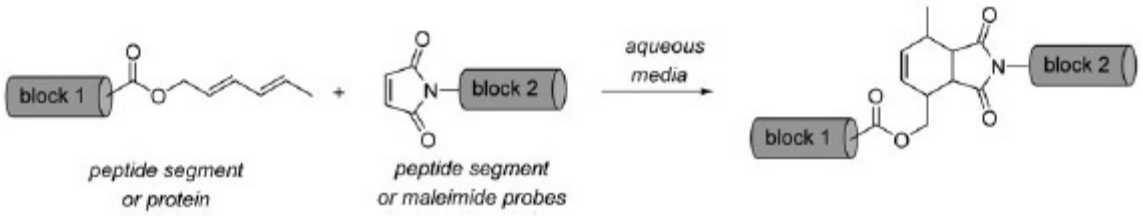


Figure 1.21. Peptide-peptide coupling via Diels-Alder reaction

Tunca and co-workers synthesized graft copolymers via Diels-Alder reaction and copper catalyzed Huisgen reaction [51], (Figure 1.23) [52].

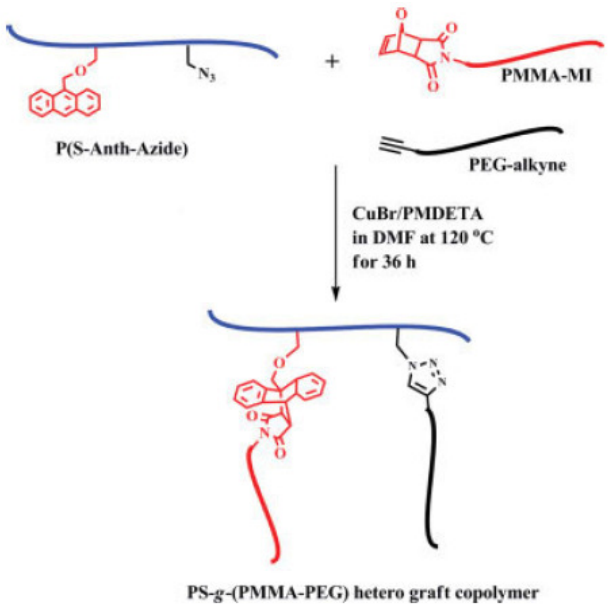


Figure 1.22. Synthesis of graft copolymer via double click reactions

2. AIM OF THE STUDY

The study is mainly composed of two parts. In the first part, 'dendronized polymers' was synthesized with novel synthetic methods which are Diels-Alder and copper catalyzed Huisgen click reaction (Figure 2.1). Second part is related to synthesis of bis-dendritic polymer via 'ROMP' and 'Click' reaction.

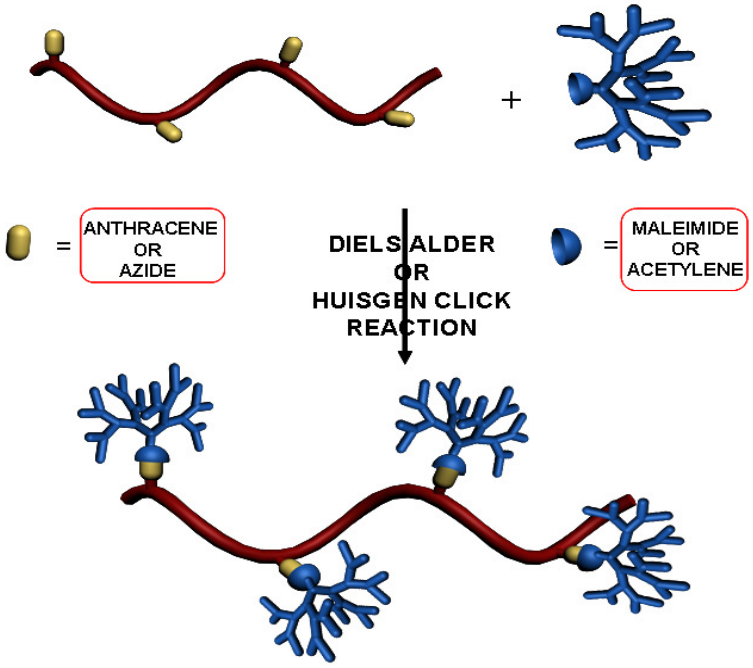


Figure 2.1. General scheme of studied dendronized polymer

The methodology discussed in the first part utilizes a Diels-Alder cycloaddition reaction based strategy for the facile post modification of polymers with dendrons. Anthracene was chosen as a side chain on the styrene based parent polymer to serve as an electron rich diene for the desired post modification via Diels-Alder reaction. Efficient thermal Diels-Alder reaction with electron deficient maleimide groups is utilized for the functionalization with dendrons. Work involves the synthesis of polymer containing anthracene groups on their side chain, synthesis of dendrons containing maleimide unit at their focal point, and the evaluation of Diels-Alder cycloaddition reactions to obtain dendronized polymers appended with first through third generation dendrons.

A modular approach towards synthesis of dendronized polymers containing two different dendrons as side chains is developed using two orthogonal Click reactions: the Huisgen Cycloaddition and Diels-Alder reaction. Polymers containing both anthracene groups and azide groups as orthogonal reactive side chains were synthesized. The anthracene groups allow functionalization using the Diels-Alder click reaction, whereas the azide group allows attachment of dendrons using the Huisgen click reaction. Initial functionalization of the polymer was carried out using the Huisgen cycloaddition between azide groups on the polymer and dendrons appended with an alkyne at their focal point. Subsequent functionalization was achieved using Diels-Alder reaction between the anthracene side chains on the polymer and dendrons containing maleimide group at their focal points. Both functionalizations were performed as a one pot reaction with tuning the temperature at a certain time intervals.

In the second part of study, bis-dendritic polyethylenes were obtained via ROMP and Click reactions (Figure 2.2). To obtain functional groups at the both edge of polyethylene, a special chain transfer agent (CTA) containing azide was synthesized. Then, cyclooctene was opened with these CTA and Grubbs' second generation catalyst resulting in polyethylene which contains azide at the both end of the polymer. This polymer was coupled with polyaryl dendrons containing acetylene at their focal point via copper catalyzed Huisgen reaction.

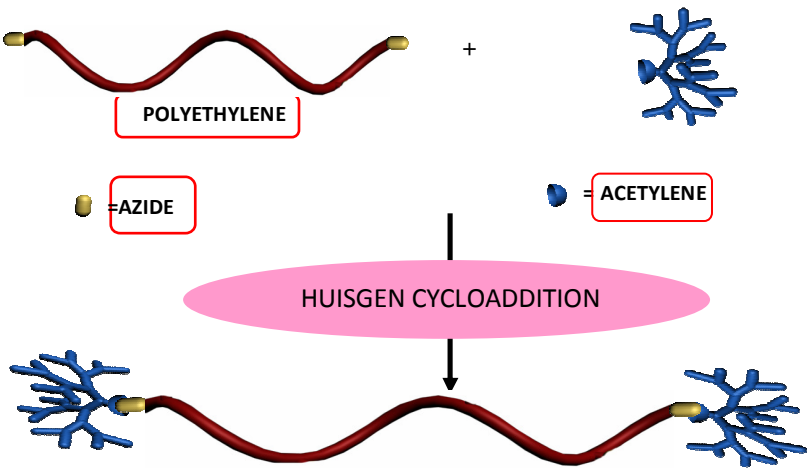


Figure 2.2. General scheme of bis-dendritic polyethylene

3. EXPERIMENTAL

3.1. Methods and Materials

All chemicals were used as received from manufacturer (Merck, Aldrich, Alfa Aesar, Riedel de Haen). Dry solvents (CH_2Cl_2, THF, toluene) was obtained from ScimatCo Purification System, other dry solvents were dried of molecular sieves. Column chromatography was performed using silicagel-60 (43-60 nm). Thin layer chromatography was performed using silica gel plates (Kiesel gel 60 F254, 0.2mm, Merck). Plates were viewed under 254 nm UV lamp. Infrared spectroscopy was carried out on Thermo Scientific Nicolet 380 FT-IR spectrophotometer. ^1H NMR (operating at 400 MHz) and ^{13}C NMR (operating at 100 MHz) were recorded on Varian Mercury-MX in $CDCl_3$ as solvent at the Advanced Technologies Research and Development Center at Boğaziçi University.

3.2. Synthesis

3.2.1. Synthesis of Polyester Dendrons

Polyester dendrons were synthesized according to the literature procedure [53], [54].

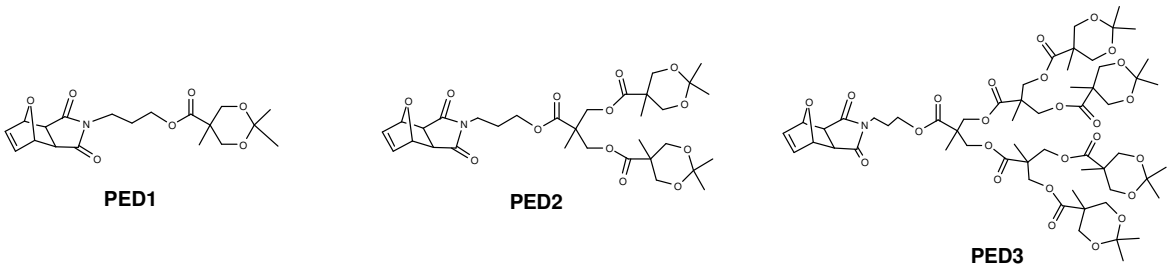


Figure 3.1. G1 through G3 polyester dendrons used in this study

3.2.2. Synthesis of Polyaryl Dendrons

Compound PAD1, PAD2 and PAD3 were synthesized according to the previously reported literature procedure [3].

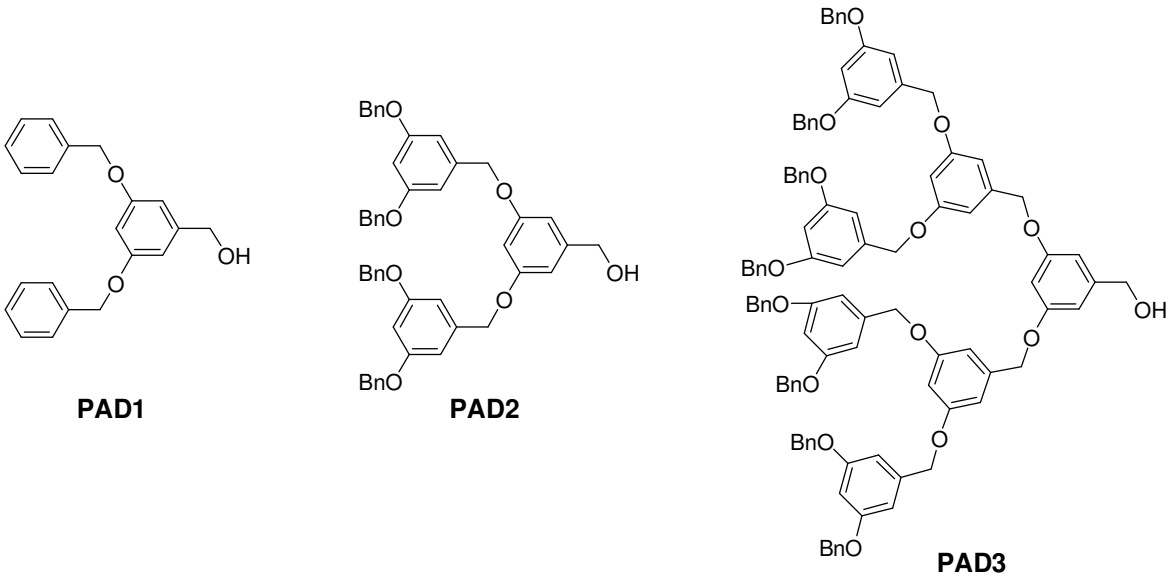


Figure 3.2. G1 through G3 polyaryl dendrons

3.2.2.1. Synthesis of G1 Dendron (PAD1)-Acetylene. To the solution of NaH (60 %, 5 equiv weight, mmol) and G1-OH (1 equiv weight, mmol) dissolved in dry THF under N_2, propargyl bromide (97 %, 3 equiv weight, mmol) was added and reaction was refluxed for 15 h. Its solvent and excess propargyl bromide was evaporated under *vacuo*. The residue was extracted with water and CH_2Cl_2. The combined organic phases were dried with Na_2SO_4, filtered and concentrated under *vacuo*. The crude product was filtrated through silica gel with ethyl acetate as an eluent to give yellow solid in Figure 3.3. ^{1}H NMR ($CDCl_3$,δ, ppm) = 7.41-7.28 (m, 10H), 6.61 (d, *J* = 2.0 Hz, 2H), 6.53 (dd, *J* = 2.0, 2.0 Hz, 1H), 5.03 (s, 4H), 4.53 (s, 2H), 4.14 (d, *J* = 2.4 Hz, 2H), 2.44 (t, *J* = 2.4 Hz, 1H) corresponding to the literature values.

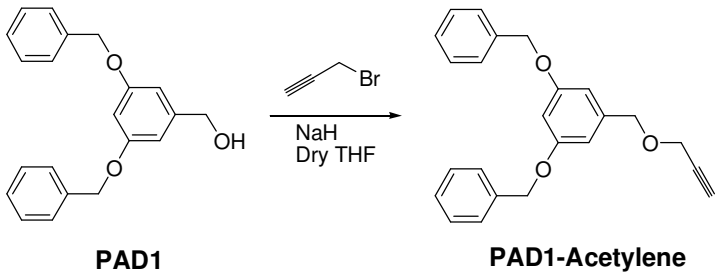


Figure 3.3. Synthesis of PAD1-acetylene

3.2.2.2. Synthesis of G2 Dendron (PAD2)-Acetylene. To the solution of NaH (60 %, 5 equiv weight, mmol) and G2-OH (1 equiv weight, mmol) dissolved in dry THF under N_2, propargyl bromide (97 %, 3 equiv weight, mmol) was added and reaction was refluxed for 15 h. Its solvent and excess propargyl bromide was evaporated under *vacuo*. The residue was extracted with water and CH_2Cl_2. The combined organic phases were dried with Na_2SO_4, filtered and concentrated under *vacuo*. The crude product was filtrated through silica gel with ethyl acetate as an eluent to give yellow solid in Figure 3.4. ^{1}H NMR ($CDCl_3$,δ, ppm) = 7.41-7.28 (m, 20H), 6.66 (d, *J* = 2.0 Hz, 4H), 6.59 (d, *J* = 2.0 Hz, 2H), 6.55 (dd, *J* = 2.0, 2.0 Hz, 2H), 6.51 (dd, *J* = 2.0, 2.0 Hz, 1H), 5.02 (s, 8H), 4.95 (s, 4H), 4.53 (s, 2H), 4.14 (d, *J* = 2.4 Hz, 2H), 2.44 (t, *J* = 2.4 Hz, 1H) corresponding to the literature values.

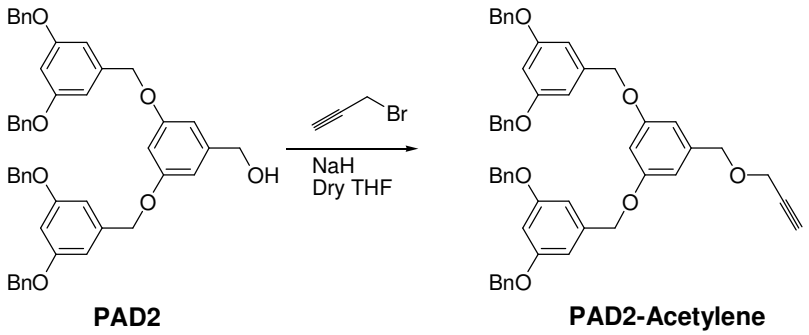


Figure 3.4. Synthesis of PAD2-acetylene

3.2.2.3. Synthesis of G3 Dendron (PAD3)-Acetylene. To the solution of NaH (60 %, 5 equiv weight, mmol) and G3-OH (1 equiv weight, mmol) dissolved in dry THF under N_2, propargyl bromide (97 %, 3 equiv weight, mmol) was added and reaction was refluxed for 15 h. Its solvent and excess propargyl bromide was evaporated under *vacuo*. The residue was extracted with water and CH_2Cl_2. The combined organic phases were dried with Na_2SO_4, filtered and concentrated under *vacuo*. The crude product was filtrated through silica gel with ethyl acetate as an eluent to give yellow solid in Figure 3.5. ^{1}H NMR ($CDCl_3$,δ, ppm) = 7.51-7.38 (m, 40H), 6.81-6.78 (m, 12H), 6.69-6.67 (m, 9H), 5.07 (s, 16H), 5.01 (s, 12H), 4.53 (s, 2H), 4.14 (d, *J* = 2.4 Hz, 2H), 2.44 (t, *J* = 2.4 Hz, 1H) corresponding to the literature values.

