

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**SURFACE MODIFICATION OF CARBON NANOTUBES (CNTs) VIA CLICK
REACTIONS**



Ph.D. THESIS

Pınar Sinem OMURTAG ÖZGEN

Department of Chemistry

Chemistry Programme

NOVEMBER 2018

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Thesis Advisor: Prof. Dr. Ümit TUNCA

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**KARBON NANOTÜP (CNTs) YÜZEYİNİN CLICK REAKSİYONLARI İLE
MODİFİKASYONU**

DOKTORA TEZİ

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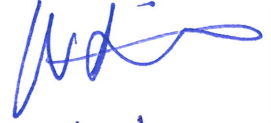


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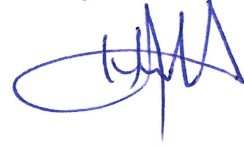
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To my parents and Emre,



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ABBREVIATIONS

^{13}C NMR	: Carbon Nuclear Magnetic Resonance Spectroscopy
^1H NMR	: Proton Nuclear Magnetic Resonance Spectroscopy
ACN	: Acetonitrile
ADCA	: Acetylenedicarboxylic acid
AIBN	: 2,2'-Azobis(2-methylpropionitrile)
ATRP	: Atom Transfer Radical Polymerization
C/LRP	: Controlled/living radical polymerization
CDCl_3	: Deuterated chloroform
CH_2Cl_2	: Dichloromethane
CNTs	: Carbon nanotubes
CuAAC	: Copper catalyzed azide-alkyne cycloaddition
DA	: Diels-Alder cycloaddition reaction
DBTTC	: S,S- Dibenzyl trithiocarbonate
DCC	: <i>N,N'</i> - Dicyclohexylcarbodiimide
DMAP	: 4-dimethylaminopyridine
DMF	: <i>N,N</i> -Dimethylformamide
DMSO-d_6	: Deuterated dimethyl sulfoxide
DOX	: Doxorubicin
DP	: Degree of polymerization
DWCNTs	: Double walled carbon nanotubes
EC	: Ethylene Carbonate
Et_3N	: Triethylamine
EtOAc	: Ethyl acetate
EtOH	: Ethanol
<i>f</i>-CNTs	: Functionalized carbon nanotubes
FLG	: Few-Layer Graphene
FPT	: Freeze-pump-thaw
FRP	: Free radical polymerization
FT-IR	: Fourier Transform Infrared Spectrophotometer
GO	: Graphene Oxide

GPC	: Gel Permeation Chromatography
MeOH	: Methanol
MI	: Maleimide
MMA	: Methyl methacrylate
MWCNTs	: Multi walled carbon nanotubes
MWD	: Molecular Weight Distribution
o-DCB	: 1,2-Dichlorobenzene
P(Ph₃)	: Triphenylphosphine
PCL	: Polycaprolactone
PEG	: Poly(ethylene glycol)
PFP	: Pentafluorophenol
PMDETA	: <i>N, N, N', N'', N''</i> , Pentamethyldiethylenetriamine
PMMA	: Poly(methyl methacrylate)
PnBA	: Poly(<i>n</i> -butyl acrylate)
PS	: Poly(styrene)
PtBA	: Poly(<i>tert</i> -butyl acrylate)
PTSA	: p-Toluenesulfonic acid
RAFT	: Reversible Addition Fragmentation Chain Transfer
rGO	: Reduced graphene oxide
RP	: Radical polymerization
St	: Styrene
SWCNTs	: Single walled carbon nanotubes
TGA	: Thermal gravimetric analysis
THF	: Tetrahydrofuran
UV	: Ultraviolet

SYMBOLS

$[M]_0/[I]_0$	: Monomer concentration to initiator concentration ratio
$^{\circ}\text{C}$	: <i>Celsius</i>
A	: Absorbance
C	: Concentration
<i>D</i>	: Dispersity Index
M	: Molarity
M_n	: The number average molecular weight
M_w	: The weight average molecular weight
M_w/M_n	: Dispersity Index
nm	: Nanometer
λ	: Wavelength



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SURFACE MODIFICATION OF CARBON NANOTUBES (CNTs) VIA CLICK REACTIONS

SUMMARY

Carbon nanomaterials have crucial importance in the science and commercial applications. Carbon-based materials like diamond, fullerene, graphite, nanotubes and nanowires are used in some applications such as electronic, optic-electronic, biomedical engineering, tissue engineering, medical implants, medical devices and sensors. New nano-hybrids obtained by hybridization of carbon-based materials with materials having different properties like metals, metal oxides and polymers have increased their area of usage.

CNTs can be defined as simply rolled graphite and can be grouped based on their layer numbers as; single walled, double walled and multi walled CNTs. Their circular curve structure is the main reason for quantum restrictions and σ - π re-hybridization. After re-hybridization, three σ bonds slightly move out of the plane and increase the elbowroom of π orbitals. These special characteristics makes CNTs to have better mechanical strength, electrical and thermal conductivity, and chemical and biological activity when it's compared to graphite. However, their area utilization is limited because of their handling restrictions, one of which is their low solubility especially in organic solvents. This results as disadvantage when they need to be purified or be treated so their usage cannot be possible unless they have been pre-modified.

Small molecules or polymers can be grafted via covalently or non-covalently approach to the surface of CNTs to increase its dispersion. Frequently used sidewall halogenation reactions, hydrogenation, Diels-alder cycloaddition, [2+1] nitrene addition, thiol-ene reaction can be examples for grafting onto the surface of the π -conjugated skeleton by covalent modification. Surface of carbon nanotubes are non-covalently functionalized by the way of adsorption of polynuclear aromatic compounds having functional groups such as anthracene, naphthalene, pyrene or porphyrin. Small aromatic molecules are attached onto the surface of CNTs via π - π stacking in non-covalent strategy. This strategy has an advantage in terms of preserving mechanical and electronic properties of CNTs' surface after modification.

In this study, increasing the usage area of hybrid materials that are obtained by the application of different click chemistries onto the surface of single and multi walled CNTs that increase their solubility in many organic solvents. The first two parts of the study The walls (surfaces) of carbon nano tubes are modified by different reactions that have significant importance for green chemistry applications.

For direct covalent modification, methodologies that does not require any metal ligand complexes are chosen such as Diels-Alder, [2+1] nitrene cycloaddition and thiol-ene reactions whereas for indirect covalent modification, active ester reactions are used by are focused on the modification of the sidewalls of carbon nanotubes by the covalent approach.

In the first part of the thesis, four model reactions between CNTs and small molecules having functional groups such as furan, maleimide, anthracene and azide were carried out to evaluate efficiency of Diels-Alder and nitrene cycloaddition reactions. Positive results obtained from model reactions proceeded the study to the next step which is mono modification of carbon nanotubes with the polymers having suitable functional groups. So, firstly, polymers having an end group (PMMA, P α BA, PS, PEG etc.) such as furan, maleimide, anthracene, azide and thiol were synthesized and characterization of them were supported by the NMR, FT-IR and GPC measurements. Diels-Alder, nitrene cycloaddition and thiol-ene click reactions were performed between these polymers and SWCNTs, MWCNTs, and MWCNT-COOH. In accordance with the results obtained from experiments, second modification methodologies such as Diels-Alder, nitrene cycloaddition and thiol-ene reaction was applied to mono-modified carbon nanotubes, which have positive results from the previous step in the presence of polymers having suitable functional groups. Besides sequential double modification, sequentially one-pot double modification methodology was applied to unmodified CNTs. Double combinations of these chemistries such as nitrene addition - thiol-ene click reaction, Diels-Alder cycloaddition - thiol-ene click reaction, nitrene addition - Diels-Alder cycloaddition were used for double modification of carbon nanotubes sequentially. And, combinations of nitrene addition - Diels-Alder cycloaddition, thiol-ene click reaction - nitrene addition and Diels-Alder cycloaddition - nitrene addition were used for one-pot double modification of CNTs by sequential approach. Thermal gravimetric analysis of the performing experiments from both approaches showed that carbon nanotubes can be functionalized with these approaches.

In the second part of the thesis, firstly grafting of amine-terminated PEG to the surface of multi walled CNTs by active ester reaction is performed. This is further followed by the grafting of azide-terminated PS polymers by nitrene reaction. Firstly, acid functions of commercially available carbon nanotubes (MWCNT-COOH) were changed to acid chloride (MWCNT-OCOCl). This reaction can be performed by the presence of thionyl chloride or oxalyl chloride together with a catalytic amount of DMF once the optimum reaction temperatures are obtained (0 °C to 60 °C). Then, pentafluorophenyl ester of MWCNTs (MWCNT-COOC $_5$ F $_6$) was synthesized by the presence of MWCNT-OCOCl pentafluorophenol and pyridine. MWCNT-COOC $_5$ F $_6$ were very active against amines and its reaction with amine-terminated PEG (PEG-NH $_2$) completed the first modification reaction of the surface. For the second surface modification, MWCNT-CONHPEG which have been obtained in the first step was dispersed in o-dichlorobenzene. Afterwards, PS-g-MWCNT-CONHPEG was obtained via nitrene addition in the presence of PS-N $_3$ on high temperatures (130 °C).