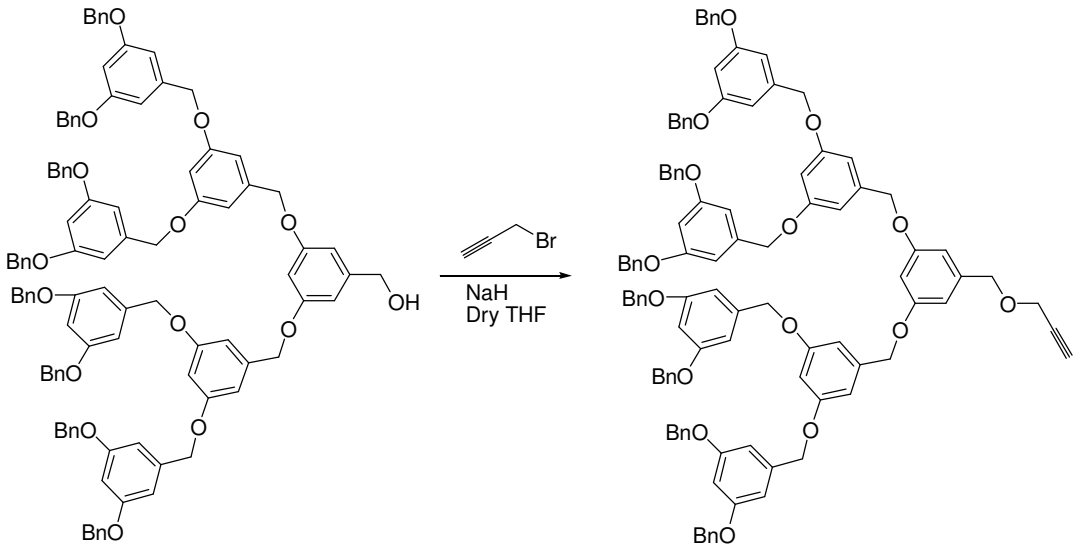


Figure 3.5. Synthesis of PAD3-acetylene

3.2.3. Synthesis of Polymers

3.2.3.1. Synthesis of RAFT Chain Transfer Agent. It was synthesized according to literature procedure [55]. All the apparatus must be dry. The solution of Mg turnings (100 mg, 4.17 mmol) and dry THF was heated to 40 °C under N_2. Approximately 15 min dropwise addition of CS_2 (0.25 mL, 4.17 mmol) to this solution resulted in dark brown solution. Methyl α-bromophenylacetate (0.68 mL, 4.54 mmol) was added into the solution and reaction temperature was increased to 80 °C and continued for 24 h. The reaction was cooled to RT and extracted with diethylether and water. Combined organic phases were dried with Na_2SO_4. After removal of solvent, flash chromatography (5 % diethylether in hexane) resulted in red oil (83 % yield) in Figure 3.6. NMR data are consistent with literature values. ^{1}H NMR ($CDCl_3$, δ, ppm) = 7.91 (dd, J = 7.26, 1.31 Hz, 2H), 7.48-7.20 (m, 8H), 5.65 (s, 1H), 3.70 (s, 3H). ^{13}C NMR ($CDCl_3$, δ, ppm) = 226.7, 167.0, 143.8, 133.2, 132.8, 129.3, 128.9, 128.8, 127.4, 126.9, 58.7, 53.0. FTIR (ATR) = 1736, 1225, 577 cm^{-1}

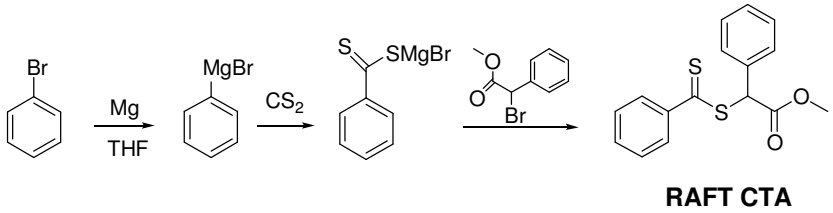


Figure 3.6. Synthesis of RAFT chain transfer agent (CTA)

3.2.3.2. Synthesis of co-(St-CMS). Monomers (Styrene and chloromethyl styrene (CMS), CTA and AIBN, which are in (450:5:1) ratio, were added into a round bottom flask. The mixture was degassed for 30 mins at room temperature and was then stirred at 90 ^{o}C. After 30 min, the flask was transferred into an ice bath to stop the polymerization process. The mixture was then added to cold methanol dropwise to obtain the copolymer as a pink precipitate. The formed solid was then filtered and dried under vacuum in Figure 3.7. ^{1}H NMR ($CDCl_3$, δ, ppm) = 7.3-6.2 (br m, 12H), 4.49 (br s, 2H), 2.0-1.2 (br m, 8H) (Figure A.4). FTIR (ATR) = 1265 cm^{-1}, $M_{n\text{-}GPC}$= 8463 , PDI=1.22, CMS:St=1/3.

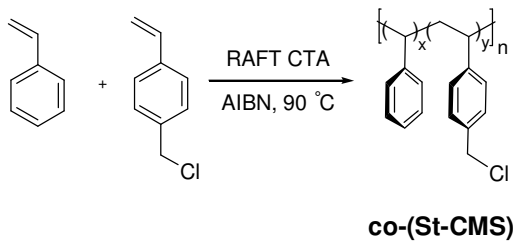


Figure 3.7. Synthesis of copolymer of styrene-chloromethylstyrene polymer

3.2.3.3. Synthesis of Anthracene co-(St-CMS). Sodium hydride (60 %, 2 equiv weight, mmol), was added to a solution of 9-anthracenemethanol (1.1 equiv) in anhydrous THF (20 mL). The reaction mixture was stirred at room temperature under nitrogen for 30 minutes followed by addition of a solution of random copolymer (1.0 CMS equiv) in anhydrous THF. The reaction mixture was refluxed for 12 h in the dark. It was then cooled to room temperature and solvent was removed in *vacuo*. The solid was dissolved in minimal amount of dichloromethane and precipitated in methanol. The product obtained upon filtration was dried for 24 h. under vacuum prior to use in Figure 3.8. NMR proves full conversion of chloros to anthracene. ^{1}H NMR ($CDCl_3$, δ, ppm) = 8.36-7.37 (br s, 5H),

7.61-6.20 (br m, 21H), 5.28 (br s, 2H), 4.51 (br s, 2H), 2.20-0.92 (br m, 13H) (Figure A.5). $M_{n\text{-}GPC}$ = 9716, $M_{n\text{-}NMR}$ = 12221, PDI = 1.53

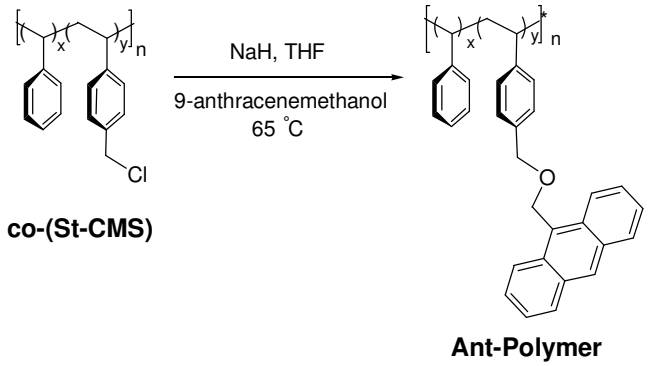


Figure 3.8. Synthesis of anthracene polymer

3.2.3.4. Synthesis of Anthracene-Azide-co(St-CMS). Sodium azide (NaN_3) (0.5 equiv weight, mmol) and co-(St-CMS) (1 equiv weight, mmol) were added and dissolved with DMF. Reaction was run at 70 °C for overnight. It was then cooled to room temperature and solvent was removed in *vacuo*. The solid was dissolved in minimal amount of dichloromethane and precipitated in methanol. The product obtained upon filtration was dried for 24 h. under vacuum prior to use. Sodium hydride (2 equiv weight, mmol) and 9-anthracenemethanol (1.1 equiv) were added into the product and dissolved with anhydrous THF (20 mL) under N_2. The reaction mixture was refluxed for 12 h in the dark. It was then cooled to room temperature and solvent was removed in *vacuo*. The solid was dissolved in minimal amount of dichloromethane and precipitated in methanol. The product obtained upon filtration was dried for 24 h. under vacuum prior to use in Figure 3.9. ^{1}H NMR ($CDCl_3$, δ, ppm) = 8.36-7.37 (br s, 8H), 7.61-6.20 (br m, 67H), 5.31 (br s, 2H), 4.51 (br s, 3H), 4.18 (br s, 1H), 2.20-0.95 (br m, 44H) (Figure A.9). FTIR (ATR) = 2095 cm^{-1}, $M_{n\text{-}GPC}$ = 11330, Azide:Anthracene = 3/4

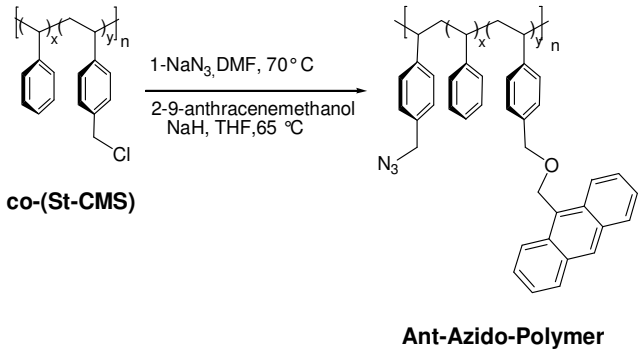


Figure 3.9. Synthesis of anthracene-azido polymer

3.2.4. Synthesis of Dendronized Polymers via Diels-Alder 'Click' Chemistry

3.2.4.1. Diels-Alder Functionalization of Anthracene Polymer with PED1. In a typical cycloaddition reaction, a solution of dendron (1.1 equiv) and the random copolymer (1.0 anthracene equiv) in toluene (10 mL) was refluxed for 24 h in the dark at 110 °C. The reaction mixture was concentrated in *vacuo*. The crude product obtained was dissolved in minimal amount of CH_2Cl_2 and then was added to methanol. The yellow precipitate was dried under vacuum for 24 h at room temperature. NMR analysis (Figure A.6) and UV-Vis Spectra showed quantitative conversion of the anthracene moiety to cycloadduct. ^{1}H-NMR for G1 adduct ($CDCl_3$, δ, ppm) = 7.46 (br s, 8H), 7.10 (br s, 5H), 6.50 (br s, 4H), 4.69 (br s, 5H), 4.16 (d, *J* = 11.2 Hz, 2H), 3.60 (d, *J* = 11.2 Hz, 2H), 3.48 (br s,2H), 3.35 (br s, 1H), 3.17 (br m, 3H), 1.85 (br s, 2H), 1.38 (s, 3H), 1.24 (s, 3H), 1.19 (s, 3H), 1.15 (s, 2H). FTIR (ATR) = 1730, 1699 cm^{-1}, $M_{n\text{-GPC}}$ = 14468, $M_{n\text{-NMR}}$ = 15320.

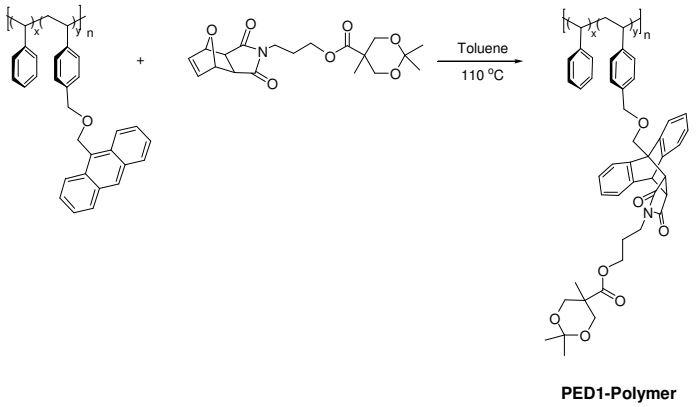


Figure 3.10. Diels-Alder functionalization of anthracene polymer with PED1

3.2.4.2. Diels-Alder Functionalization of Anthracene Polymer with PED2. Above procedure was applied (Figure 3.11). NMR analysis (Figure A.7) and UV-Vis Spectra showed quantitative conversion of the anthracene moiety to cycloadduct. ^{1}H NMR data of G2 adduct ($CDCl_3$, δ, ppm) = 7.46 (br s, 8H), 7.10 (br s, 5H), 6.50 (br s, 4H), 4.69 (br s, 5H), 4.31 (s, 4H), 4.16 (d, *J* = 11.2 Hz, 4H), 3.62 (d, *J* = 11.2 Hz, 4H), 3.44 (br m, 3H,), 3.17 (br m, 3H), 1.76 (br m, 2H), 1.40 (br s, 6H), 1.34 (br s, 6H), 1.29 (br s, 3H), 1.14 (br s, 6H). FTIR (ATR) = 1733, 1698 cm^{-1}, $M_{n\text{-}GPC}$ = 17003, $M_{n\text{-}NMR}$ = 20221

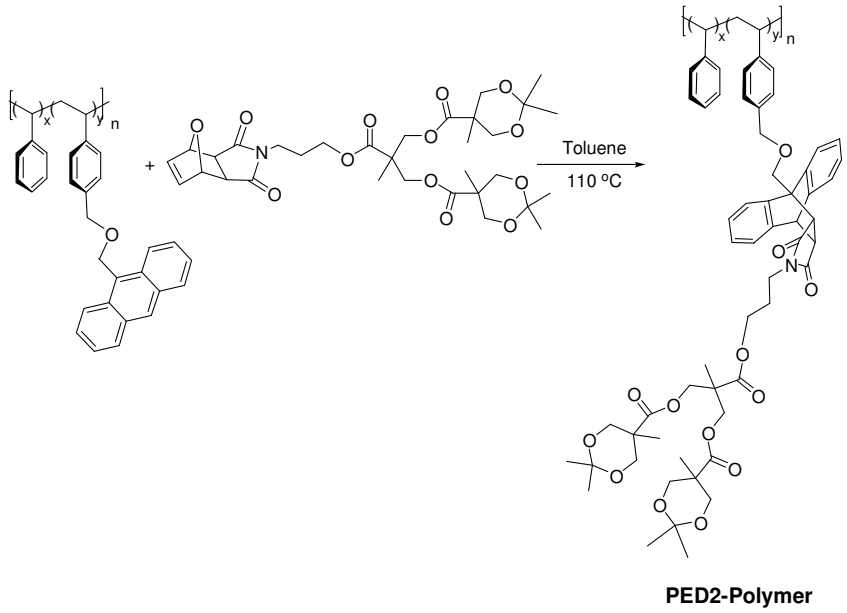


Figure 3.11. Diels-Alder functionalization of anthracene polymer with PED2

3.2.4.3. Diels-Alder Functionalization of Anthracene Polymer with PED3. Above procedure was applied (Figure 3.12). NMR analysis (Figure A.8) and UV-Vis Spectra showed quantitative conversion of the anthracene moiety to cycloadduct. ^{1}H NMR data of G3 adduct ($CDCl_3$, δ, ppm) = 7.45 (br s, 9H), 7.10 (br s, 5H), 6.49 (br s, 4H), 4.69 (br s, 5H), 4.30 (br s, 9H), 4.25 (br s, 4H), 4.11 (d, *J* = 11.7 Hz, 8H), 3.61 (d, *J* = 11.7 Hz, 8H), 3.42 (br m, 3H), 3.17 (br s, 2H), 1.73 (br m, 2H), 1.38 (br s, 12H), 1.33 (br s, 12H), 1.26 (br s, 9H), 1.13 (br s, 12H). FTIR (ATR) = 1732.8, 1700.2 cm^{-1}, $M_{n\text{-}GPC}$ = 19682, $M_{n\text{-}NMR}$ = 30024

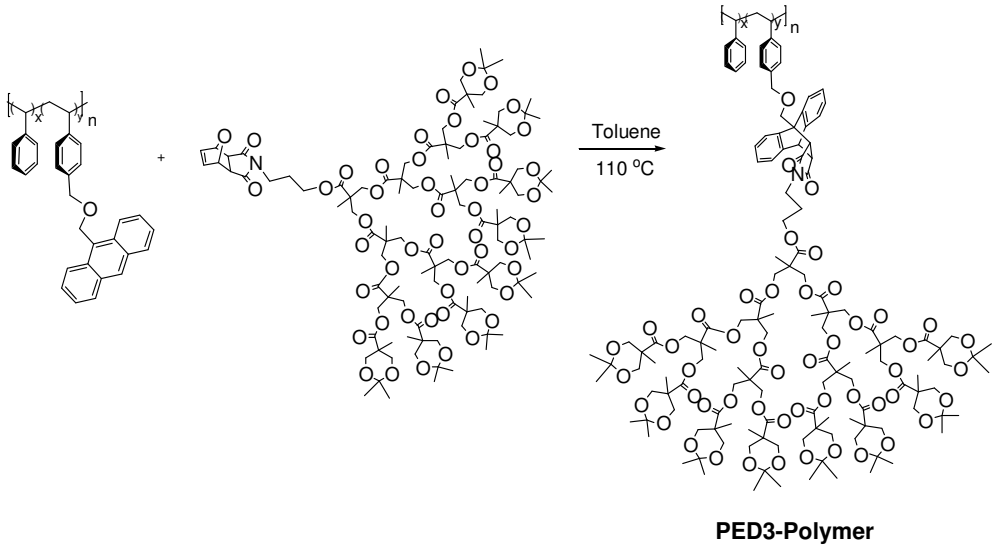


Figure 3.12. Diels-Alder functionalization of anthracene polymer with PED3

3.2.5. Orthogonal Functionalization of Anthracene-Azide Polymers via Diels-Alder and Huisgen Cycloaddition

3.2.5.1. Click-Click Functionalization of Anthracene-Azide Polymer with PED1 and PAD1. Anthracene-Azido polymer (1 equiv weight, mmol), PED1 (10 equiv weight, mmol), PAD1 (10 equiv weight, mmol), Cu(I)Br (2 % equiv weight, mmol) and BHT (catalytic amount) were dissolved with dry DMF under N_2. PMDETA (2 % equiv weight, mmol) was added into this solution. The reaction was run at RT for 24 h. Remaining azide was checked with FTIR. Then, the reaction was heated to 120 °C for 24 h. Remaining anthracene was checked with UV-Vis spectroscopy. Solution was concentrated in *vacuo*. The crude product was dissolved in minimal amount CH_2Cl_2, and then precipitated into cold MeOH. The yellow precipitate was dried under vacuum for 24 h at room temperature. NMR analysis (Figure A.10) showed quantitative conversion of the anthracene and azide moieties to cycloadduct in Figure 3.13. ^{1}H-NMR for adduct ($CDCl_3$, δ, ppm) = 7.65-6.2 (br m, H), 5.3 (br s, 2H), 4.96 (br s, 4H), 4.88-4.54 (br m, 5H), 4.50 (br s, 2H), 4.17 (br d, J = 10.9 Hz, 2H), 3.61 (br d, J = 11.2 Hz, 2H), 3.48 (br s,2H), 3.35 (br s, 1H), 3.18 (br m, 3H), 2.0-0.8 (br m, 13H).

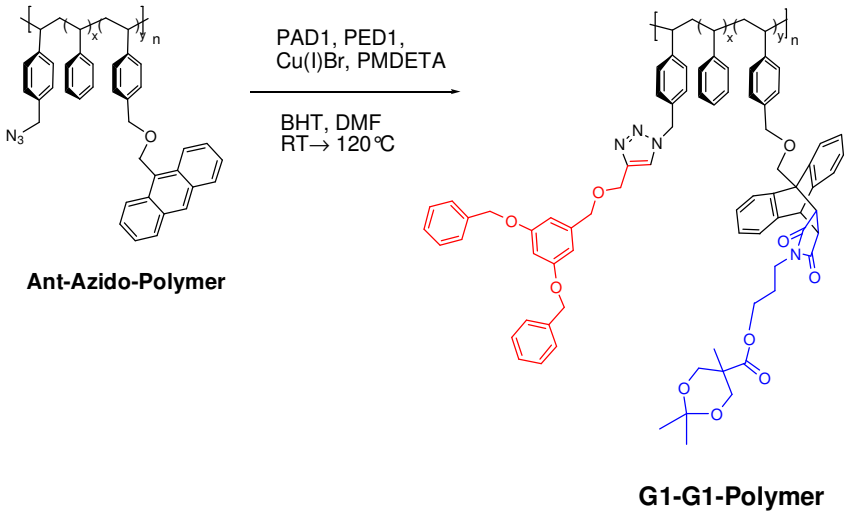


Figure 3.13. Synthesis of G1-G1-Polymer via double clicks

3.2.5.2. Click-Click Functionalization of Anthracene-Azide Polymer with PED2 and PAD2. Above procedure was applied. NMR analysis (Figure A.11) showed quantitative conversion of the anthracene and azide moieties to cycloadduct in Figure 3.14. ^{1}H-NMR for adduct ($CDCl_3$, δ, ppm) = 7.65-6.2 (br m, H), 5.3 (br s, 2H), 4.97 (br s, 8H), 4.91 (br s, 4H), 4.72-4.53 (br m, 5H), 4.50 (br s, 2H), 4.30 (br s, 4H), 4.12 (br d, *J* = 11.4 Hz, 4H), 3.60 (br d, *J* = 11.7 Hz, 4H), 3.55-3.25 (br m, 3H), 3.16 (br m, 2H), 2.0-0.8 (br m, 23H).

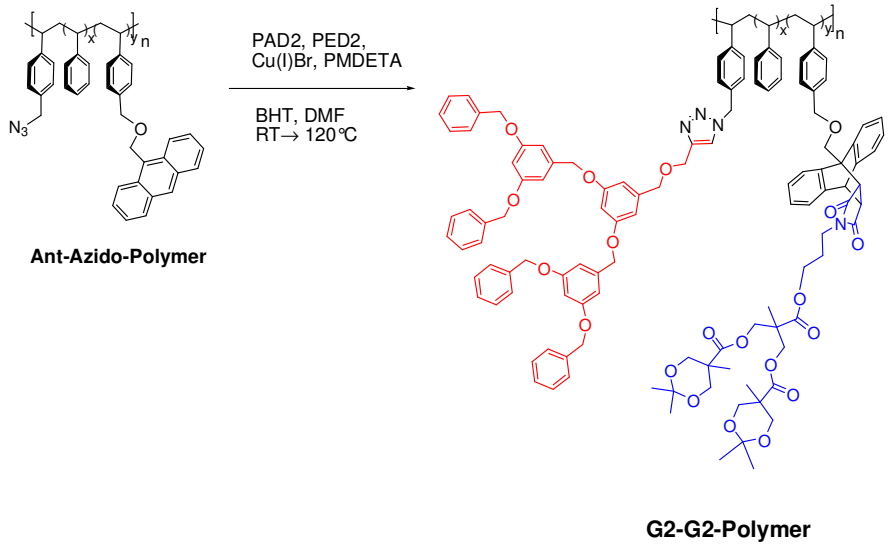


Figure 3.14. Synthesis of G2-G2-Polymer via double clicks

3.2.5.3. Click-Click Functionalization of Anthracene-Azide Polymer with PED3 and PAD3. Above procedure was applied. NMR analysis (Figure A.12) showed incomplete conversion of the anthracene and azide moieties to cycloadduct in Figure 3.15. ^{1}H-NMR for adduct ($CDCl_3$, δ, ppm) = 7.65-6.2 (br m, H), 5.3 (br s, 2H), 5.02-4.74 (br m, 28H), 4.73-4.52 (br m, 5H), 4.50 (br s, 2H), 4.29 (br s, 9H) 4.25 (br s, 4H), 4.12 (br d, *J* = 11.5 Hz, 8H), 3.58 (br d, *J* = 11.5 Hz, 8H), 3.50-3.25 (br m, 3H), 3.16 (br m, 2H), 2.0-0.8 (br m, 47H).

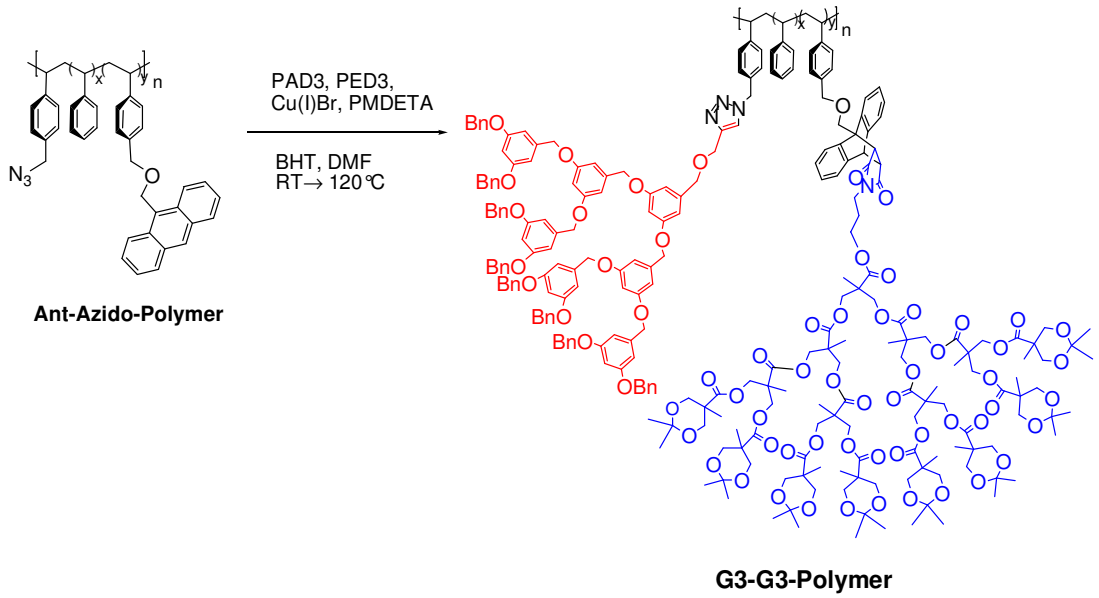


Figure 3.15. Synthesis of G3-G3-Polymer via double clicks

3.2.6. Synthesis of Bis-Dendritic PE via ROMP and Click Chemistry

3.2.6.1. Synthesis of Azido CTA. 11-Bromoundecanoic (3.0 g, 11.4 mmol), sodium azide (3.7 g, 56.8 mmol) and KI (0.94 g, 5.7 mmol) were dissolved with DMSO (25 mL). The mixture was heated to 80 °C for 48 h, after which H_2O (25 mL) was stirred for 30 min, and extracted with EtOAc (3 x 15 mL). The combined organic phases were washed with brine, dried with Na_2SO_4, filtered and the solvent was evaporated under to give pale yellow oil (2.5 g, 98 %). The product was dried under high vacuum for 24 h at RT. The product (2.5 g, 11 mmol), cis-butene-1,4-diol (0.3 mL, 3.67mmol), DCC (5 g, 24.2 mmol) and DMAP (3 g, 24.2 mmol) were dissolved with anhydrous CH_2Cl_2. The reaction was run for 24 h at RT. Solvent was evaporated and formed dicyclohexylurea (DCU) was filtrated.

Purification by flash chromatography (5 % EtOAc in hexane) resulted in colorless liquid in Figure 3.16. ^{1}H NMR ($CDCl_3$,δ, ppm) = 5.73 (dt, *J* = 4.0, 1.2 Hz, 1H), 4.68 (dd, *J* = 4.0, 1.2 Hz, 2H), 3.25 (t, *J* = 7.0 Hz, 2H), 2.30 (t, *J* = 7.2 Hz, 2H), 1.65-1.55 (br m, 2H), 1.40-1.25 (br m, 12H) (Figure A.14).

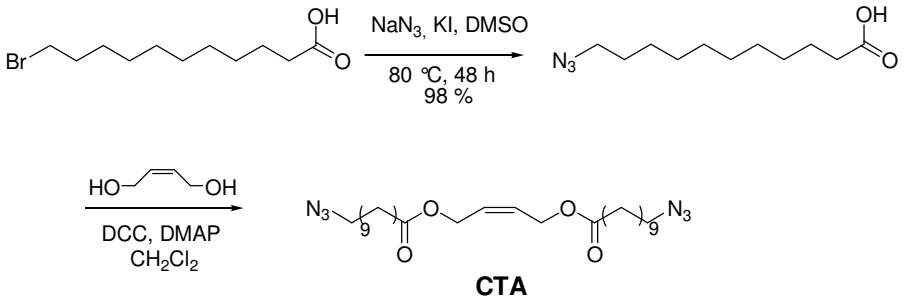


Figure 3.16. Synthesis of Azido CTA

3.2.6.2. Synthesis of Polyethylene via Azido CTA. Cylooctene (0.5 mL, 7.8 mmol) was added into solution of 2nd Generation Grubbs catalyst (1.6 mg, 1.9 μmol) dissolved with THF (1 mL) in microwave tube under N_2. The mixture was degassed for 30 min prior polymerization. The reaction was run for 24 h at RT. Polymer was concentrated in *vacuo* and precipitated in cold EtOAc, filtered and dried under high vacuum for 24 h at RT in Figure 3.17. ^{1}H NMR ($CDCl_3$,δ, ppm) = 5.73 (dt, *J* = 1.2, 1.1 Hz, 1H), 5.40-5.30 (m, 290H) 4.48 (dd, *J* = 6.4 Hz, 2H), 3.23 (t, *J* = 7 Hz, 2H), 2.30 (t, *J* = 7.2, 6.4 Hz, 2H), 2.03-1.90 (br m, 580H), 1.53 (br m, 4H), 1.33-1.20 (br m, 1160H) (Figure A.15). $M_{n\text{-GPC}}$ = 19526, PDI = 2.36

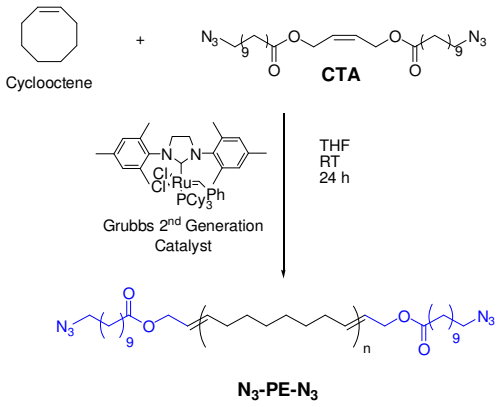


Figure 3.17. Synthesis of bis-azido PE

3.2.6.3. Functionalization PE with PAD1-Acetylene. PMDETA (2 % equiv weight, mmol) was added to solution of bis-azido-PE (1 equiv weight, mmol), PAD1 (2.2 equiv weight, mmol) and Cu(I)Br (2 % equiv weight, mmol) dissolved in anhydrous THF under N_2. The reaction was run for 24 h at RT. Reaction was followed with FTIR. Polymer in Figure 3.18 was concentrated in *vacuo* and precipitated in cold EtOAc, filtered and dried under high vacuum for 24 h at RT. NMR (Figure A.16) and FTIR (Figure A.18) prove the full attachment of dendron onto polymer. ^{1}H-NMR ($CDCl_3$, δ, ppm) = 7.47 (br s, 2H), 7.42-7.28 (m, 20H), 6.60 (br s, 4H), 6.53 (br s, 2H), 5.73 (m, 1H) 5.40-5.29 (br m, 380H), 5.01 (br s, 8H),4.65 (br s, 2H), 4.52 (br s, 4H), 4.30 (t, J = 7.2 Hz, 2H), 2.27 (t, J = 7.4 Hz, 2H), 1.94 (br s, 760H), 1.53 (br s, 4H), 1.26 (br s, 1520H). $M_{n\text{-GPC}}$ = 24581, PDI = 1.52

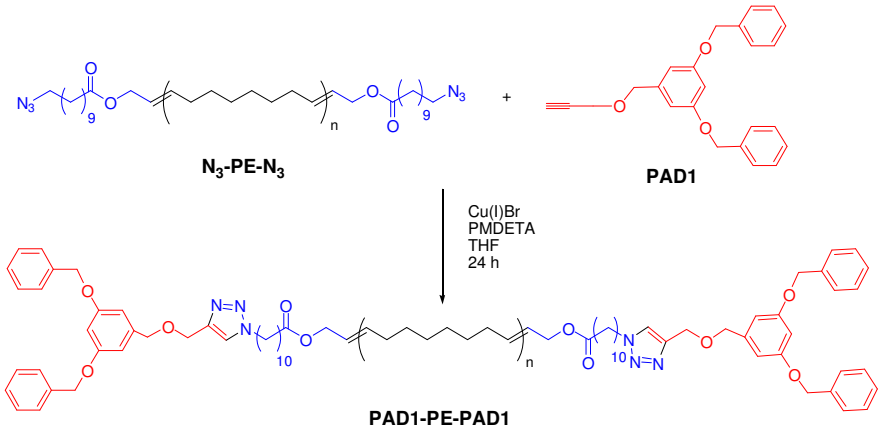


Figure 3.18. Synthesis of bis-PAD1 PE via Huisgen click reaction

3.2.6.4. Functionalization PE with PAD3-Acetylene. PMDETA (2 % equiv weight, mmol) was added to solution of bis-azido-PE (1 equiv weight, mmol), PAD3 (2.2 equiv weight, mmol) and Cu(I)Br (2 % equiv weight, mmol) dissolved in anhydrous THF under N_2. The reaction was run for 24 h at RT. Reaction was followed with FTIR. Polymer in Figure 3.19 was concentrated in *vacuo* and precipitated in cold EtOAc, filtered and dried under high vacuum for 24 h at RT. NMR (Figure A.17) and FTIR (Figure A.18) prove the full attachment of dendron onto polymer. ^{1}H-NMR ($CDCl_3$, δ, ppm) = 7.45 (br s, 2H), 7.40-7.26 (m, 80H), 6.67-6.46 (br s, 42H), 5.73 (m, 1H), 5,39-5.30 (br m, 430H), 4.99 (br s, 32H), 4.93 (br s, 24H), 4.62 (br s, 2H), 4.50 (br s, 2H), 4.24 (t, J = 7.2 Hz, 2H), 2.25 (t, J = 7.4 Hz, 2H), 2.03-1.87 (br m, 860H), 1.53 (br s,4H), 1.28 (br s, 1720H). $M_{n\text{-GPC}}$ = 27413, PDI = 1.59

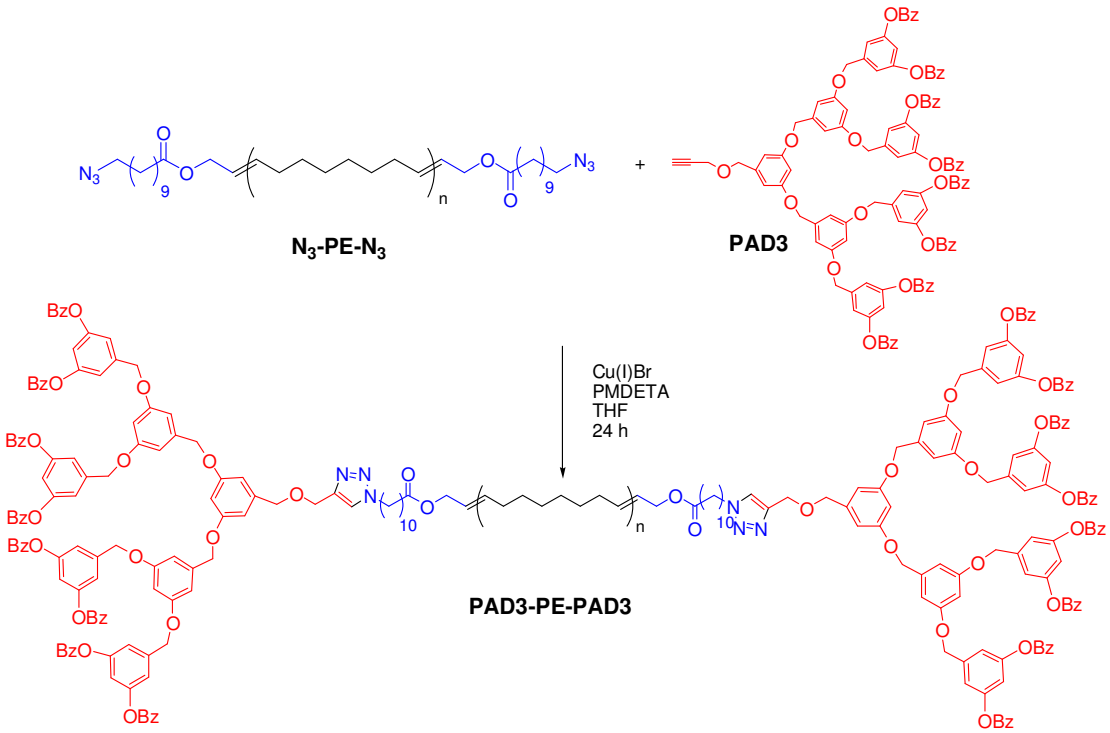


Figure 3.19. Synthesis of bis-PAD3 PE via Huisgen click reaction

4. RESULTS AND DISCUSSION

Copolymer of styrene and chloromethyl styrene (CMS) was synthesized by using the reversible addition-fragmentation chain transfer (RAFT) polymerization method at 90°C. RAFT was chosen as preferred polymerization method to obtain polymer with low polydispersity. More importantly, the method allows incorporation of monomers containing benzyl halides. The attachment of electron rich anthracene group was accomplished via etherification reaction with 9-anthracenemethanol according to a literature protocol [51] The copolymer composition was determined by comparing the ratios of peak areas around 4.5 ppm, which corresponds to the two side chain methylene protons of CMS, and the total area between 6.5 and 7.1 ppm, corresponding the total aromatic protons in ^{1}H-NMR spectra. It was found that each repeating unit is composed of one CMS monomer and three styrene monomers. Efficiency of anthryl pendant group attachment into the backbone of the copolymer could be evaluated from ^{1}H-NMR spectra of the formed product. In the ^{1}H-NMR spectra the new peaks arising from methylene protons of anthracene ring at 5.3 ppm and aromatic protons of anthracene ring between 7.3 and 8.4 ppm were identified (Figure 4.1). The integral ratio of methylene protons adjacent to the anthryl and benzylic positions were found to be equal thus indicating complete replacement of the chloride groups by anthryl subunit.