In the last part of the thesis, surface of carbon nanotubes was functionalized by polyesters containing pyren via non-covalent adsorption interaction which is an advantageous method in terms of preserving mechanical, electronic properties of CNTs. Polymers having polynuclear aromatic group were attached onto the surface of CNTs via π - π stacking in non-covalent strategy. So firstly, five different of polyesters (P1-P5) containing electron deficient internal alkyne units derived from acetylene dicarboxylic acid in the main backbone were synthesized. Afterwards, firstly, polyesters gave Huisgen type 1,3-dipolar copper free cycloaddition reaction with pyrene-1-ylmethyl 3-azidopropanoate. One of the choosen polyester backbone (P2) which was previously synthesized gave Huisgen type 1,3-dipolar copper free cycloaddition reaction with pyrene-1-ylmethyl 3-azidopropanoate and the second molecule which

had azide function (2-azidoethanol, 3-azidopropionic acid, prop-2-yn-1-yl 3-azidopropanoate). Eight polyesters having pyrene which is a polynuclear aromatic compound were employed as a polymeric platform in the non-covalent modification of carbon nanotubes. The 1,3-dipolar cycloaddition reactions were performed at 40 °C in 1,4-dioxane for 4 hours. Characterization of polymers was supported by the NMR and GPC measurements. Synthesized polyesters were adsorbed into the sidewalls of MWCNTs for 10 days reaction time by non-covalent approach. Characterization of polyester modified MWCNTs were performed with TGA, UV and HR-TEM measurements.





KARBON NANOTÜP (CNTs) YÜZEYİNİN CLICK REAKSİYONLARI İLE MODİFİKASYONU

ÖZET

Günümüzde nanoteknoloji devrinin başlamasıyla karbon nanomalzemeler büyük önem kazandı. Nanoteknolojide uygun malzeme seçimi ve malzemenin işlenebilirliği önemlidir. Karbon elementi bu bakımdan eşsizdir. Karbondan oluşan makroskopik boyuta sahip malzemelere başlıca örnek olarak elmas, grafit, grafen oksit (GO), karbon fiberler, karbon nanotüpler (CNT) ve fulleren verilebilir.

Karbon nanomalzemeler, bilim dünyasında ve ticari uygulamalarda oldukça önemlidir. Elektronik, optikelektronik, biyomedikal mühendislik, doku mühendisliği, medikal implantlar, medikal cihazlar ve sensör uygulamalarında elmas, fulleren, grafit, nanotüpler, nanokablolar ve nanoşeritler gibi karbon bazlı malzemeler kullanılmaktadır. Karbon bazlı bu malzemelerin metal, metal oksit ve polimerler gibi farklı özelliklerdeki malzemelerle hibritlenmesiyle elde edilen yeni nano-hibritler kullanım alanlarını arttırmıştır.

Karbon nanotüpler (CNTs), üstün mekanik, elektronik, yüksek elastik modülüs gibi özellikleri ve düşük ağırlığından dolayı ilgi görmüştür. Basitçe yuvarlanmış grafen olarak ifade edebileceğimiz karbon nanotüpler levha sayısına göre; tek-duvarlı CNT, çift-duvarlı CNT ve çok-duvarlı CNT olmak üzere sınıflandırılabilir. Karbon nanotüplerin dairesel eğri yapısı, kuantum sınırlamasına ve σ - π tekrar hibritleşmesine neden olur. Tekrar hibritleşme ile üç σ bağı az oranda düzlem dışına çıkar ve π orbitalleri tübün dışında hareket alanını artırır. Bu özellikleri karbon nanotübü grafitten mekanik olarak daha güçlü, elektriksel ve termal olarak daha iletken, kimyasal ve biyolojik açıdan da daha aktif yapar. Bu eşsiz malzemenin kullanımı, muamele edilmesindeki zorluklar nedeni ile kısıtlanmaktadır. Bu zorlukların başında organik çözücülerde çözünürlüğünün olmayıp, zayıf dipersiyon göstermesi gelir. Ayrıca organik çözücülerde çözünürlüğünün az olması, saflaştırma ve işlem görmesi sırasında da sorun yaratmaktadır. Bu nedenle öncü bir modifikasyon olmadan CNT'ün kullanımı düşünülemez.

Çözünürlüğü arttırmak için CNT yüzeyine küçük molüküller veya polimerler kovalent veya non-kovalent yolla aşılanabilir. Kovalent bağ ile π -konjuge iskelet yüzeyine aşılama örnek olarak sıklıkla kullanılan yan duvar halojenlendirme tepkimeleri, hidrojenlendirme, Diels-Alder siklokatılma tepkimesi, [2+1] nitren katılma tepkimesi, tiyol-en tepkimesi verilebilir. Non-kovalent adsorpsiyon etkileşimi ile karbon nanotüplerin yüzeyleri, antrasen, naftalin, piren veya porfirin fonksiyonu içeren çeşitli polinükleer aromatik bileşikler vasıtasıyla fonksiyonlandırılır. Non-kovalent stratejide, küçük aromatik moleküller CNT yüzeyine π - π istiflenmesi ile tutunur. Bu strateji modifikasyondan sonra CNT yüzeyinin mekanik, elektronik özelliklerini koruması açısından avantajlıdır.

Polimer zincirlerinin karbon nanotüp yüzeyine kovalent bağlarla bağlanması ise yüzeye doğrudan bağlanma (grafting to) ve yüzeyden dolaylı olarak büyüme (grafting

from) olmak üzere iki başlık altında toplanır. Yüzeye bağlanma yöntemi, önceden hazırlanmış fonksiyonel uç gruba sahip polimer zincirleri ile karbon nanotüp yüzeyindeki uygun fonksiyonel gruplar arasında gerçekleşen tepkimelerle yüzeyin fonksiyonlandırılmasıdır. Diğer yöntem ise gerekli başlatıcı fonksiyonlitesi karbon nanotüplerin yüzeyine kazandırılıp çeşitli monomerlerin yüzeyden büyüterek polimerleşmeleri ile sağlanır.

Bu çalışmada tek duvarlı CNT ve çok duvarlı CNT yüzeylerine farklı ‘click’ kimyaları uygulandıktan sonra elde edilen hibrit malzemelerin çeşitli organik çözücülerdeki çözünürlüğünün artması ile kullanım alanının da arttırılması amaçlanmıştır.

Çalışmanın ilk iki kısmında kovalent yaklaşım ile karbon nanotüp duvarlarının modifikasyonuna odaklanılmıştır. Karbon nanotüplerin duvarları yeşil kimya uygulamaları açısından önemli yere sahip olan tepkimeler kullanılarak modifiye edilmiştir. Doğrudan kovalent modifikasyon için Diels-Alder ve [2+1] nitren siklokatılma tepkimeleri ile birlikte tiyol-en tepkimesi gibi metal ligand kompleksleri olmadan gerçekleşen kimyalar kullanılmıştır. Dolaylı kovalent modifikasyon için ise aktif ester reaksiyonları tercih edilmiştir. Bu kimyaların nitren katılması - tiyol-en click reaksiyonu, Diels-Alder siklokatılma - tiyol-en click reaksiyonu, nitren katılması - Diels-Alder siklokatılma ve aktif ester reaksiyonları - nitren katılması gibi çiftli kombinasyonları karbon nanotüplerin modifikasyonu için tercih edilmiştir.

Diels-Alder (DA) tepkimesi bir dienofil ve konjuge bir dien (4π elektron sistemi) arasındadır. Diels-Alder tepkimelerinde dienofildeki elektron çekici ve diendeki elektron verici grupların varlığı tepkimeyi hızlandırır. Ayrıca sıcaklık, basınç veya Lewis asitlerinin kullanımı da tepkimeyi hızlandırır. Diels-Alder [4+2] siklo katılma tepkimesi önceden dikkatlice seçilmiş uygun uç gruba sahip polimer ile karbon nanotüp, fulleren veya grafen yüzeyine aşılanabilir.