Anthracene functionalized polymer was reacted with dendrons containing furan protected maleimide groups at their focal points by refluxing in toluene. At such elevated temperature, unmasking of the reactive maleimide functional group at the focal point of the dendrons take place via the retro-DA reaction. Thus generated dienophile appended dendrons generated in situ reacts with anthracene containing copolymer via [4+2] cycloaddition reaction resulting in dendron grafted polymer.

High efficiency in the formation of DA adduct on the copolymer was clearly evident in the ^{1}H-NMR spectra of the dendronized polymers. Characteristic aromatic proton peaks of anthracene between 7.3 and 8.4 ppm completely disappeared as expected and a new peak corresponding to the bridgehead proton appeared at around 4.7 ppm as a broad peak,

due to the overlapping with the peaks corresponding to methylene protons of CH_2 adjacent to anthracene and phenyl ring (Figure 4.1).

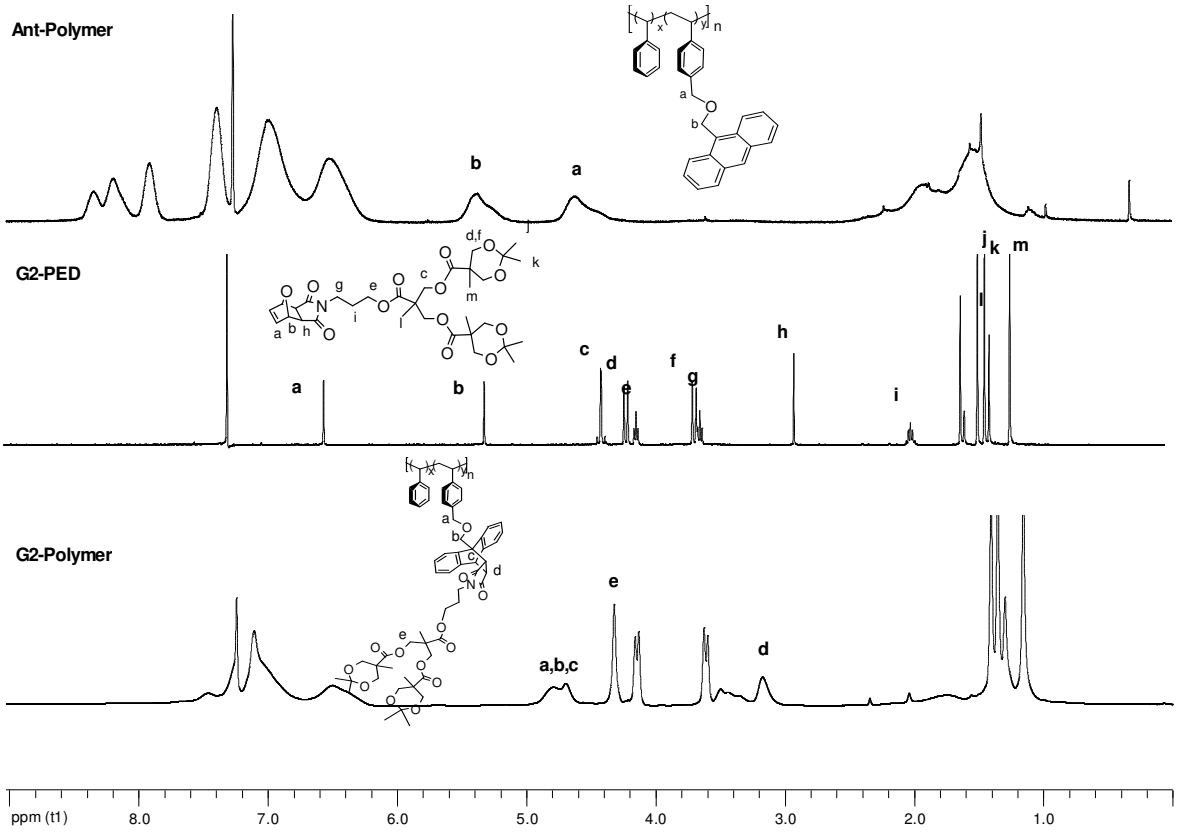


Figure 4.1. ^{1}H-NMR of Ant-Polymer, G2-PED and G2-Polymer

Insertion of the dendrons to the backbone of the copolymer during the DA reaction was monitored by UV spectroscopy where disappearance of characteristic finger like anthracene peaks at around 300-400 nm verifies the quantitative cycloadduct formation. The increase in the hydrodynamic volume of the dendronized polymers upon attachment of higher generation dendrons was monitored by the evolution of GPC traces of the dendrons grafted polymers. Molecular weight increase of dendronized polymers upon attachment of higher generation dendrons was evident from the GPC traces, although the values were much lower than expected (Table 4.1), (Figure 4.1). It has been noted earlier by other research groups that SEC underestimates the real molecular weights of the dendronized polymers [56].

Table 4.1. Molecular weights of dendronized polymers via GPC

Compound	$M_{n\text{-theoretical}}$[a]	$M_{n\text{-GPC}}$[b]	M_w/M_n
Anthracene Polymer	12221	9716	1.53
G1-Polymer	15320	14468	1.41
G2-Polymer	20221	17003	1.41
G3-Polymer	30024	19682	1.45

[a] $M_{n\text{-Theo}} = M_{n\text{-GPC(Anth-Polymer)}} + (N_{Anth} * M_{n\text{-Dendron}})$

[b] Determined by GPC relative to linear PS standards.

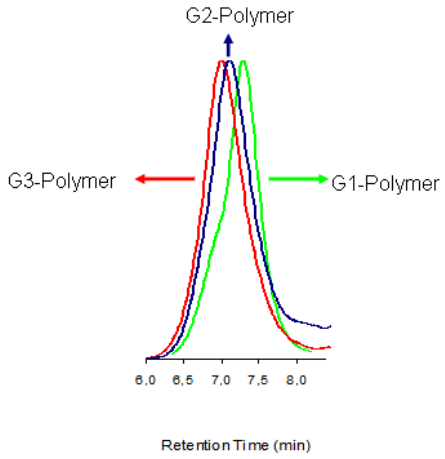


Figure 4.2. GPC traces of dendronized polymers

Kinetic study regarding G1 and G3 dendron attachment onto anthracene polymer were carried out via UV spectroscopy. Surprisingly, the generation of dendrons did not seem to have any effect at the rate of cycloaddition. Both dendrons showed the same rate profile due to the slow releasing of furan from dendrons. This observation can be explained on the basis that the rate determining step is the release of furan from the dendrons focal point. It is likely that the unmasking of the maleimide for G1 and G3 dendrons is independent of the dendrons generation. To probe this further, the cycloaddition reaction was followed using deprotected dendrons. As expected, the kinetic study of DA reaction reveals that the deprotected G1 dendron reacts faster than the deprotected G3 dendron

(Figure 4.2). This stems from larger steric bulk of G3 dendron compared to the G1 dendron. Importantly, the reaction goes to completion upon prolonged heating.

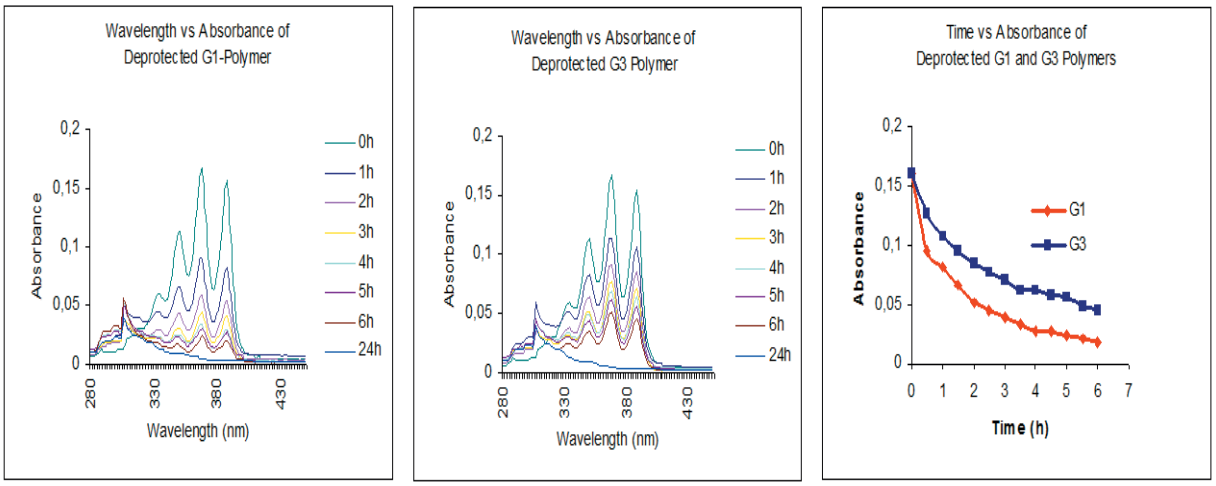


Figure 4.3. UV-Vis analysis of effect of dendron generation on grafting efficiency

Dendronization of polymers is effective in modulating the physical and chemical characteristics of the parent polymer. In our case, one can envision that deprotection of the acetal groups on the appended dendrons will render the polymer hydrophilic. This is indeed the case, the G3-dendron appended polymer that is insoluble in a polar protic solvent like methanol becomes soluble in methanol once the acetal groups are transformed to hydroxyl groups upon deprotection with an acidic resin such as DOWEX-H^+. As expected, this also changes the surface characteristics of films coated using these polymers. A static contact angle measurement demonstrates the change in surface wetting characteristics of such a film (Figure 4.3).

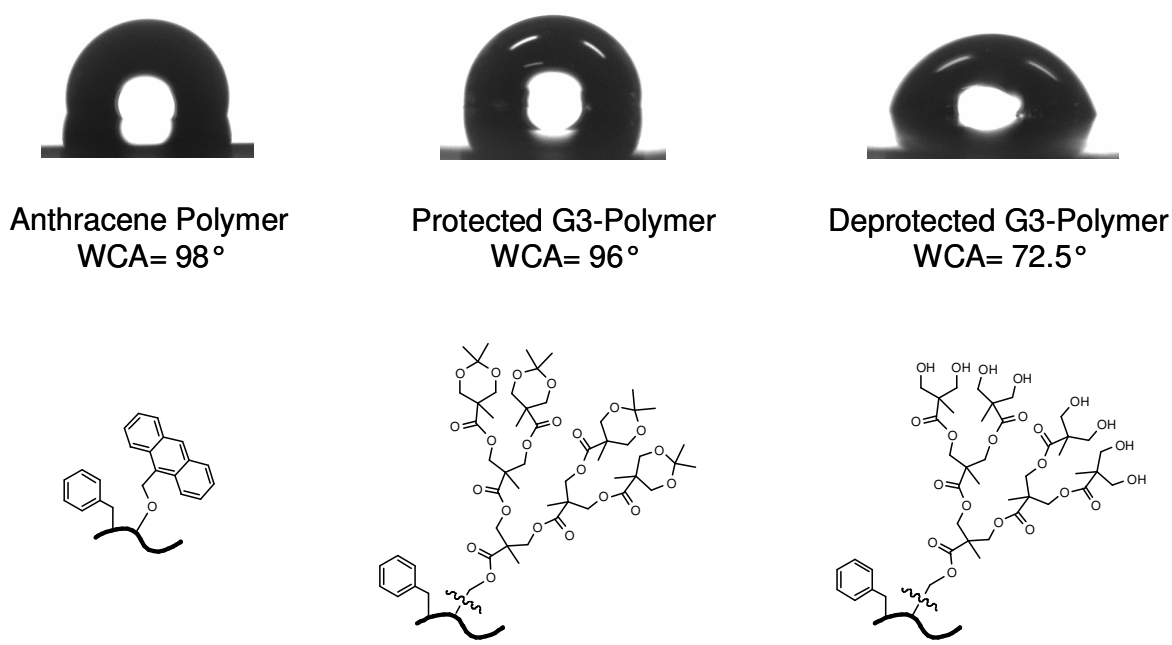


Figure 4.4. Contact angle of water on films of dendronized polymers

In order to produce orthogonally double dendronized polymer, polymer containing both anthracene and azido functional was synthesized. In the ^{1}H-NMR spectra in addition to peak at 5.31 ppm corresponding to methylene protons of anthracene, a new peak corresponding to methylene protons of CMS adjacent to azide at 4.18 appeared (Figure A.9).

Anthracene and azido functional are orthogonal groups at certain temperature. It is expected that azide is supposed to make Huisgen click reaction with terminal acetylene, and antracene is supposed to make Diels-Alder reaction with maleimide. Surprisingly, it is known that at a certain temperature (50-55 °C) azide can couple with maleimide. Under the light of this knowledge, two pathways, either stepwise or one pot adjusting the temperature at certain time interval, may help the synthesis of doubly dendronized polymers.

In the stepwise route, copper catalyzed Huisgen reaction was first done with poly aryl dendron containing acetylene at their focal point. Then, Diels-Alder reaction with polyester dendron containing maleimide at their focal point follows purification steps of first reaction. Again, a new purification is needed. After a long procedure desired product is obtained but it is time consuming and waste of the final product.

In the one pot route, all the reagents are present together in the same round bottom flask. The reaction was run at room temperature for overnight for the completion of copper catalyzed Huisgen click reaction. Then, the reaction was heated to elevated temperature (120 °C) for overnight, without any purification step following the first part. The completion of Huisgen click reaction was checked with the disappearance of azide absorbance peak at 2094 cm^{-1} in the FTIR (Figure A.13). The completion of Diels-Alder reaction is also followed with disappearance of characteristic absorbance peaks of anthracene between 300-400 nm in the UV-Vis spectra. Unfortunately, in the functionalization of the main polymer with the generation 3, copper catalyzed Huisgen reaction went to completion but Diels-Alder reaction did not manage to the completion according to the UV-Vis spectra and ^{1}H-NMR spectra due to steric crowding.

^{1}H-NMR spectra gave useful data for the reaction to be carried out. The explanations related to Diels-Alder reaction were mentioned detailed in the first part of the study which was Diels-Alder functionalization of anthracene polymer with polyester dendrons. After the Huisgen click reaction methylene protons of CMS adjacent to azide shifted from 4.2 ppm to 5.3 ppm. Proton of triazole comes at 7.4 ppm but it cannot be seen due to peaks of aromatic regions (Figure A.10).

Molecular weight increase of doubly dendronized polymers was also followed with GPC (Table 4.2), (Figure 4.4).

Table 4.2. Molecular weights of doubly dendronized polymers via GPC

Compound	$M_{n\text{-theoretical}}$[a]	$M_{n\text{-GPC}}$[b]	M_w/M_n
Ant-Azido-Polymer	11401	11330	1.47
G1-G1-Polymer	15254	13342	1.39
G2-G2-Polymer	19118	14706	1.44
G3-G3-Polymer	26882	18250	1.42

[a] $M_{n\text{-Theo}} = M_{n\text{-GPC(Anth-N3-Polymer)}} + (N_{Anth} * M_{n\text{-PED Dendron}}) + (N_{N3} * M_{n\text{-PAD-Dendron)}}$

[b] Determined by GPC relative to linear PS standards.

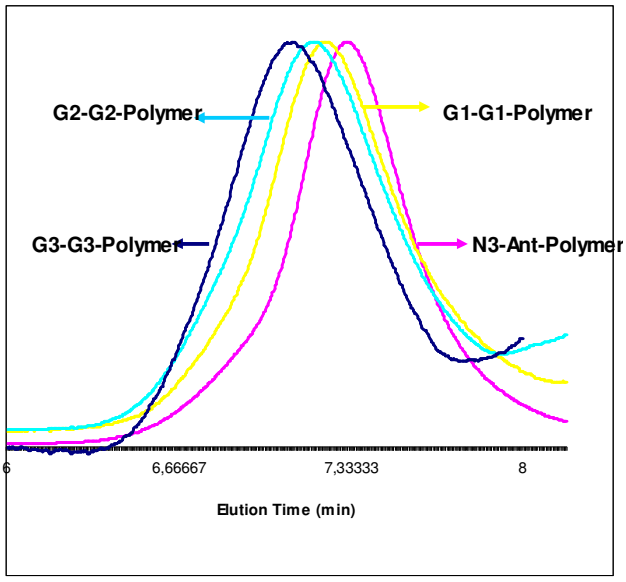


Figure 4.5. GPC traces of double clicks

After functional polyethylene (PE) was synthesized, acetylene containing dendrons at its focal point were combined to it via copper catalyzed Huisgen reaction. Reaction was monitored by the disappearance of azide absorbance peaks at 2094 cm^{-1} with FTIR (Figure A.18). Second characterization method was ^{1}H-NMR spectroscopy. After click reaction, methylene protons adjacent to azide shifted from 3.2 ppm to 4.30 ppm. Proton of triazole ring also came at 7.47 ppm. Aromatic and benzylic protons appeared at around 6.5-7.5 ppm and 4.65-5.01 ppm, respectively (Figure A.15).

Table 4.3. Molecular weights of bis-dendritic polyethylenes

Compound	$M_{n\text{-theoretical}}$[a]	$M_{n\text{-GPC}}$[b]	M_w/M_n
Bis-N_3-PE	16960	19526	2.36
G1-PE-G1	22620	24581	1.52
G3-PE-G3	27920	27413	1.59

[a] $M_{n\text{-Theo}} = I_{5.3}/2 * M_{cyclooctene}$

[b] Determined by GPC relative to linear PS standards.