Azid fonksiyonuna sahip moleküller yıllar geçtikçe artan bir şekilde kimya, biyoloji ve malzeme biliminde kullanım alanı bulmuşlardır. Azid içeren bileşiklerden yola çıkarak nitren ara ürünü termal, fotokimyasal ya da bazı metal katalizörler kullanılarak elde edilebilir. Nitrenler, karbenlere benzetilir fakat farklı özelliklere sahiptirler. Azidlerin kovalent bozunması sonucu N_2 molekülü eliminasyonu ile elde edilirler. Termal veya fotokimyasal olarak üretilen nitrenlerin alkenler ile moleküller arası siklo katılmasında aziridinler elde edilir. Termoliz ile bir azido grubu singlet hal nitren (iki dolu p-orbitalli) ve triplet hal nitren (bir dolu p-orbitali ve eşleşmemiş elektronları içeren iki p-orbitali) olmak üzere iki tip reaktif ara ürünü meydana getirebilir. Her iki tip nitren de karbon nanotüpün konveks yüzeyinde elektrofilik [2+1] siklo katılmasıyla aziridin halkası oluşturabilir.

Son yıllarda, tiyol bazlı moleküllerin elektronca zengin veya fakir karbon-karbon bağına serbest radikal katılması ile gerçekleşen tepkimeler tiyol-en tepkimesi olarak anılmaktadır. Tiyol-en kimyası bazı kaynaklarda yeni bir ‘click’ tepkimesi olarak anılmakta ve üstün performans ile biyokonjuge polimerler, polimerlerin ve yüzeylerin modifikasyonu, yıldız polimerleri ve dendrimerlerin sentezinde kullanılmaya başlanmıştır. Tiyol-en tepkimeleri termal veya fotokimyasal olarak ılımlı sıcaklıklarda oksijen varlığında sülfenil radikal kenetlenmesi gibi yan ürün oluşturmada gerçekleşir. Bu tepkimenin en önemli avantajı ise çevre dostu, yeşil kimyaya uygun, oksijen veya neme duyarlı olmadan, tek bir regioselektif ürün veren, çözücüsüz veya çözücü ortamında gerçekleşmesi ve potansiyel toksik metaller kullanılmadan oluşturulan tepkime koşullarına sahip olmasıdır.

Aktif ester reaksiyonlarına, peptit sentezinde ve organik kimyada sıklıkla başvurulmaktadır. Peptit bağı oluşumu için katı ile sıvı fazda da gerçekleşmesi ve ılımlı reaksiyon ortamı oluşturmaya açısından yöntem avantaj sağlamaktadır. Literatürde çok sayıda aktif ester örneklerine rastlanmakla birlikte bunların arasından perflorofenil esteri dikkat çekmektedir.

Tezin ilk bölümünde, CNT'ler ile furan, maleimid, antrasen ve azid gibi fonksiyonel gruplara sahip küçük moleküller arasındaki Diels-Alder ve nitrene siklokatılma tepkimelerinin etkinliğini değerlendirmek için dört model reaksiyon gerçekleştirilmiştir. Model reaksiyonlardan elde edilen olumlu sonuçlar çalışmayı bir sonraki adım olan karbon nanotüplerin uygun fonksiyonel gruba sahip polimerlerle tekli modifikasyonuna taşımıştır. Bu amaçla ilk olarak maleimid, antrasen, furan, azid ve tiyol uç gruba sahip polimerler (PMMA, PBA, PS, PEG vb.) sentezlenmiş, karakterizasyonları NMR, FT-IR ve GPC ölçümleri ile desteklenmiştir. Bu polimerle tek duvarlı, çok duvarlı ve ticari olarak temin edilmiş çok duvarlı asit fonksiyonuna sahip karbon nanotüplerle tekli Diels-Alder, nitren veya tiyol-en reaksiyonları gerçekleştirilmiştir. Deneylerden elde edilen sonuçlar doğrultusunda tekli modifikasyonlarından olumlu sonuç alınan tekli modifiye olmuş karbon nanotüplere ikinci modifikasyon olarak uygun fonksiyonel gruba sahip polimerlerle uygulanmıştır. Sıralı çift modifikasyona ek olarak modifiye olmamış karbon nanotüplere one-pot fakat sıralı olarak uygulanmıştır. Bu amaçla karbon nanotüplerin sıralı çift modifikasyonu için nitren katılması - tiyol-en click reaksiyonu, Diels-Alder siklokatılma - tiyol-en click reaksiyonu, nitren katılması - Diels-Alder siklokatılma reaksiyonları ve one-pot fakat sıralı modifikasyon için ise nitren katılması - Diels-Alder siklokatılma, tiyol-en click reaksiyonu - nitren katılması ile Diels-Alder siklokatılma - nitren katılması gibi çiftli kombinasyonları tercih edilmiştir. Her iki yaklaşımın sonucunda elde edilen karbon nanotüplerin termal gravimetrik analiz sonuçları, karbon nanotüplerin bu yaklaşımlarla fonksiyonlandırılabilirliğini başarı ile göstermiştir.

Tezin ikinci bölümünde ise çok duvarlı karbon nanotüpün duvarlarına ilk olarak aktif ester katılmasıyla amin sonlu PEG ve daha sonra nitren katılma reaksiyonu ile azid sonlu PS polimerlerinin aşılınması hedeflenmiştir. Deneylere ilk olarak ticari olarak temin edilmiş çok duvarlı asit fonksiyonuna sahip karbon nanotüplerdeki (MWCNT-COOH) asit fonksiyonu asit klorüre (MWCNT-OC(=O)Cl) dönüştürülür. Bu reaksiyon, uygun reaksiyon sıcaklığında (0 °C'den 60 °C'ye) tiyoni klorür veya oksalil klorür ile katalitik miktarda DMF varlığında gerçekleştirilir. Sonrasında elde edilen MWCNT-OC(=O)Cl pentaflorofenol ile piridin varlığında reaksiyona girerek MWCNT'ün pentaflorofenil esteri (MWCNT-COOC₅F₆) sentezlenir. Aktif ester içeren MWCNT-COOC₅F₆ aminlere karşı çok aktiftir ve MWCNT-COOC₅F₆'nin amin sonlu PEG (PEG-NH₂) ile verdiği tepkime sonucu MWCNT yüzeyinin birinci modifikasyonu gerçekleştirilmiş olur. Daha sonra MWCNT yüzeyinde ikinci kovalent modifikasyonun gerçekleşmesi için bir önceki basamakta elde edilen MWCNT-CONHPEG o-diklorobenzen içerisinde dispers edilir ve yüksek sıcaklıkta (130 °C) PS-N₃ ile nitren katılması vererek çift modifiye edilmiş PS-g-MWCNT-CONHPEG elde edilir.

Tezin son kısmında, CNT yüzeyinin mekanik, elektronik özelliklerinin korunması açısından avantajlı bir metot olan non-kovalent adsorpsiyon etkileşimi ile karbon nanotüplerin yüzeyleri, piren fonksiyonu içeren polimerler vasıtasıyla fonksiyonlandırılır. Non-kovalent stratejide, polinükleer aromatik grup içeren polimerler CNT yüzeyine π - π istiflenmesi ile tutunur. Bu amaçla ilk olarak, asetilen

dikarboksilik asitten elektron eksikliği olan iç alkine sahip beş farklı poliestер (P1-P5) ana iskeleti sentezlendi. Daha sonra ilk olarak, poliestерler piren-1-ilmetil 3-azidopropanoat ile Huisgen tipi 1,3-dipolar bakırsız siklokatılma reaksiyonu vermiştir. Sentezlenen poliestер ana zincirlerinden seçilen bir tanesi (P2) ise piren-azid ile birlikte bir azid fonksiyonuna sahip ikinci bir molekül (2-azidoetanol, 3-azidopropiyonik asit, prop-2-in-1-il 3-azidopropanoat) ile Huisgen tipi 1,3-dipolar bakırsız siklokatılma reaksiyonu vermiştir. Polinükleer aromatik bir bileşik olan piren içeren bu sekiz poliestер karbon nanotüplerin non-kovalent modifikasyonu için polimerik platform olarak kullanılmıştır. 1,3-dipolar siklo-katılma reaksiyonları, 4 saat boyunca 1,4-dioksan kullanılarak 40 °C’de gerçekleştirildi. Polimerlerin karakterizasyonları NMR ve GPC ölçümleri ile desteklenmiştir. Sentezlenen poliestерler MWCNT’ün duvarlarına non-kovalent yaklaşım ile 10 günlük reaksiyon süresi sonunda başarıyla adsorblanmıştır. Elde edilen poliestерlerle fonksiyonlandırılmış MWCNT’lerin karakterizasyonu TGA, UV ve HR-TEM ile gerçekleştirilmiştir.



1. INTRODUCTION

Iijima's finding of multiple walled carbon nanotubes (MWCNTs) in 1991 have enlightened the details of carbon-based materials and have been a milestone for the following researchers [1]. Carbon nanotube-based nanomaterials show great physical and mechanical properties, which make them a primary raw material for various composites in quite a number of fields such as electronics, computers, drug delivery, imaging and hydrogen storage [2]. In addition to these, they can also be used for the removal of pollutants, thanks to their great specific surface area, high hydrophobicity, and diversity of functional groups [3]. Poor solubility and having a tendency to aggregate into bundles are the primary concerns of pristine CNTs [4]. Hence, key aspect to overcome these issues is the functionalization of CNTs. Two main methodologies have been reported, which are formation of covalent bonds and non-covalent interactions (van der Waals forces, π - π stacking interactions) [5-8].

Previous studies indicated that many different modification ways are possible on the surface of carbon nanotubes directly or indirectly. Both direct and indirect functionalization approaches have been examined in the first two sections of this research. Diels-Alder cycloaddition, nitrene addition and thiol-ene reaction as direct modification approaches and parafluoro reaction as indirect modification approach have been the main focus of these two sections and the results obtained from these four approaches will be discussed. The possibility of CNTs for reacting with dienes or dienophiles via Diels-Alder reaction has been argued since 2002, and some publications have approved this experimentally [9]. Diels-Alder [4 + 2] cycloaddition reaction can be applied under moderate conditions to the surface of carbon nanotube, fullerene, or graphene, in the presence of polymer having the suitable end groups [10]. Also Barner-Kowollik and co-workers succeeded in Diels-Alder [4+2] cycloaddition reaction of single-walled carbon nanotubes (SWCNTs) as dienophile with diene end-capped polymers without pre-modification [11]. Zydziak et al. reviewed the literature and reported that CNTs can behave as both diene and dienophile when proper reaction conditions are provided [10-12].

In the literature, several modification examples of carbon-based materials via thiol-ene click chemistry have been issued. For instance, Arsu and co-workers studied on grafting of multiwall carbon nanotubes in the presence of AIBN as thermal initiator with thiol end-functional polystyrene [13]. As reported by Yagci and co-workers in 2012, thiol-ene chemistry was applied to obtain a single modified-C60 product. In the first step of the research, polystyrene polymer carrying a ω -bromine chain-end functionality was obtained by atom-transfer radical polymerization (ATRP) technique and the bromine end group was converted to -SH function. Then, resulted PS-SH polymer was grafted to C60 in favor of the thermal route, since there was less chance of side reaction in the presence of the radical initiator AIBN [14].

In another approach for modification of carbon nanotubes is called “nitrene addition”. Strained alkyl-substituted alkenes and electronically weak/ rich alkenes (such as fullerenes, CNTs) can act as dipolarophile to give aziridines in the presence of organoazides [15]. Nitrene intermediate can be obtained by using thermal, photochemical reactions or in the presence of some metal catalysts. N_2 molecules are evolved by the elimination of covalent decomposition of the azides. Aziridines are obtained by addition of thermally or photochemically produced nitriles to alkenes via intermolecular cycloaddition reaction. Starting from the paper published by Hirsch and co-workers, nitrene addition approach has been introduced into the studies of carbon nanomaterials. In this seminal study, the [2+1] cycloaddition of nitrenes to SWCNTs surface achieved in the presence of 200-fold excess of alkyl azidoformate [16, 17].

The condensation reaction between a carboxylic acid and an amine results in the formation of an amide bond. For this reason, activating the acid accelerates amide bond formation. The carboxylic acid with a leaving group facilitates the formation of the amide bond in the presence of the amine. There are many ways in the literature to convert the acid function into a good leaving group by forming an active ester. Changing acid function into an acyl chloride in the presence of thionyl chloride or oxalyl acid is one of the most preferred methods, but production of HCl as a byproduct can be a drawback for some cases (e.g. biological systems). Therefore, the active ester-amine method is the most preferred method. Following the introduction of strongly electron withdrawing coupling reagents to carbonyl group such as *N*-hydroxysuccinimide or pentafluorophenyl ester, forming a stable amide bond by the reaction between amine and these reagents, becomes easier. Pentafluorophenyl (PFP)

ester strategy was first reported by Kisfaludy et al. for the peptide synthesis and then became popular in polymer science [18-22]. Having a long shelf life, reaction temperatures between 0 °C and ambient temperature, and no byproducts such as urea are the advantages of these of PFP activated esters.

Tunca and co-workers reported novel trifunctional polyurethanes for triple-click strategy combining active ester substitution, CuAAC and Diels-Alder reaction in 2016 [23]. They also showed that pentafluorophenyl ester-functional acyclic diene metathesis polymers could be synthesized and used for post-functionalization [24]. In 2008, Tsumoto et.al synthesized a number of methano[60]fullerene carboxylic acids which are suitable for getting several esters and amides by condensation with alcohols and amines, respectively, using a condensation reagent [25]. In the same year, Theato and co-workers reported MWCNTs which were modified with the active pentafluorophenyl ester to synthesize transparent conductive multilayered film in four steps [26].

Double modification strategy is one of the most preferred strategies for macromolecular architecture. The double modification strategies, which consist of a combination of different click reactions, permit the preparation of polymers in different topologies and the diversification of polymers that can not be achieved using only one type of reaction [27]. However, introducing new functional groups into sidewalls of carbon nanotubes is a challenging matter. Therefore, organic synthesis methods and ‘click reaction’ strategies in polymer science have been started to be applied to this kind of “nano” materials in order to overcome aforementioned solubility problems of carbon nanotubes.

The objective of the first part of the thesis is the application of various dual combinations of the Diels-Alder, nitrene addition and thiol-ene click reactions to perform double modification strategy into the carbon nanotubes (MWCNTs, MWCNT-COOH, SWCNTs) for their surface modification. For this purpose, first of all, well-defined anthracene, maleimide, furan, nitrene and thiol-terminated various polymers were prepared by using several controlled/“living” radical polymerization methods. In addition to these polymers, some small molecules with anthracene, maleimide, furan, and azide functionality were used for modeling reactions. The unique aspect of this study is to obtain double surface modification of MWCNTs with

covalent bonding and “*grafting to*” method sequentially by using reactions, such as Diels–Alder cycloaddition, nitrene addition or thiol-ene reaction.

In the second part of the thesis, polyethylene glycol (PEG) and polystyrene (PS) were used for double modification of carbon nanotubes. PEG is an adequate polymer due to its biocompatibility, low toxicity, and great solubility properties in water and other common solvents. PS is a hydrophobic vinyl polymer having a long hydrocarbon chain with a phenyl group attached to every other carbon atom. Different chemical methods have also been applied to MWCNTs’ surface and different polymers have been chosen in order to diversify the functionalities. Hence, active ester substitution and nitrene addition reactions have been chosen, and their combination was suggested as a new route for double modification of sidewalls of MWCNTs. The present study concerns with the synthesis of amine terminated PEG and azido terminated Styrene polymers for the application of double modification strategy (active ester substitution and nitrene addition) in sequential process.

In the last part of the thesis, five different polyesters (P1-P5) containing electron deficient internal alkyne units that are derived from acetylene dicarboxylic acid in the main backbone, were synthesized. Afterwards, these polyesters gave first Huisgen type 1,3-dipolar copper free cycloaddition reaction with pyrene-1-ylmethyl 3-azidopropanoate. And then, one of the chosen polyester backbone (P2) reacted with a molecule with azide function (2-azidoethanol, 3-azidopropionic acid, prop-2-yn-1-yl 3-azidopropanoate) together with pyrene-1-ylmethyl 3-azidopropanoate which resulted as Huisgen type 1,3-dipolar copper free cycloaddition reaction. The 1,3-dipolar cycloaddition reactions were performed at 40 °C in 1,4-dioxane for 4 hours. Eight polyesters having pyrene which is a polynuclear aromatic compound were used as a polymeric platform for non-covalent modification of carbon nanotubes. Characterization of polymers were supported with the NMR and GPC measurements. Synthesized polyesters were adsorbed into the sidewalls of MWCNTs in 10 days reaction time by non-covalent approach. Characterization of polyester modified MWCNTs were performed with TGA, UV and HR-TEM measurements.

2. SCIENTIFIC BACKGROUND

2.1 Nanomaterials

Nanotechnology can be considered as a field of science that related with the materials which are nanomaterials if one half or the better part of the component particles have at least one external dimension between 1 and 100 nm size ranges or if its volume-specific surface area is above $60 \text{ m}^2\text{cm}^{-3}$. According to this definition, fullerenes, graphene and carbon nanotubes with at least one external dimensions under 1 nm are clearly accepted as nanomaterials (Figure 2.1) [28].