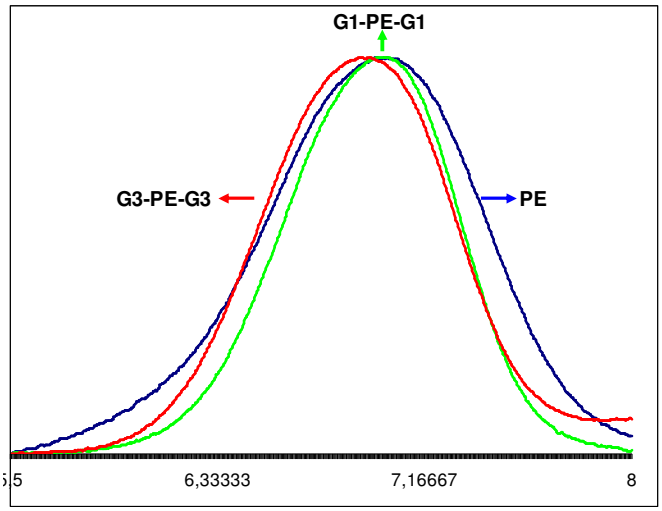


Figure 4.6. GPC traces of bis-dendritic polyethylenes

5. CONCLUSIONS

A new strategy towards synthesis of dendronized polymers via the “Click” reactions was designed. Polymers incorporating only an anthracene group and both anthracene and azide in the side chain were utilized as a reactive backbone.

Biodegradable latent-reactive dendrons containing furan protected maleimide groups at their focal points were used as dendrons. In situ thermal deprotection of the focal points of the dendrons exposes the reactive maleimide dienophile that undergoes efficient Diels-Alder cycloaddition reaction with the anthryl moieties on the polymer side chain. First through third generation of dendrons are efficiently ‘grafted to’ a polymer back bone using the aforementioned strategy. Dendronized polymers thus obtained could be converted to hydroxyl group jacketed polymers and could be cast as hydrophilic films. The hydroxyl groups on these films should be amenable to further functionalization with molecules of interest to fabricate functional surfaces.

Kinetic study regarding G1 and G3 dendron attachment onto anthracene polymer was performed. Furan masked dendrons did not demonstrate different rate profile due to fact that the rate determining step is release furan from dendrons. The same study was applied to unmasked dendrons and it was seen that unmasked G1 dendron reacts faster than unmasked G3 dendron due to steric bulkiness of G3 dendron compared to G1 dendron.

Orthogonally double click reactions were done onto polymers containing both antracene and azide in the appended side chains. While azide moiety can make cycloaddition reaction with polyaryl dendron containing acetylene at their focal point via Cu (I) catalyzed Huisgen click reaction, antracene moiety can make cycloaddition reaction with polyester dendron containing maleimide at their focal point via Diels-Alder reaction in one pot. It is known that azide can make Huisgen reaction with maleimide that is why the reaction temperature was altered at appropriate time schedule.

Bis-dendritic polyethylene was synthesized via ROMP and Click chemistry. For this purpose after the synthesis of azide containing polyethylene at the both end of the polymer,

polyaryl dendrons containing acetylene at their their focal point added to this polymer via copper catalyzed Huisgen click reaction.

For the all works, the characterizations of the products were carried out by ^{1}H-NMR, ^{13}C-NMR, UV-Vis Spectroscopy and FTIR.

As a future work, bis-azido-polyethylene will be coupled with anthracene-acetylene changing to ends of the polymer from azide to anthracene which is a potential diene for Diels-Alder reaction. Then, polyester dendrons containing maleimide at their focal point will be bound to this polymer via Diels-Alder reaction.

APPENDIX A: SPECTROSCOPY DATA

^{1}H, ^{13}C NMR and IR spectroscopy of the synthesized products are included. Necessary expansions were made on the NMR data.

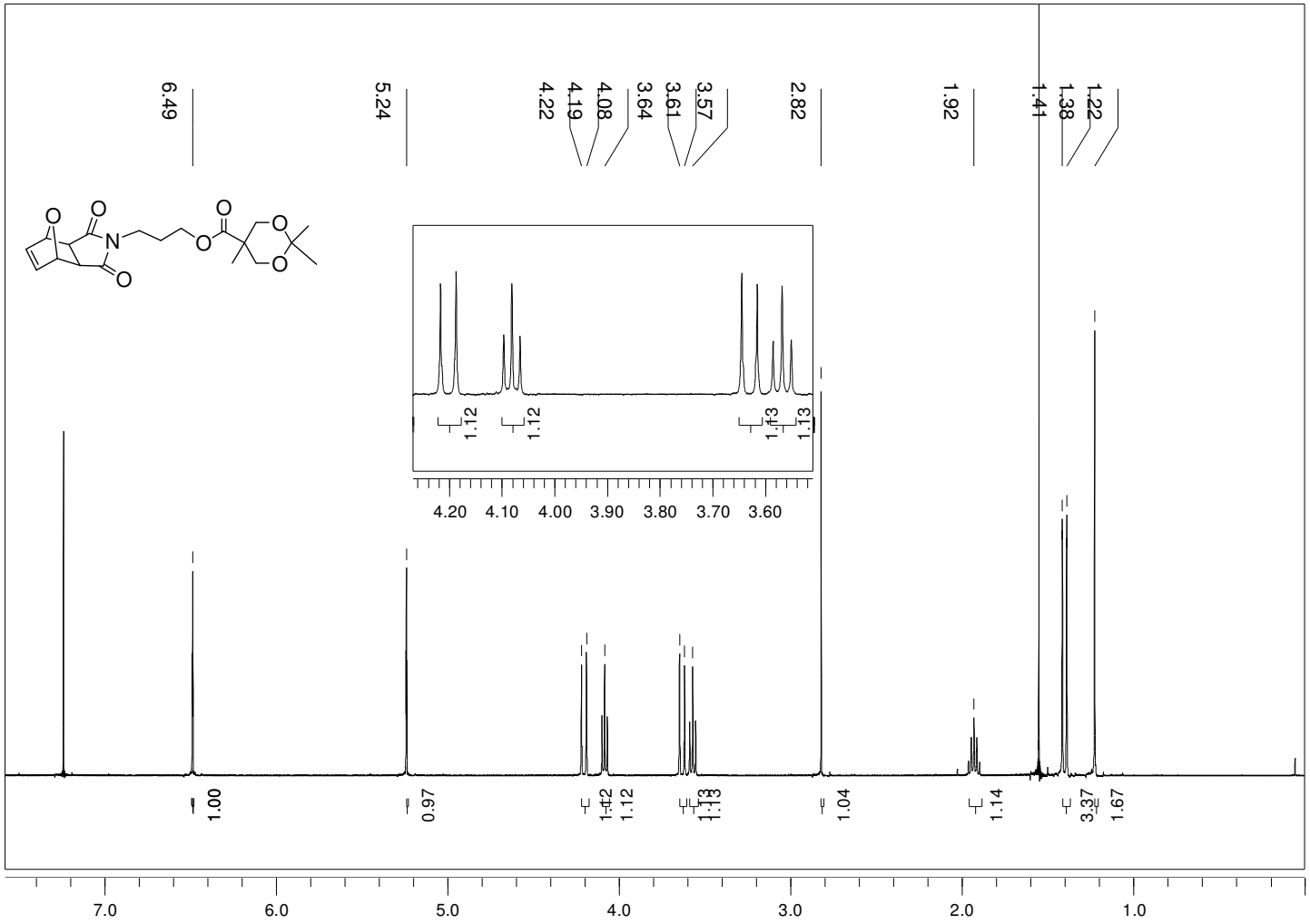


Figure A.1. ^{1}H-NMR of PED1

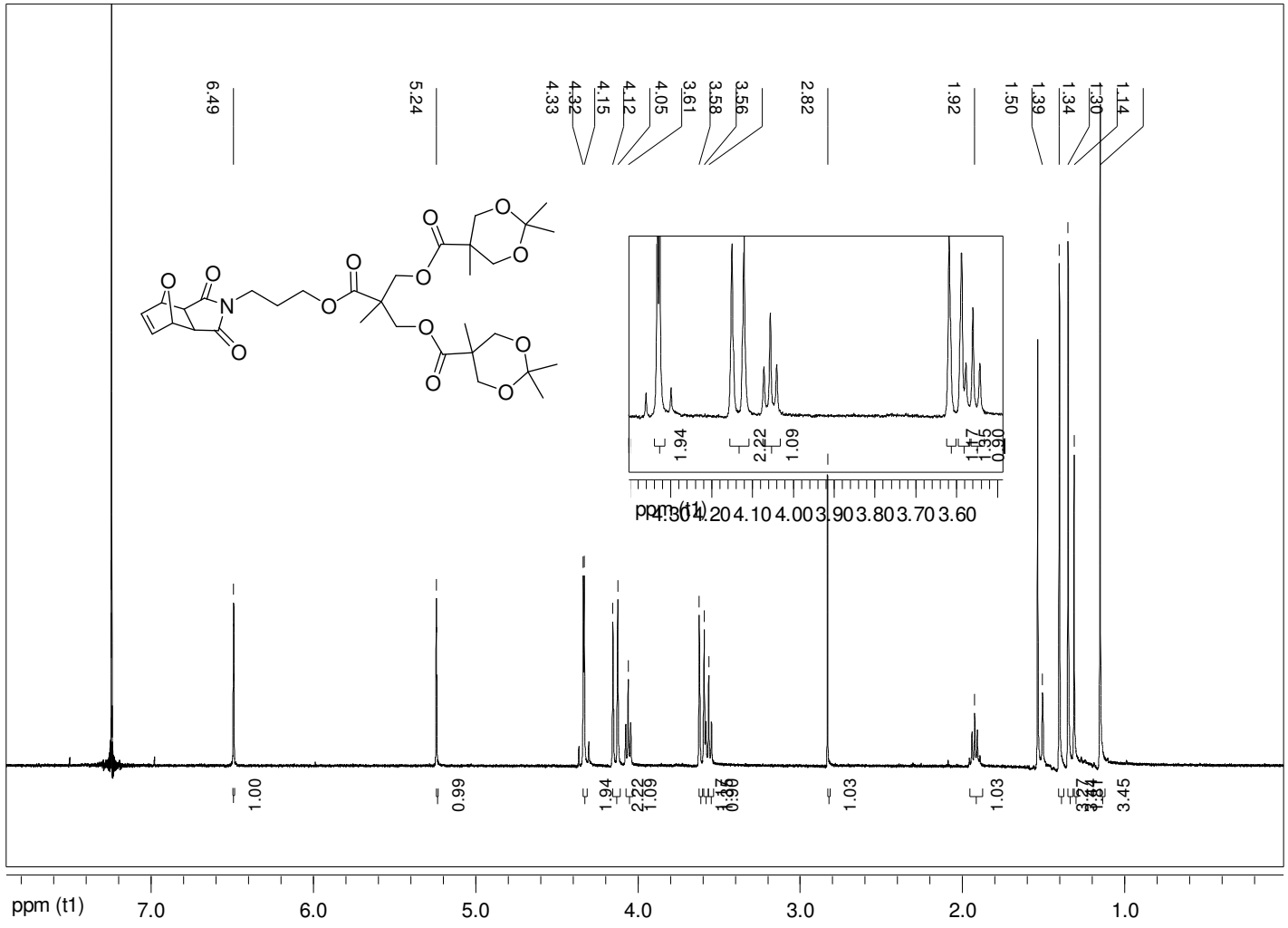


Figure A.2. ^{1}H-NMR of PED2

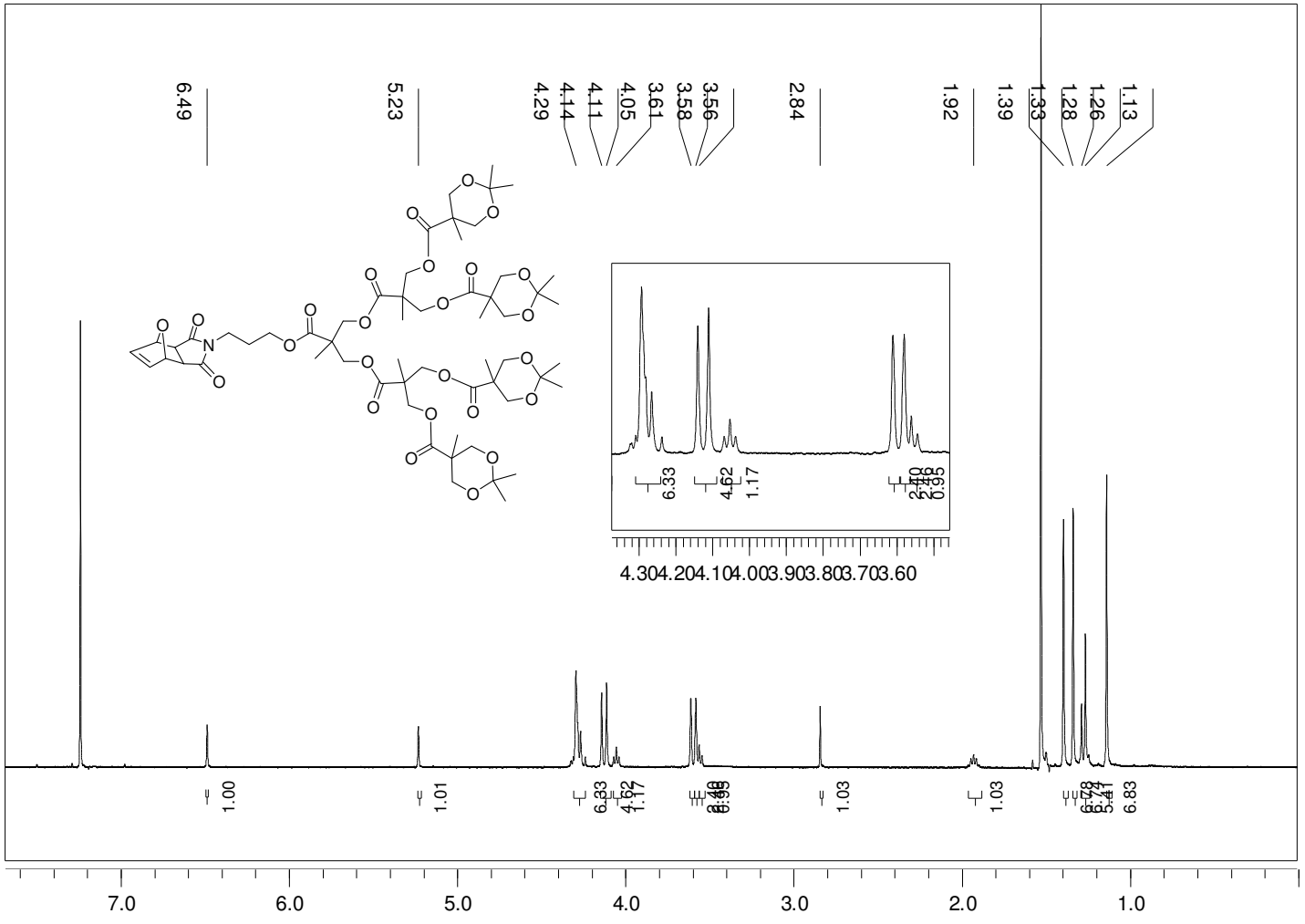


Figure A.3. ^{1}H-NMR of PED3

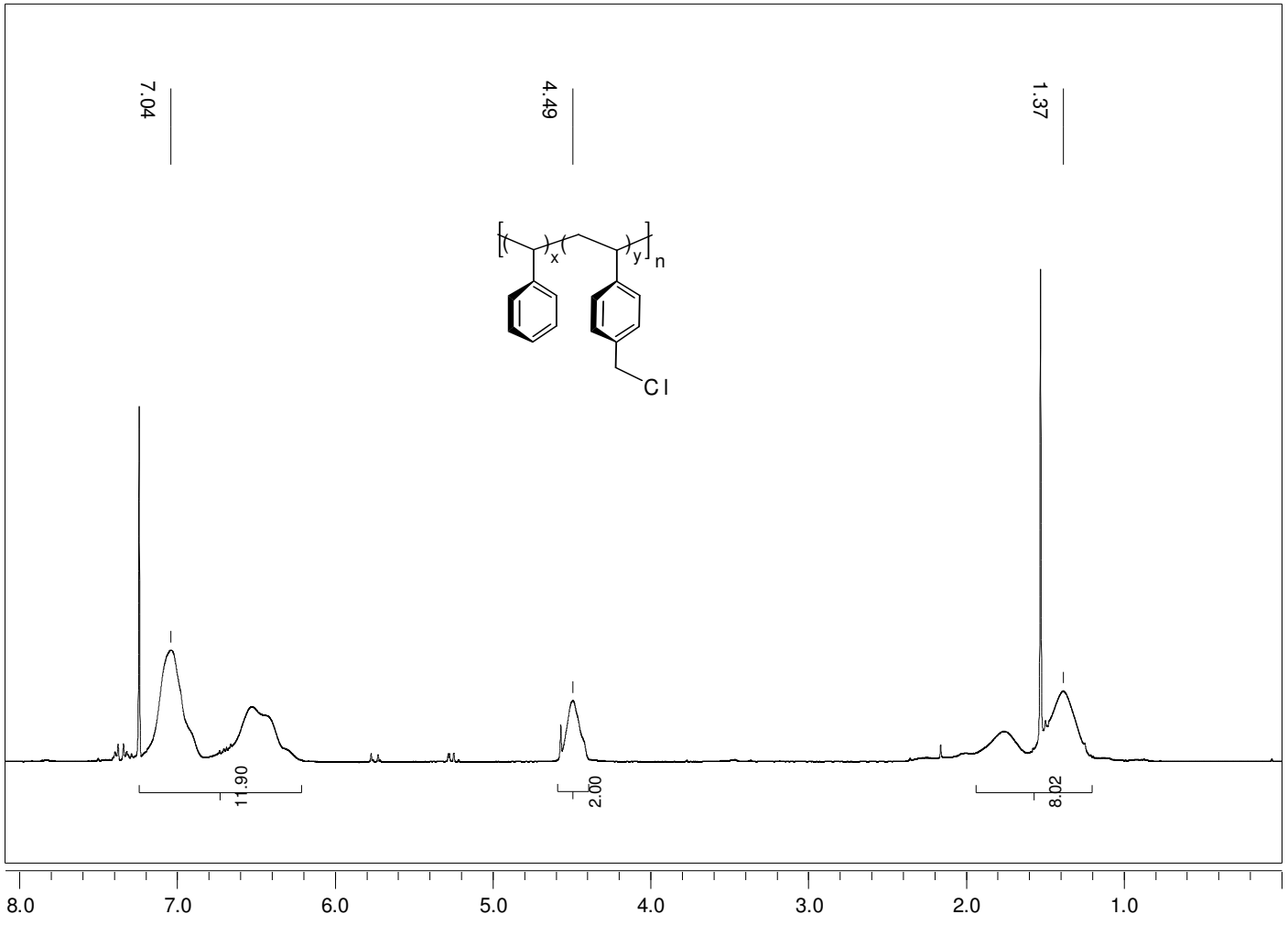


Figure A.4. ^{1}H-NMR of co-(St-CMS)