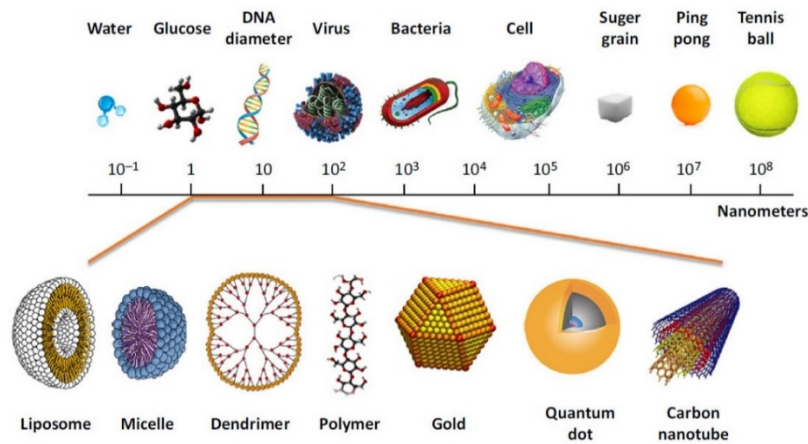


Figure 2.1 : For delivering genetic matter to the cells, non-viral vectors or nanoparticles can be benefited from based on the nanoscale (1-100 nm) [29].

In recent years, the emergence of nanotechnology is rapidly heading to different scientific areas such as aerospace, military, and medicine. Especially, polymer science has a big part in the investigation of nanoscale hybrid materials in almost all technical disciplines. Polymer-based biomaterials, drug delivery with nanoparticles, mini-emulsion particles, and fuel cell electrode polymer bound catalysts, polymer films that self-assembled layer-by-layer, electro spun nanofibers, polymer blends and nanocomposites can be given as more detailed examples for current research areas. In addition to improvements in nanotechnology, new, beneficial and powerful characterization techniques have been developed to investigate composition, size, thickness, crystallinity, crystal phase, defects, oxidation states, and electronic states of nanomaterials developments [30].

For the classification of nanomaterials that can be accepted as a keystone in nanotechnology, not only size but also shape is an important criterion. Shape is an important property to classify nanomaterials in terms of dimension or aspect ratio. Zero dimensional (0D) substances have nanometer magnitude in every directions; one-dimensional (1D) substances (carbon nanotubes, silicon nanowires) have nanometer size in two magnitudes and the length of third magnitude should be larger than nanoscale; two-dimensional (2D) substances (graphene) are thin sheets of materials, and three-dimensional (3D) substances are nanoporous or nanostructured materials (Figure 2.2) [30, 31]. Nanomaterials are also found in single, merged, aggregated structure with spherical, tubular and irregular forms.

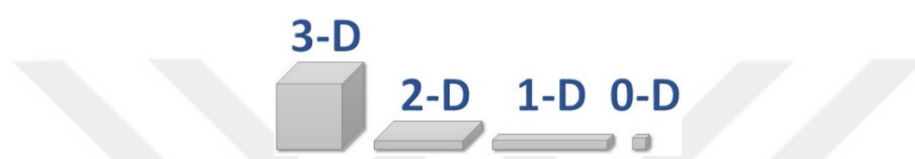


Figure 2.2 : Schematic showing of 0-D, 1-D, 2-D, and 3-D nanomaterials based on their shape.

Individuality of nanomaterials and nanostructured materials is based on their mechanical properties. Shorter bond length gives strength and stiffness to the material. Formation of the possibility of potential defects is reduced due to the restricted size of the units of the material; such as grain boundaries are infrequent in tiny nanoparticles. The strongest bonds which are carbon-carbon bonds in solids are located in in the hexagonal lattice of graphite [31].

2.2 Classification of Carbon-Based Nanomaterials

The most resourceful element in the table of elements is carbon due to its strength and capability of forming more than one bond with other elements. Because of the coordination of electrons around the nucleus of atom, carbon has unique properties. There are three allotropic solid form exist: graphite, diamond and buckminsterfullerene (Figure 2.3) [31].

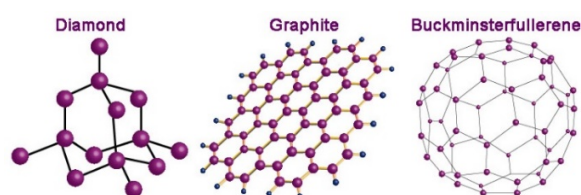


Figure 2.3 : Allotropic forms of carbon.

After 1980s following the finding of molecular carbon allotropes such as fullerenes, CNTs, and 2-D graphene, the members of carbon family has been extended and it was not restricted to graphite and diamond [32].

Each carbon atom in diamond hybridized sp^3 and is bounded to four others in tetrahedral arrangement. Crystalline structure of diamond causes its hardness and excellent heat conduction properties. Layered planer sheets are formed, since to sp^2 hybridized of carbon atoms in graphite bonded in a hexagonal network. Due to the geometry of chemical bonds, graphite gains some properties such as being soft, slippery, opaque, and electrically conductive. A spheroidal or cylindrical structure which is occurred from fully sp^2 hybridized carbon atoms is called fullerene.

2.2.1 Graphene

Almost 500 years, naturally existing graphite has been accepted as a mineral. Graphene, fundamental of graphite, was theoretically risen in 1940. In 1962 thin plates of carbon distinguished via chemical reduction of graphite oxide and heating, but in the beginning of 2004, single-layer graphene was considered as thermodynamically unsteady under atmospheric conditions. In consequence of this discovery, the “thinnest” known material graphene that has good electrical conductivity, mechanical flexibility, optical transparency, thermal conductivity, and low coefficient of thermal expansion (CTE) behavior was introduced to almost all research fields in science [33].

Mechanical lamination of graphite flakes repeatedly using adhesive tape or grown on substrates for electronics applications by chemical vapor deposition or decomposition of carbide phase could be isolation ways to obtain graphene from graphite (Figure 2.4) [34].

Graphene sheets have numerous wide range of properties, which can compete with graphite in terms of their thermal conductivity and mechanical stiffness. Over the last decade, graphene has become popular research interest due to its superior characteristics [35, 36].

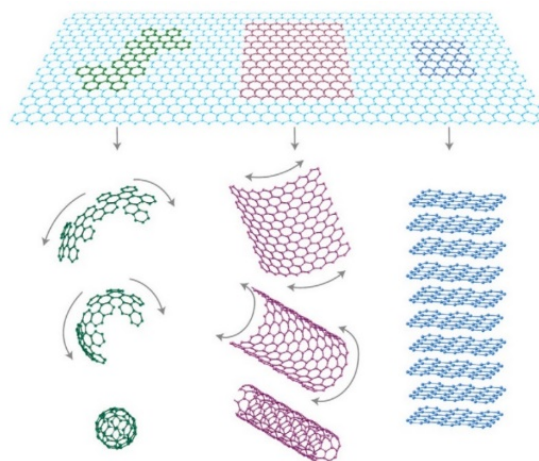


Figure 2.4 : Representation of all forms for graphite [37].

2D graphene is created by one-atom-thick planar sheets, which are formed in the presence of the hexagon lattice with 0.141 nm distance between two sp^2 hybridized carbon atoms. The thickness of graphene have been measured from 0.35 nm to 1.00 nm by different research groups [33].

Graphene nanomaterial family has a few members such as few-layer graphene (FLG), graphene oxide (GO) and reduced graphene oxide (rGO) (Figure 2.5).

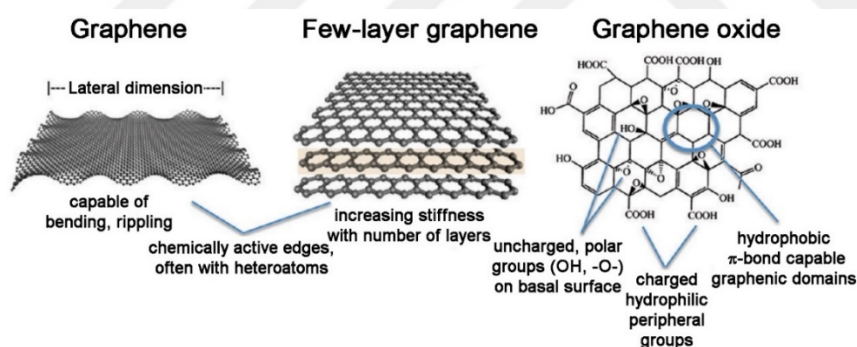


Figure 2.5 : Example members and some properties of the graphene nanomaterial family [34].

Gathering of 2-10 graphene layers together is called few-layer graphene (FLG). During fabrication of monolayer graphene, few-layer graphene comes out as byproduct of the process [34].