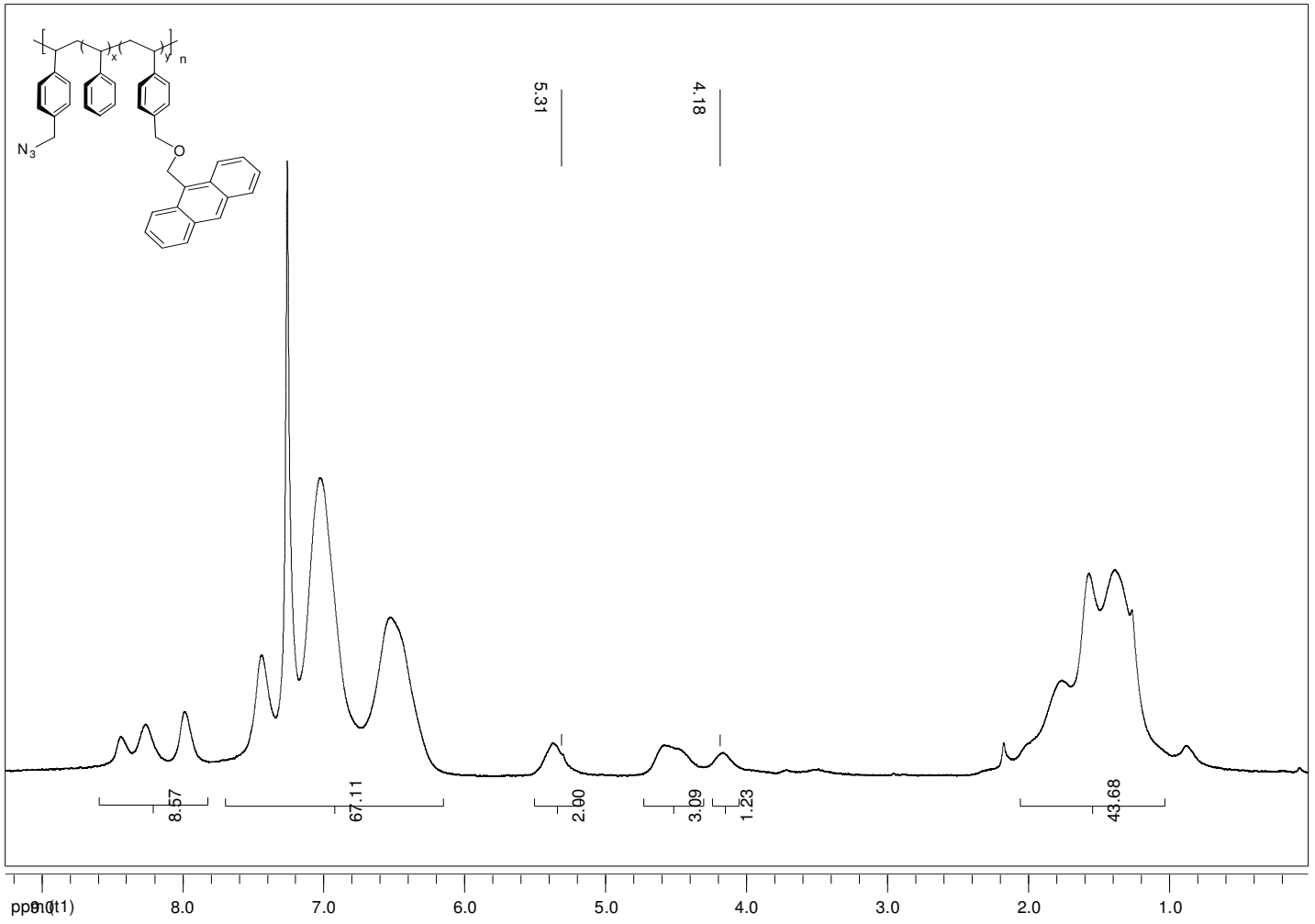


Figure A.5. ^{1}H-NMR of ant-polymer

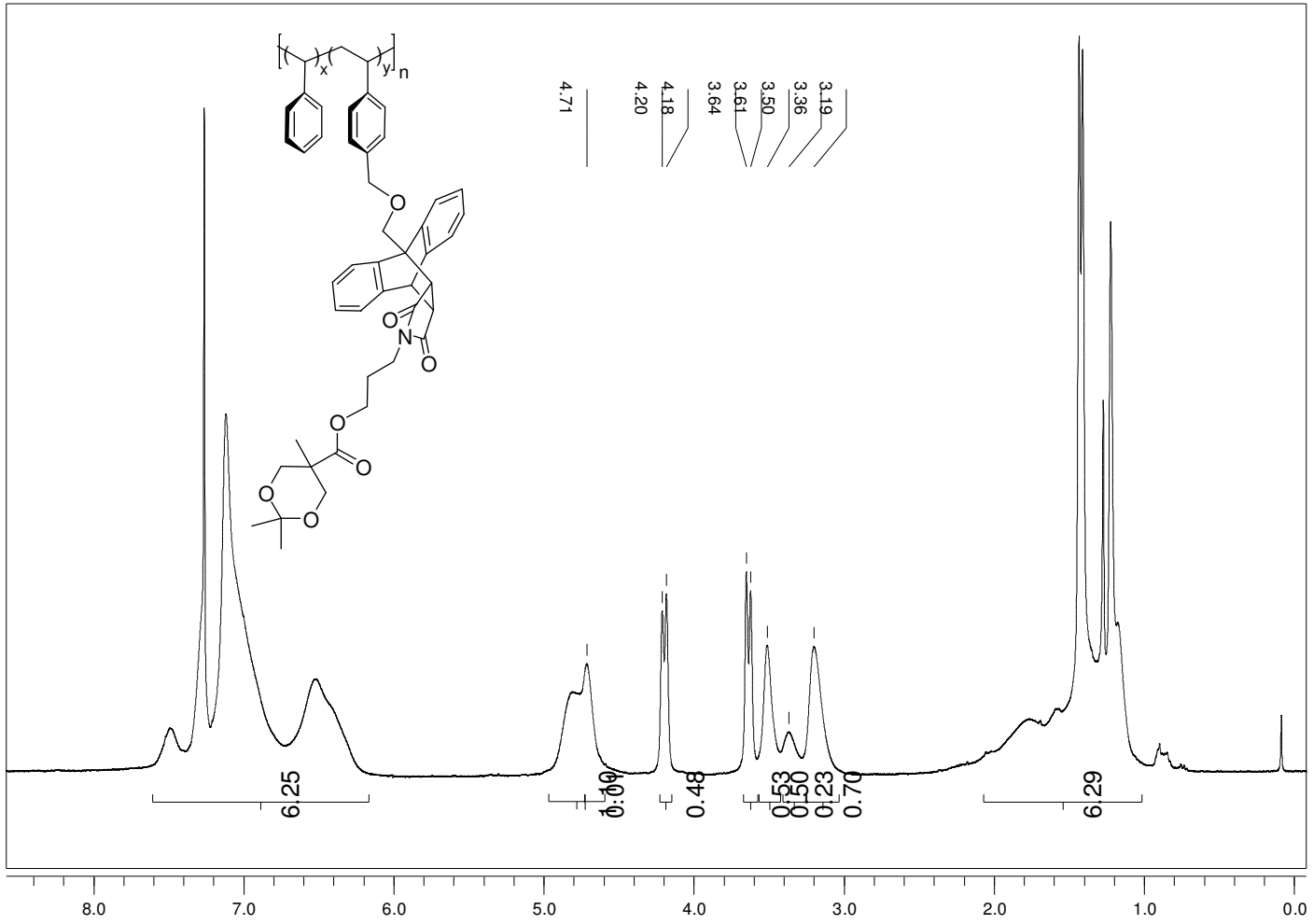


Figure A.6. ^{1}H-NMR of PED1-Polymer

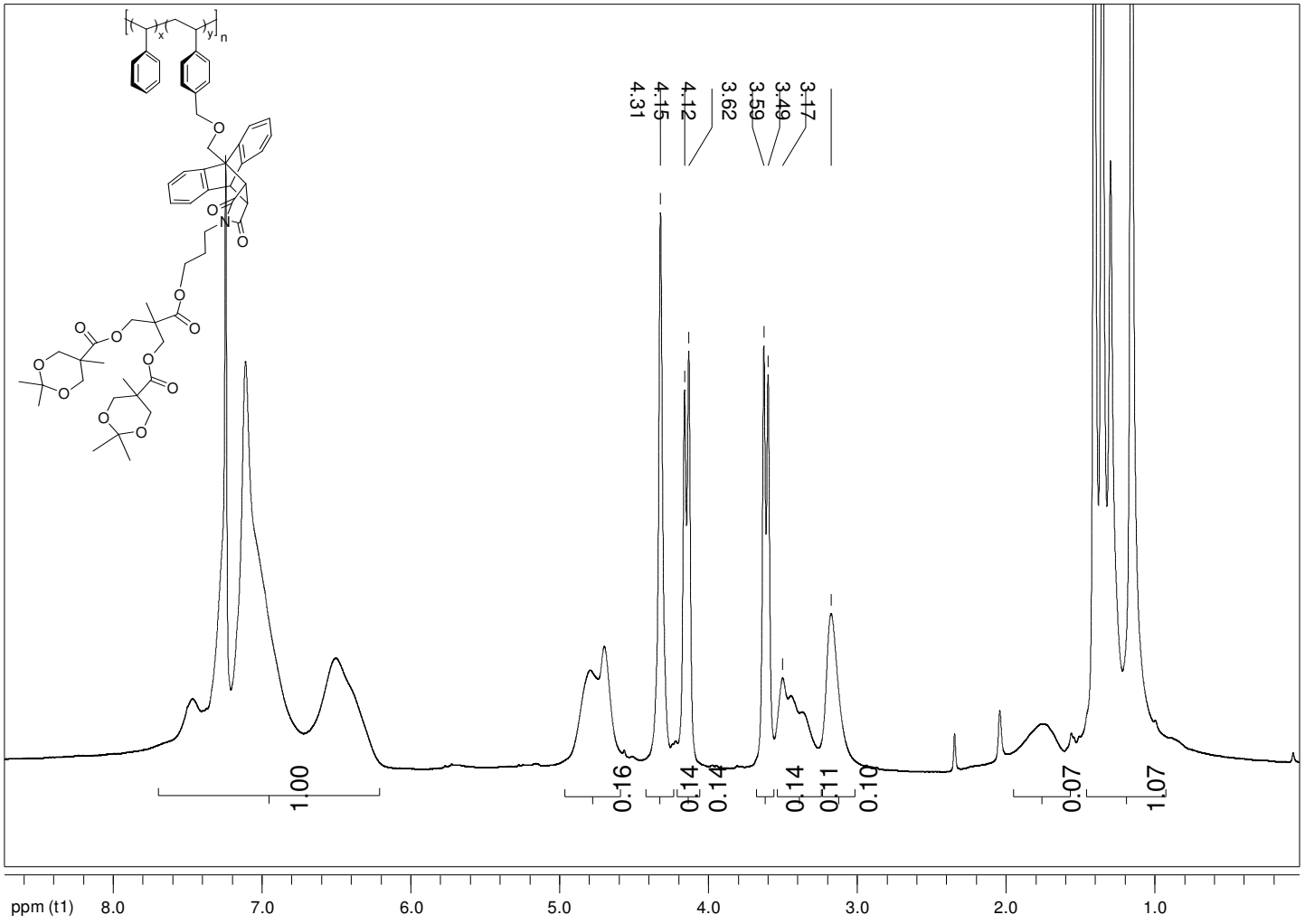


Figure A.7. ^{1}H-NMR of PED2-Polymer

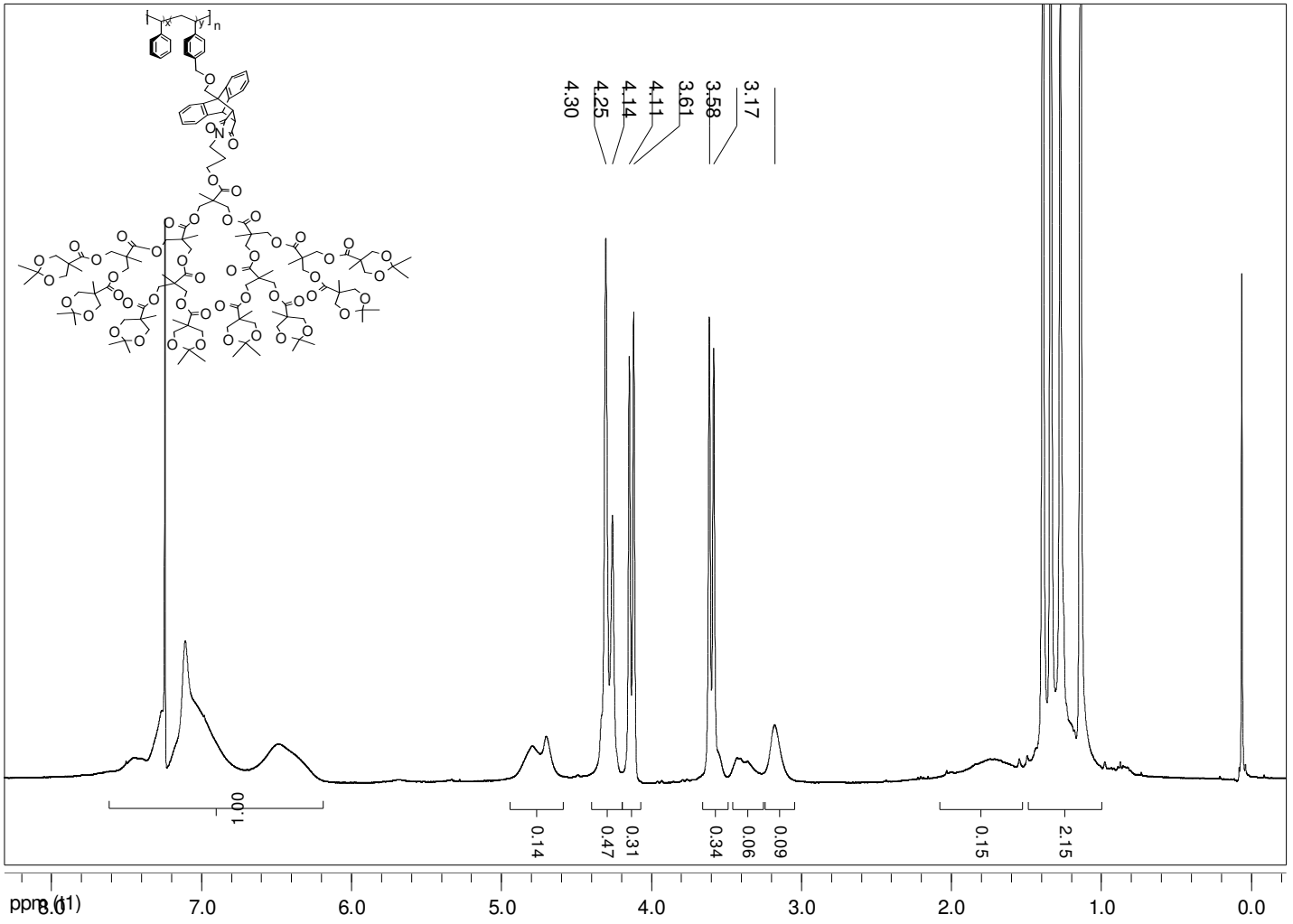


Figure A.8. ^{1}H-NMR of PED3-Polymer

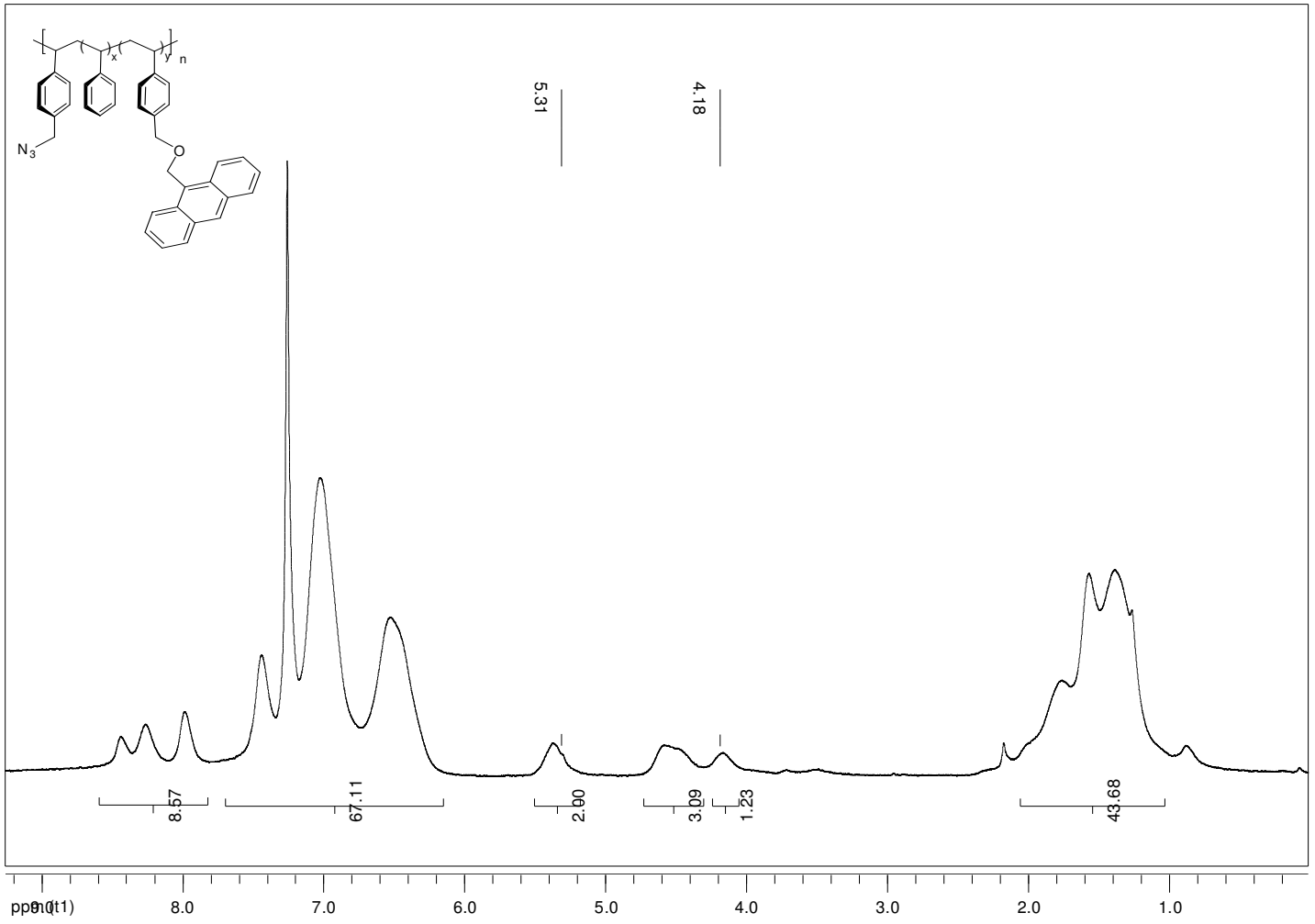


Figure A.9. ^{1}H-NMR of Azido-Ant-Polymer