Graphene oxide (GO) that is a monolayer form of graphene is produced after applying harsh oxidation conditions to graphene. The periphery structure of GO contains carboxylate groups which gives to GO pH dependent negative surface charge and colloidal stability. Hydrophilicity is provided by the carbonyl and carboxyl groups at the edge of GO. Dispersion of GO sheets in water becomes easier due the presence of

this hydrophilic groups in GO sheets [33]. Uncharged and polar hydroxyl (OH) and epoxide (O) functional groups are located on the basis of GO (Figure 2.6) and hydrophobic, unmodified graphenic surface on basal planes prepare a substructure for π - π interactions adsorption of some drugs or dye molecules [34]

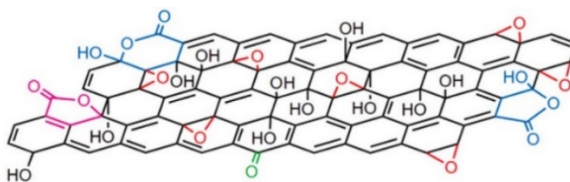


Figure 2.6 : Functional groups on the surface of GO graphitic plates [38].

Reduced graphene oxide (rGO) is the product of treating GO under reducing conditions, like high-temperature thermal treatment and chemical treatments in the presence of hydrazine (N_2H_4) or other reducing agents. Although GO reduction may change some GO properties, reduction process of GO enhances its electrical conductivity and hydrophobicity, reduces oxygen content and water dispersibility [34].

2.2.2 Fullerene

Starting from finding of C_{60} by Kroto et.al. in 1985 and production in gram quantities in 1990, it becomes promising study field in science [39-41].

Fullerenes are convex carbon cages combining hexagons and total 12 pentagons. The curved π -conjugation within hybrid hexagon-pentagon C-C networks provide fullerene unique properties. During last decades, fullerene [60] and its homologues have been an outstanding topic of some researches in terms of their curved π -conjugation and aromaticity related chemistry (Figure 2.7).

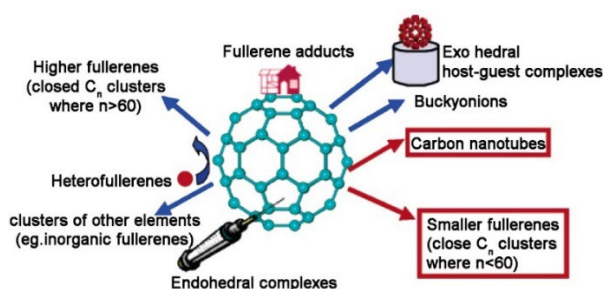


Figure 2.7 : Research areas centered on fullerene C_{60} [41].

Isolation of the most stable fullerene derivatives from the others is easy due to surrounding by five hexagons. Their perfect photochemical, electrochemical, and magnetic properties are still challenging to do research. Apart from these good properties, it is hard to manufacture C_{60} molecules in industry because of the poor

processability. There are some ways to overcome processability problems one of which is grafting of polymers onto C_{60} [14].

Lipid-like systems and Fullerene- C_{60} can be aggregated with ease in order to intersect their cell membranes by means of their spherical structure and powerful nonpolar character [42].

Fullerenes are insoluble however in prevalent organic solvents and water, their solubility increases sparingly. Strong van der Waals binding energy and π - π stacking make difficult to dissolve carbon-based materials such as CNTs, fullerene and graphene in either aqueous or nonaqueous solvents. Consequently, to overcome this chemical functionalizations' problems, various methods are developed [43].

2.2.3 Carbon nanotubes (CNTs)

Iijima's finding about multi walled carbon nanotubes (MWCNTs) in 1991 has enlightened the details carbon based materials and has been a milestone for the following researches [1].

Mechanical, thermal, and electrical measurements were performed on MWCNTs long before SWCNTs, since manufacturing of MWCNTs in large scale is easier and cheaper than SWCNTs. Carbon nanotube based nanomaterials show great physical and mechanical properties, which make them a preferable raw material for various composites in quite a number of fields such as electronics, computers, medical drug delivery, therapy and imaging, and hydrogen storage [2]. Since CNTs show poor solubility and have a tendency to aggregate into bundles, usage of pristine CNTs can be a problem [4]. In addition to these areas of utilization of CNTs, they can be used in removal of pollutants, due to the their great specific surface area, high hydrophobicity, and diversity of functional groups [3].

Carbon nanotubes are one-dimensional materials which differs from other one-dimensional materials. Extended tubes with hemisphere fullerene caps at both ends are formed by rolling-up nano-scaled graphene sheets.[44]. Bonding type is sp^2 for carbon nanotubes. However, the radial bending leads quantum confinement and σ - π rehybridization in which three σ bonds are barely out of plane, the π orbital is more delocalized outside the tube. Consequently, when a comparison has been made between carbon nanotubes and graphite, carbon nanotubes are stronger in terms of mechanical properties, more conductive in electrically and thermally, more active

chemically and biologically [45]. In spite of their unique properties, their small size, challenges during defect-free manufacturing of CNTs and poor quality of several growth methods are still a problematic issue for CNTs. Three fundamental techniques can be counted for production of CNTs: arc discharge, laser ablation, and chemical vapor deposition [46].

In general, CNTs can be classified according to the number of walls: single-walled carbon nanotubes (SWCNTs), and multi-walled carbon nanotubes (MWCNTs). The length of cylinder-shaped SWCNTs can be reach almost 20 cm, although their diameters are almost a nanometer [47]. In addition, there are three types of SWCNTs, which are classified due to their helicity: armchair, zigzag and chiral (Figure 2.8 (a)) [48].

As described in Figure 2.8 (a), SWCNTs can be defines as a single graphene sheet rolled into a cylinder, while MWCNTs consist of more than two concentric cylindrical shells of graphene sheets coaxially arranged leading to a central hollow core through van der Waals forces between adjacent layers. CNTs, with two concentric cylinders is a special case of MWCNTs, which is stated as double-walled carbon nanotubes (DWCNTs).

Changes on the surface of SWCNTs, which can be happened due to the chemical functionalization, affect the mechanical and electrochemical properties of it, while those changes happened only outer layer of DWCNTs and MWCNTs. Therefore, inner layer of DWCNTs and MWCNTs protects their mechanical and electrochemical properties (Table 2.1) [49].

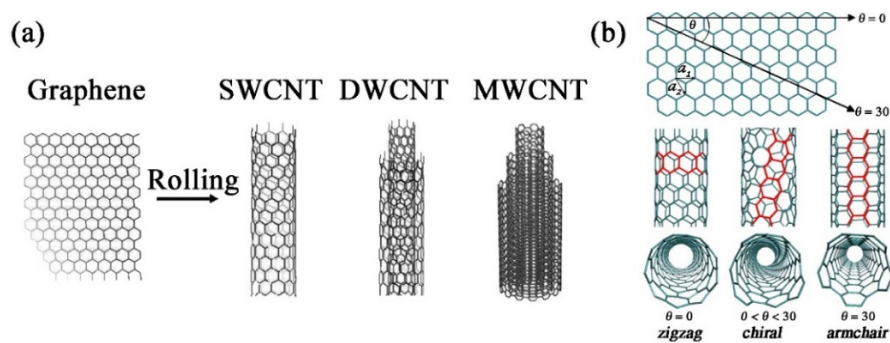


Figure 2.8 : (a) CNTs types based on number of walls [50]. (b) Definition of the roll-up vector as linear combinations of base vectors a_1 and a_2 . Zigzag: $\theta = 0$ (n, 0), armchair: $\theta = 30$ (n, n), chiral: $0 < \theta < 30$ (n, m) [51].

Table 2.1 : Differences between SWCNTs, DWCNTs and MWCNTs [52].

Property	SWCNTs	DWCNTs	MWCNTs
Tensile Strength (GPa)	50 – 500	23 – 63	10 – 60
Elastic Modulus (TPa)	~ 1	–	0.3 – 1
Elongation At Break (%)	5.8	28	–
Density (g/cm ³)	1.3 – 1.5	1.5	1.8 – 2.0
Electric Conductivity (S/m)		~ 10 ⁶	
Thermal Stability		> 700 °C (in air)	
Typical Diameter	1 nm	~ 5 nm	~ 20 nm
Specific Surface Area		10 – 20 m ² /g	

As shown in Figure 2.8 (b), according to the different rolling angle of the graphene sheet, which is called helicity, the chirality of CNTs has a noteworthy impact on their transport properties and the electrical conductivity. The simplest morphology is pertained to SWCNTs due to their the orientation of the tube axis with respect to the hexagonal lattice, the structure of a nanotube can be simply defined through its chiral vector, which is defined by the chiral indices (n, m) [47]. The chiralities of each nanotube are various in MWCNTs, so it is difficult to predict the physical properties of them. The helicity of carbon nanotubes is stated by chiral vector C_h in terms of a set of two integers (n, m) and chiral angle (θ).

$$C_h = n \cdot a_1 + m \cdot a_2 \quad (2.1)$$

Differences in chiral angles of carbon nanotubes divided into three group: armchair ($n = m$, $\theta = 30^\circ$), zig-zag ($m = 0$, $n > 0$, $\theta = 0^\circ$), and chiral ($0 < |m| < n$, $0 < \theta < 30^\circ$). Electronic properties of carbon nanotubes are directly affected by differences in chiral angle. For example, armchair structures have metallic, zig-zag and chiral structures have semi-metallic or quasi-metallic properties [45].

Another important parameter for carbon nanotubes is called specific surface area (SSA). SSA is parameter used in material science for powders or porous materials to determine their gas adsorption mostly N_2 at 77 K based on the Brunauer–Emmett–Teller (BET) isotherm. Due to this calculation, MWCNTs are accepted as mesoporous (pore size 2 to 50 nm) and SWCNTs are microporous (up to 2 nm) [53]. Surface area properties of CNTs can be influenced by tube diameter, bundling, agglomeration, surface functionalization, type of the production and number of walls. In particular, surface area has better correlation with such receptor moieties for biosensing applications than other parameters [53, 54].

Dispersion of CNTs in organic solvents or water is a challenging area for research due to their high tendency to agglomerate. However, it is possible to improve solubility of CNTs by using chemical or physical modification approaches. Functionalization gives carbon nanotubes to vary their properties and possible uses [55].

Some techniques has been developed to enhance dispersion of CNTs in organic solvents or water such as ultrasonication, calendaring process, ball milling, mechanical stirring and extrusion [56]. Simply, loading a mechanical energy or specific force onto the system separate the individual tubes from the agglomerates of CNTs. Ultrasonication is the most frequently referred method for enhancing dispersion of CNTs in low viscosity solvents. If the sonication process is excessive and/or too long, CNTs can be impaired.

2.3 Surface Modification Techniques For Carbon Nanotubes

As mentioned before, CNTs have numerous applications such as new composites, electronics, sensors, actuators, field emission and energy storage devices, drug delivery vehicles, as well as tools for high-resolution and biomedical imaging [57]. Insolubility of carbon nanotubes is always an obstacle for all these applications, so functionalization of carbon nanotubes' surface is a key point to improve usage of them. Even though there are many methodologies to functionalize carbon nanotubes' surface, these methods may be divided into two main sub-groups as covalent and non-covalent functionalization. Both have advantages and drawbacks based on the place that it will be used.

In non-covalent functionalization, the molecules are adsorbed by the polyaromatic surface with the effect of van Der Waals, π - π stacking, electrostatic forces or hydrophobic forces, while more strong unity has been afforded via functional groups in covalent functionalization.

When carbon nanotubes noncovalently functionalized, their affinity for aggregation and formation of bundles due to strong intermolecular interactions between surfaces of carbon nanotubes such as van der Waals forces, dipole-dipole interactions is unavoidable. Undesirable aggregation of carbon nanotubes leads to change in their physiochemical properties such as mechanical and electrical properties, and reduce the aspect ratio. Therefore, covalent functionalization can be preferred in terms of to insert

functional groups (hydroxyl, epoxy, and carboxylic groups) into the surface of nanotubes directly (Figure 2.9) [58].

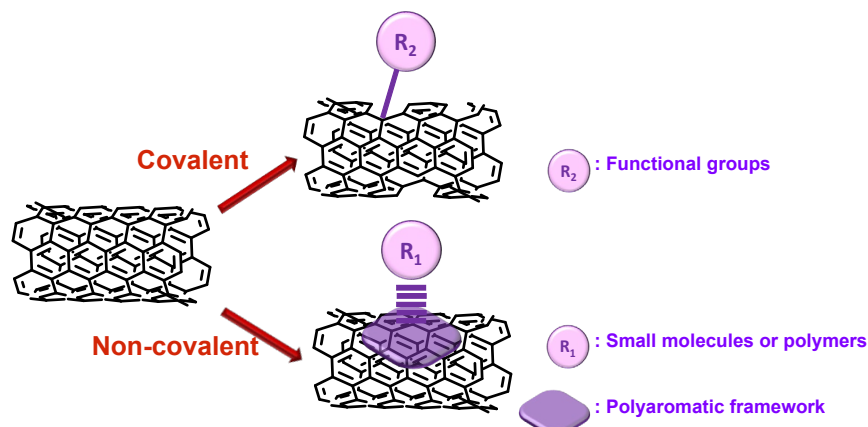


Figure 2.9 : General representation of CNTs functionalization methods [59].

There are some methods which are applied at the end of the CNTs modification process (non-covalently or covalently) to remove unbounded or unreacted structures like polymer or organic molecules. These methods are listed as dialysis, filtration/washing cycle and centrifugation/decantation [59]. The most preferred technique for removing unbounded structures is filtration/washing process, which is shown as schematic illustration in Figure 2.10.

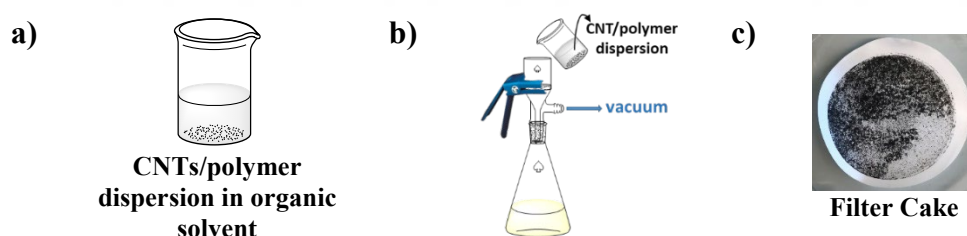


Figure 2.10 : Schematic illustrations of the filtration process in three steps.

2.3.1 Non-covalent attachments

When it is desired to modify the surface of carbon nanotubes, it is very important to maintain properties such as structural and electrical. While covalent modifications alter nanotube sidewalls and give damage to sp^2 graphene lattice of carbon nanotube, noncovalent modifications are more preferred as they retain all properties of the nanotubes. In addition, noncovalent modification procedures are often easy and fast. Modification can be achieved by mixing at room temperature or short-time sonication processes and purified by simple processes such as centrifugation and filtration.

Since the sidewalls of carbon nanotubes are composed of sp^2 carbon honeycomb lattice, they can be interacted with π -conjugated structures. Thereafter, the idea of

dispersing carbon nanotubes in organic or aqueous media has emerged by using aromatic molecules, which are regarded as π -conjugated systems. Modification via π - π stacking or hydrophobic interactions, also known as supramolecular interaction, do not affect the quantum efficiency and their electronic properties adversely because they do not cause defects in the carbon nanotube walls and do not distort the conjugate system in the nanotube walls [60].

For this purpose between carbon nanotubes and aromatic compounds, polycyclic derivatives like coronene [61], phenanthrene [62], anthracene [63, 64], pyrene [8, 65-67], various biological molecules like flavin [68, 69] and porphyrin [70] were able to create nanohybrid materials through supramolecular interactions. Structures of polyaromatic compounds are shown in Figure 2.11.

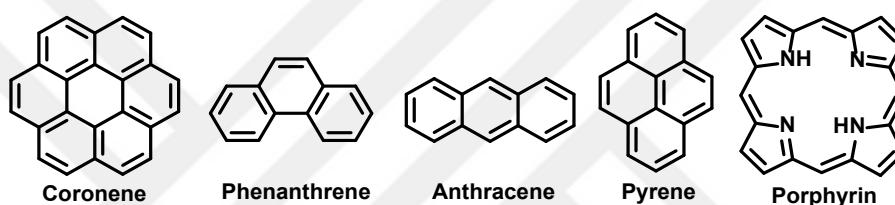


Figure 2.11 : Structures of polyaromatic compounds that used in noncovalent functionalization of carbon nanotubes.

It is seen from the studies about non-covalent attachment that the most preferred polynuclear aromatic moiety is pyrene. In 2002, Naotoshi et al. introduced a new perspective on the functionalization of nanotubes. In the literature, SWCNTs dispersed in water by sonication in the presence of pyrene-carrying ammonium ion and sidewalls of SWCNTs were modified by non-covalent interaction (Figure 2.12 (a)) [71]. Gorur et al. first published decoration of carbon nanotubes with star polymers containing pyrene moiety in 2011. In the study, MWCNTs were modified with hexa-armed and pyrene end-capped ϵ -caprolactone star polymer noncovalently linked [72]. In 2012, Durmaz et al. reported pyrene bearing amphiphilic miktoarm star polymer for π - π stacking to the surface of MWCNTs (Figure 2.12 (b)). Then, dispersion stability of MWCNTs/ pyrene-PS-PEG-PMMA was investigated in common organic solvents [8].