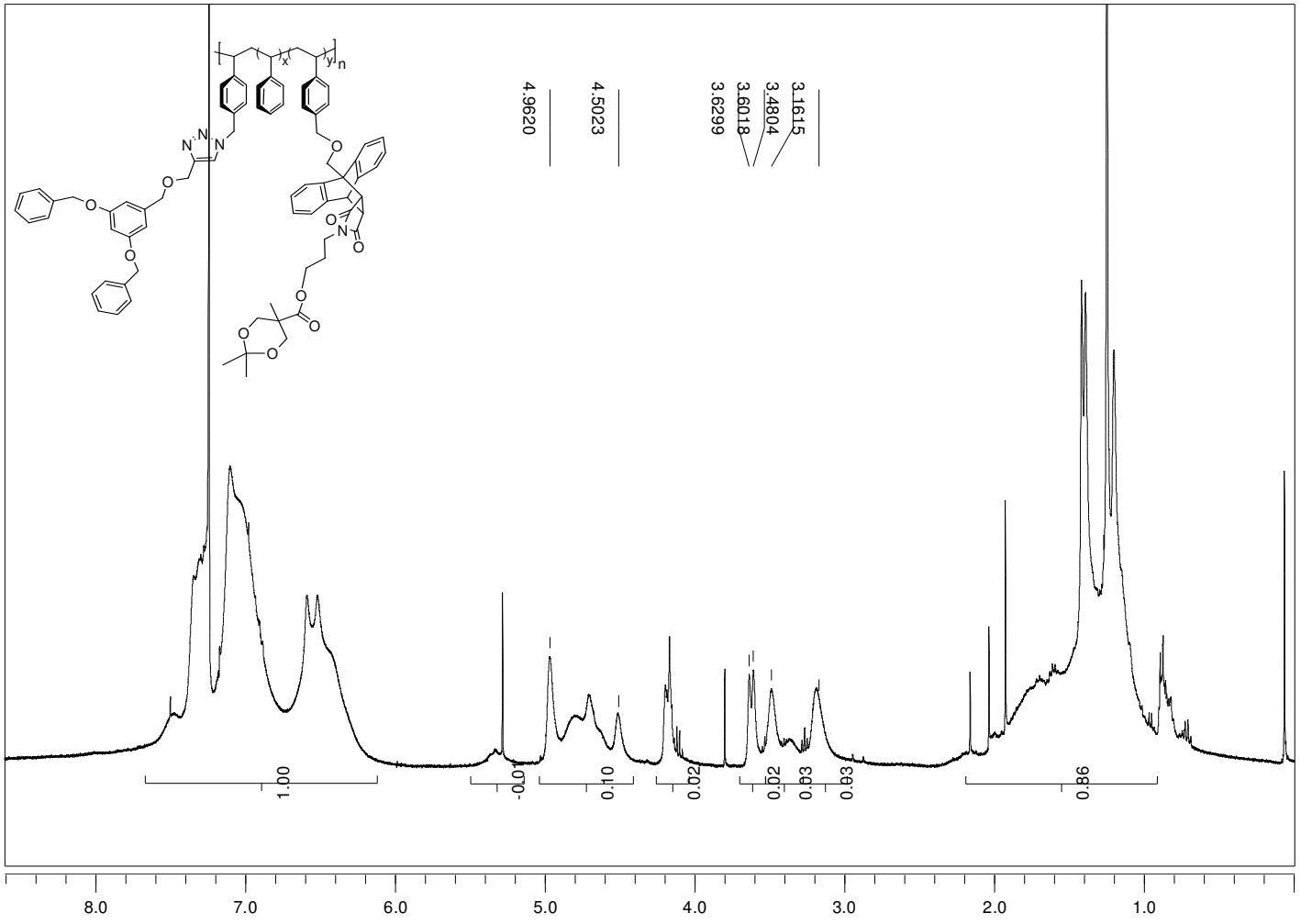


Figure A.10. ^{1}H-NMR of G1-G1-Polymer double click

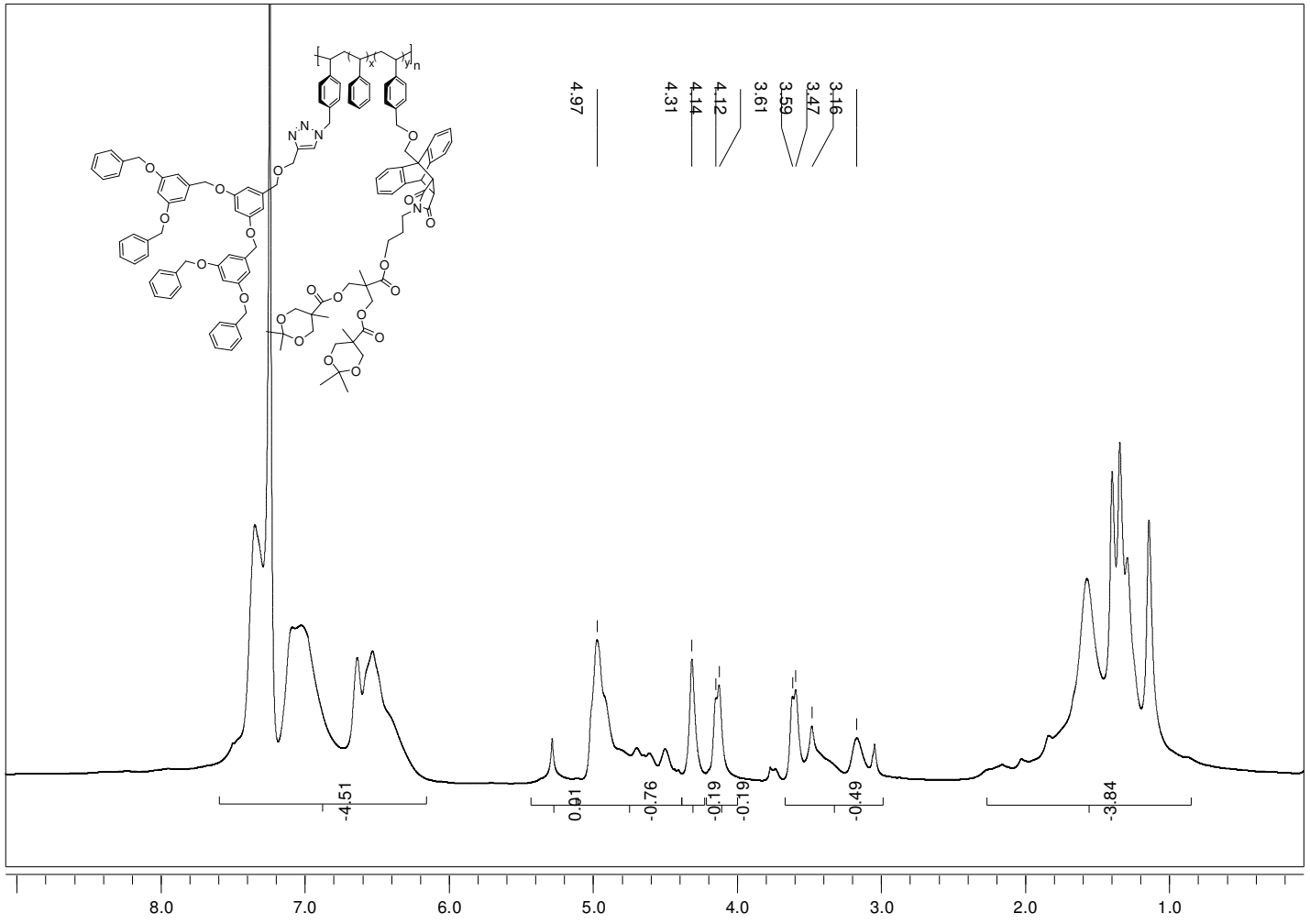


Figure A.11. ^{1}H-NMR of G2-G2-Polymer double click

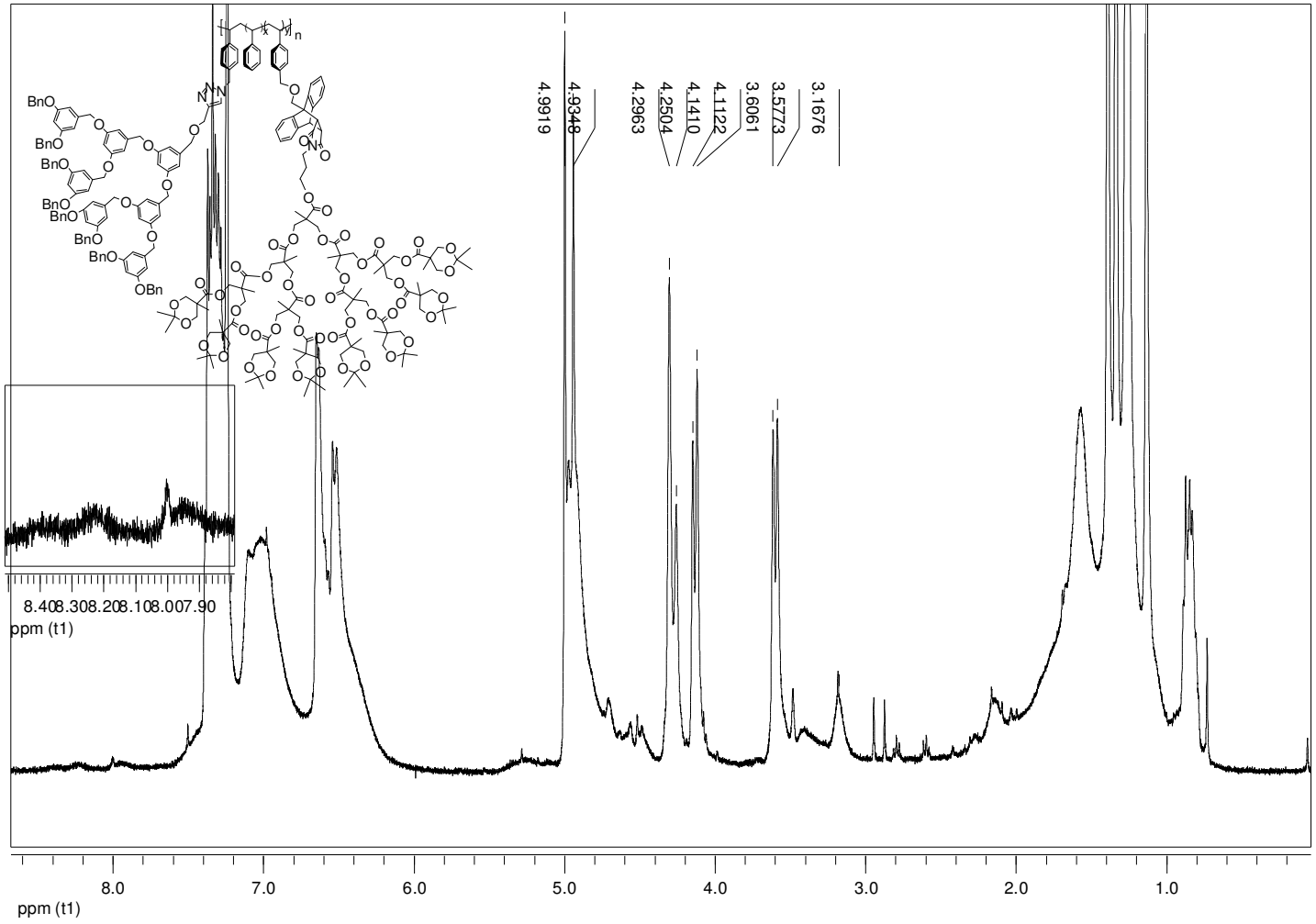


Figure A.12. ^{1}H-NMR of G3-G3-Polymer double click

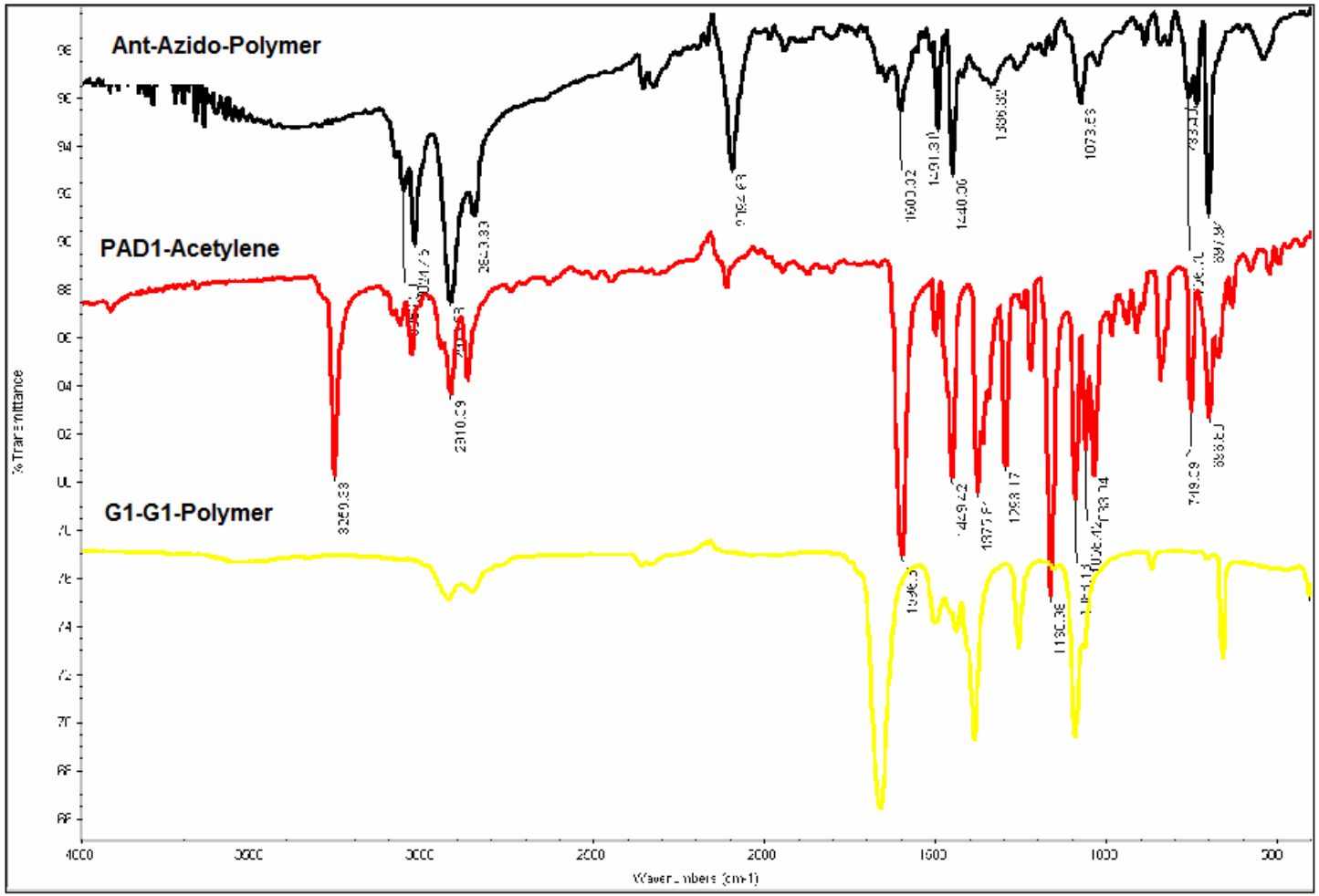


Figure A.13. Following the double click reactions with FTIR

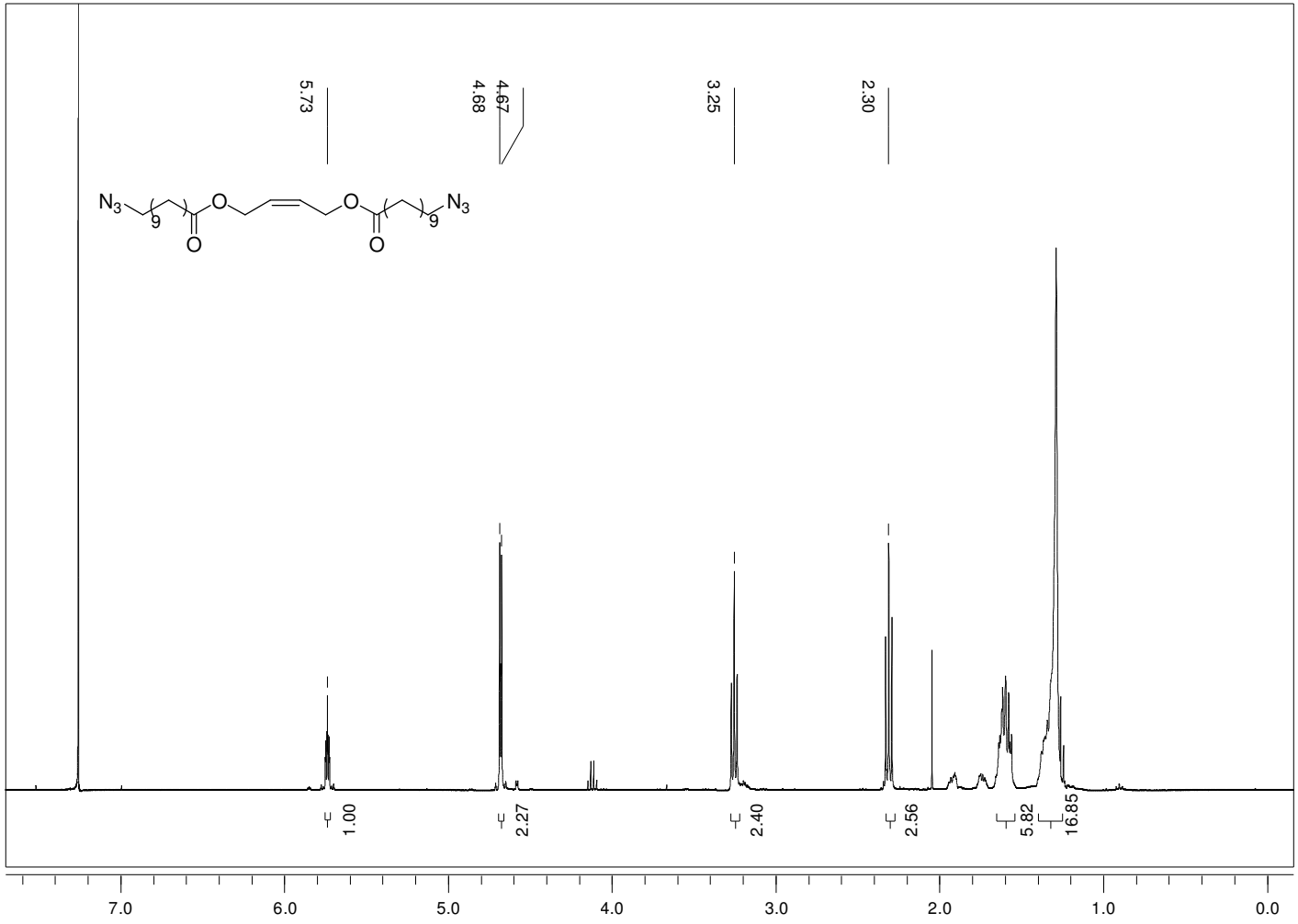


Figure A.14. ^{1}H-NMR of CTA

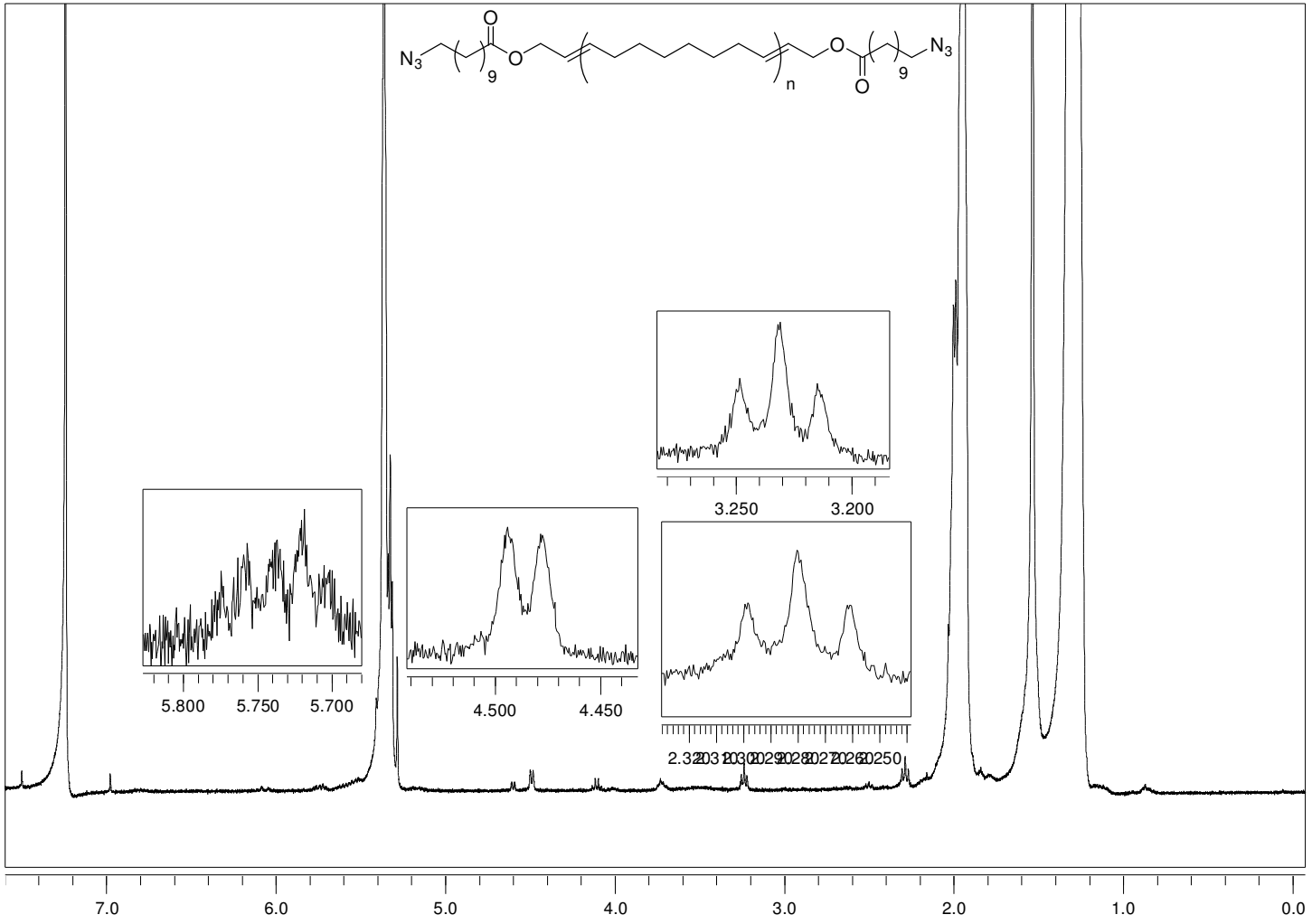


Figure A.15. ^{1}H-NMR of PE via CTA

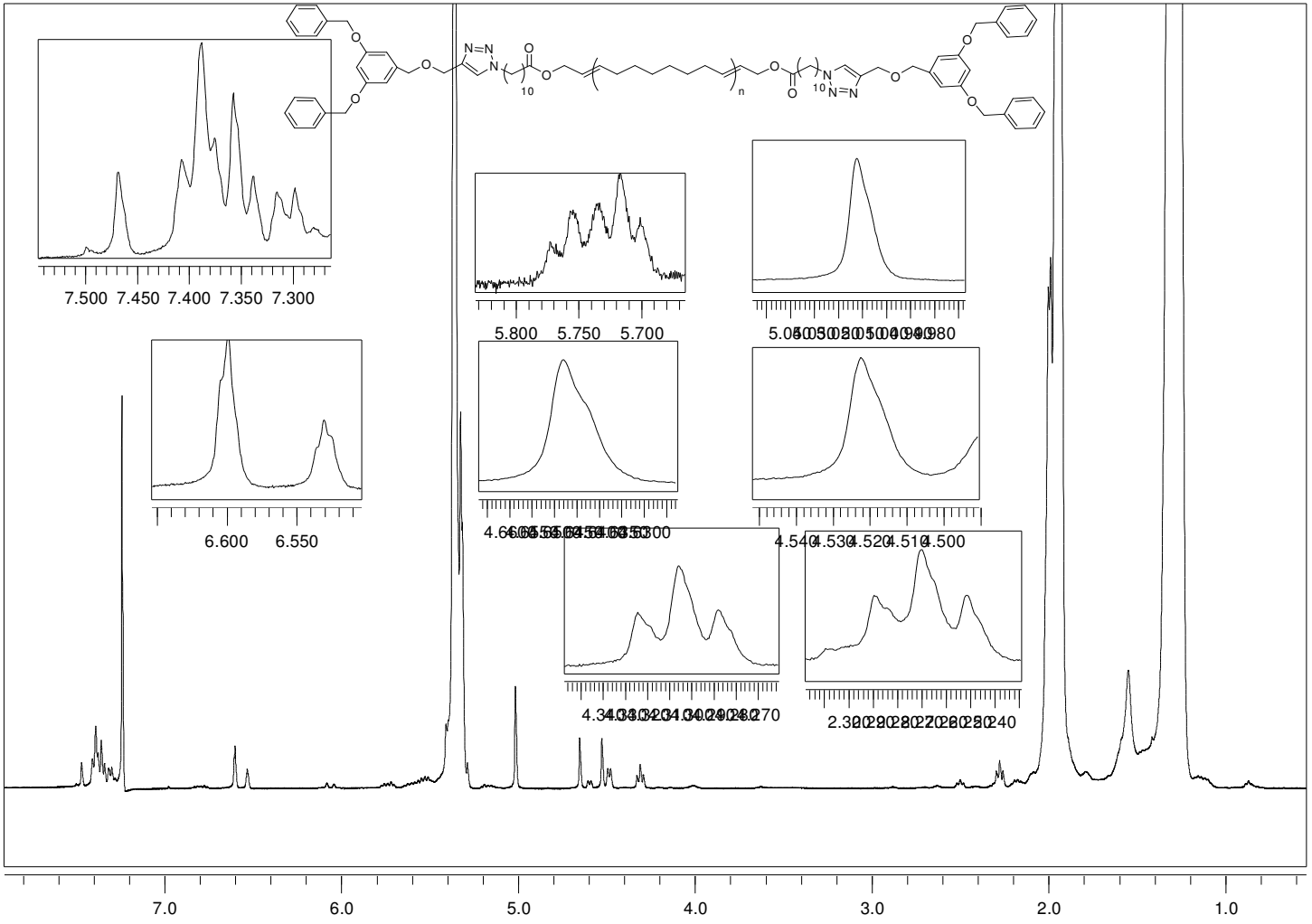


Figure A.16. ^{1}H-NMR of PAD1-PE-PAD1

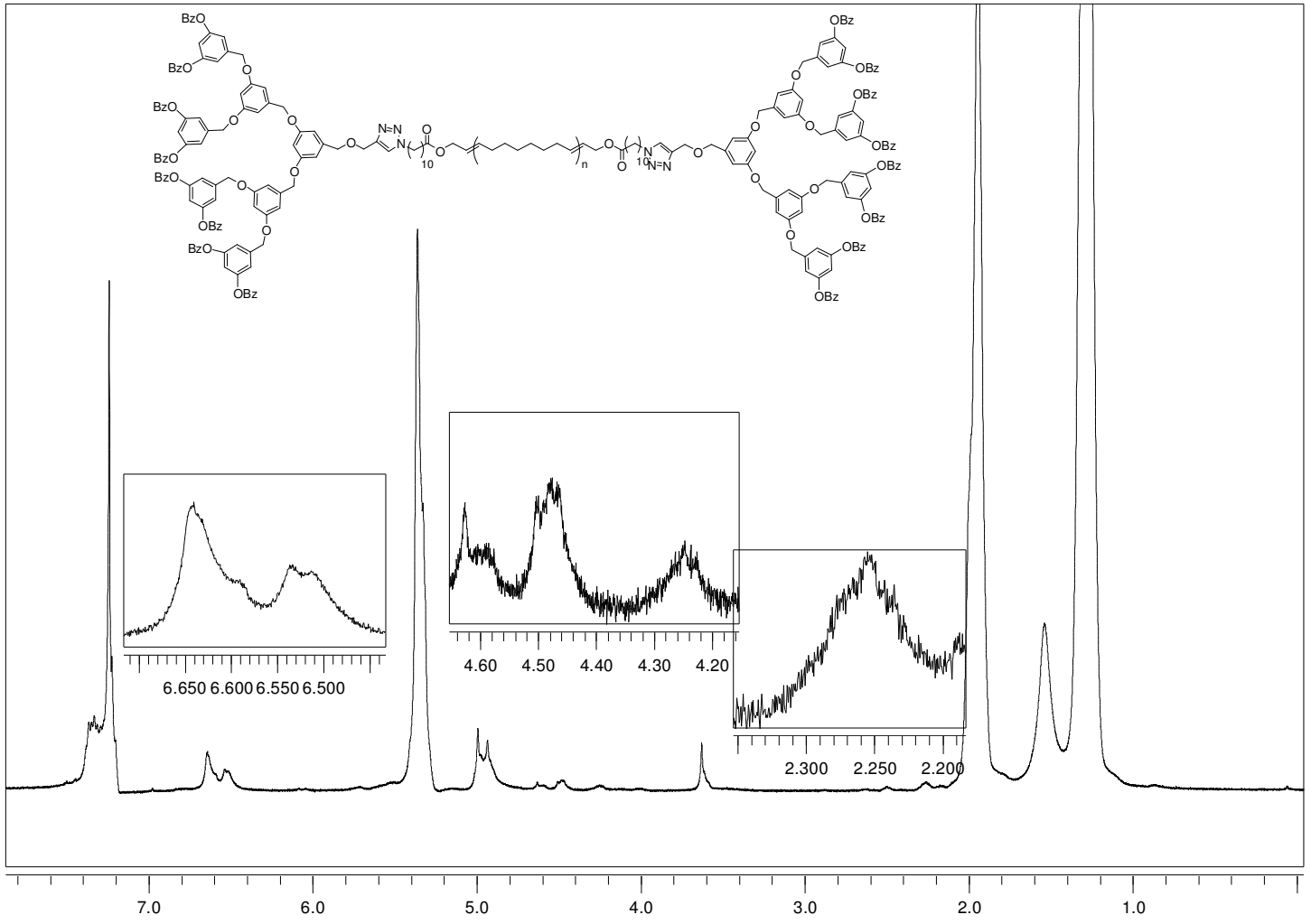


Figure A.17. ^{1}H-NMR of PAD3-PE-PAD3

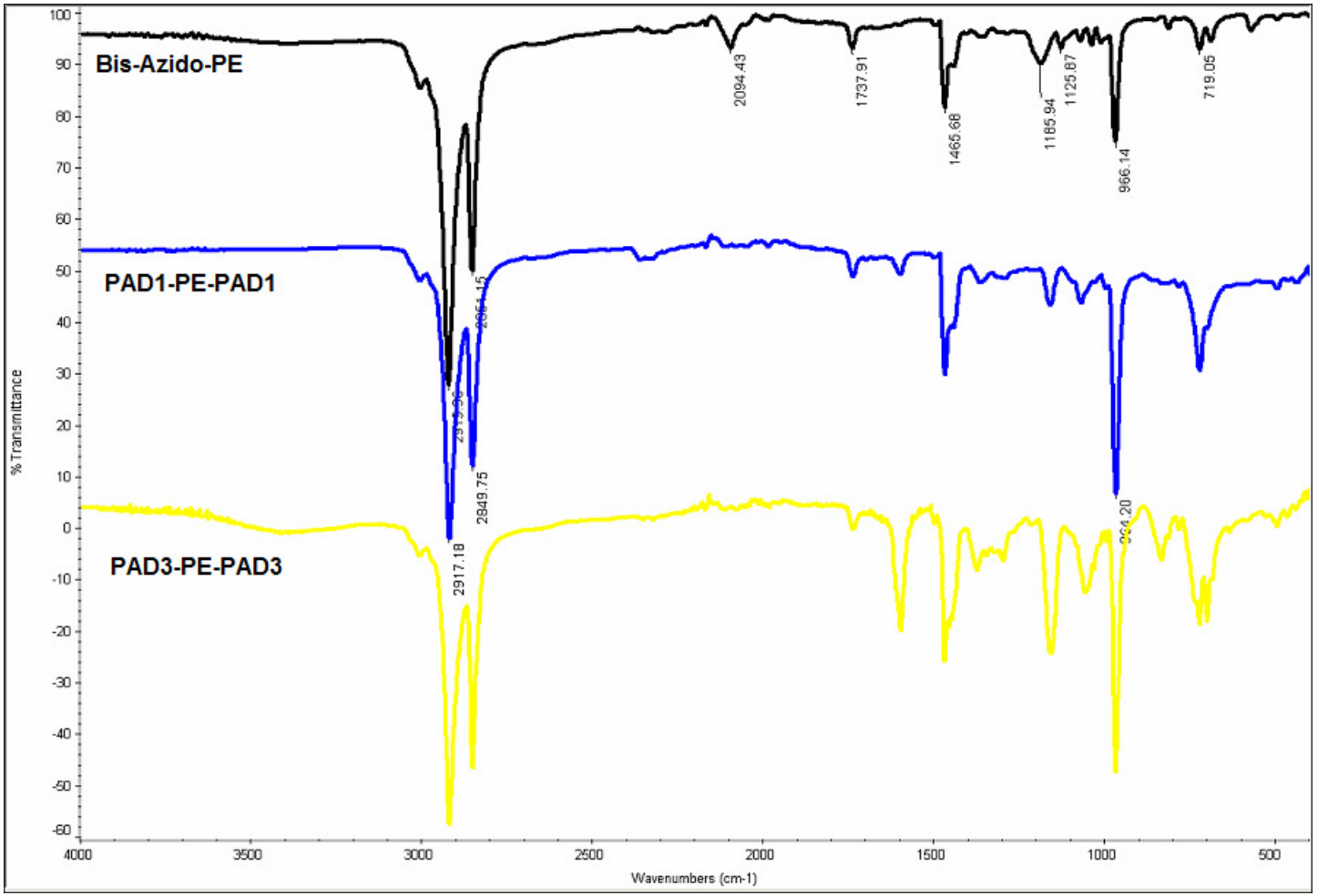


Figure A.18. FTIR traces of bis-dendritic-PEs

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