A carbon-stabilizing agent, flavin mononucleotide (FMN), was used to wrap with helically manner carbon nanotube surface by choosing vibrational ball milling process by Kim et al. Isoalloxazine unit inside FMN interacted with MWCNTs surface via π -

π stacking (Figure 2.12 (c)). Due to the modification, thermal stability of MWCNTs is improved [69]

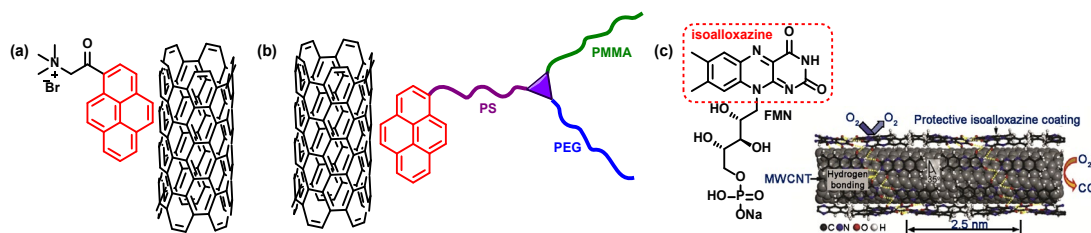


Figure 2.12 : **a)** First example of modification of SWCNTs' sidewalls with pyrene carrying structure [71] **b)** modification of MWCNTs with pyrene bearing amphiphilic miktoarm star polymer [8] **c)** helically wrapping, non-covalent interactions between MWCNTs and FMN [69].

Since carbon nanotubes are nano-scaled structures, scientists wondered anticancer effects of the combination of anticancer drugs with carbon nanotubes. Some of the antineoplastic drugs that used for this purpose are doxorubicin [73-77], methotrexate [78, 79], taxanes (taxoid [80] and paclitaxel [81]), 10-hydroxycamptothecin (HCPT) [82], and platinum analogues [83, 84].

Although doxorubicin (DOX, Figure 2.13 (a)) is known as an anthracycline class of chemotherapeutic agent with the drawbacks such as systemic toxicity and drug resistance, scientists still use DOX for the handling of human cancer like aggressive non-Hodgkins lymphoma. Dai and coworkers introduced a chemotherapeutic product with some therapeutic advantages such as extended circulation in the blood, enhanced tumor drug uptake, and increased therapeutic effectiveness. This formulation was containing carbon nanotube to carry chosen chemotherapeutic drug (DOX). And, DOX was loaded to sidewalls of nanotube via supramolecular π - π stacking approach (Figure 2.13 (b)) [73]. CNTs can be covalently or non-covalently linked with drugs containing aromatic moiety. Mostly non-covalent attachments would preferred to protect properties of CNTs. Therefore, DOX is loaded through hydrophobic interactions into the sidewalls of CNTs [74]. Adam and coworkers choose non-covalent approach to take advantage of large surface area of MWCNTs and high drug loading capacity. Firstly, oxidation of MWCNTs carried out in the presence of concentrated HNO_3 . Then, oxidized MWCNTs (*o*-MWCNTs) covalently modified with chosen peptide (SMSIARL), following that DOX non-covalently linked to the material [85]. Heister et al. successfully accomplished modification of SWCNTs with three different agents by combining non-covalent and covalent approach. DOX

attached to the surface of CNTs via non-covalent approach for the following cellular uptake process. Fluorescein which is used as a marker for SWCNTs and carcinoembryonic antigen antibodies were bonded to sidewalls of nanotubes via covalent attachment (Figure 2.13 (c)) [86].

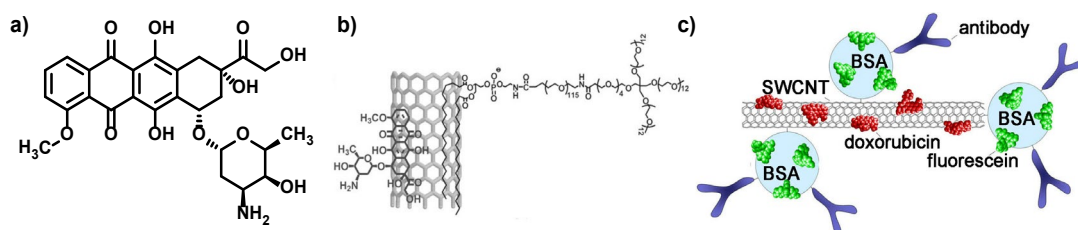


Figure 2.13 : a) Structure of doxorubicin, schematic representation the b) SWCNTs–DOX complex and, c) DOX–fluorescein–BSA–antibody–SWCNTs complex.

During non-covalent modification of nanotube, not only polymers or small molecules but also surfactants are used. Whereas polymers wrap sides of carbon nanotube via π - π , CH- π , NH- π etc., surfactants mostly interact via hydrophobic interactions. When polymers have multiple interaction centers such as pyrene, porphyrin etc., they easily wrap nanotubes by non-covalent modification [59].

2.3.2 Covalent attachments

It is good to start giving a definition of what is covalent functionalization with carbon nanotubes. Covalent functionalization is the modification that occurs when the chemical group is covalently bonded to the cylindrical carbon nanotube surface. In this case, at least one pair of electrons is shared between the carbon nanotube and the present chemical group. In covalent functionalization of carbon nanotubes, it is also important to consider increasing the solubility, processability and reactivity of nanotubes in organic solvents while overcoming the problem of agglomeration. As a result, the physicochemical properties of carbon nanotubes can be tailored to the desired application areas such as nanotube-based composites or hybrid systems.

Two parts of CNTs can be functionalized covalently one of which is structural defects through the sidewalls or tips of nanotubes and the second one is double bonds through the whole nanotube arrangement. The meaning of “defect sides” is disorders or malformations within the fused benzene motif along the sidewalls of carbon nanotube (Figure 2.14). For covalent modification, defect sides can be useful in terms of change in reactivity in the presence of five- and seven-membered rings different from typical

two six-membered rings and the rehybridization of carbon atoms from sp^2 to sp^3 . Another reason for the formation of defects is methods applied to CNTs to remove metal impurities. When CNTs are heated or sonicated with strong acids (HNO_3 or H_2SO_4), different functional groups exist in the nanotube backbone. Carboxyl, carbonyl, and hydroxyl groups can be given as examples of these groups [87].

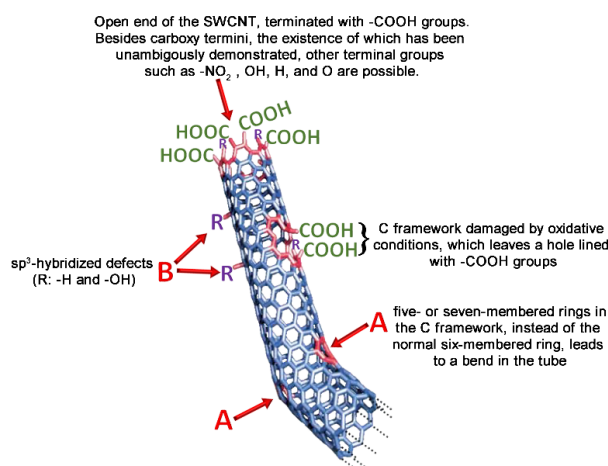


Figure 2.14 : Representation of typical defects in a SWCNTs [6].

Another approach for direct functionalization is done between species containing functional groups and highly reactive sidewalls of CNTs. This method is more challenging compared to the defect-based approach because of the rehybridization of from the sp^2 carbon atoms into sp^3 configuration [87]. Cycloadditions and electrophilic or nucleophilic attacks along sidewalls of nanotube can be given as example for direct covalent modification approach.

Considering all these information, many different modification ways are possible on the surface of carbon nanotubes directly or indirectly. Here, the most preferred cycloaddition reactions (Diels-Alder and nitrene addition) and thiol-ene reaction for direct functionalization approach, and parafluoro addition reaction for indirect functionalization approach will be discussed briefly.

2.3.2.1 Cycloaddition reactions

Cycloaddition reactions are comparatively plain and simple in terms of no need for additional reagents such as catalysts or expensive processes. Cycloaddition reactions take place when two unsaturated moieties yielded a cyclic product in an atom efficiently way. These cycloaddition reactions can be explained by considering that movement of electrons proceeds from the highest occupied molecular orbital (HOMO)

of one molecule to the lowest unoccupied molecular orbital (LUMO) of the other molecule based on frontier orbital (FO) theory.

The most commonly studied cycloaddition reactions with carbon nanotubes are $[2 + 1]$, $[2 + 2]$, $[2 + 3]$ and $[4 + 2]$ cycloadditions. Some of selected cycloaddition reactions applied to carbon nanotube surface directly is shown in Figure 2.15. Here, the cycloaddition reactions will be summarized as nitrene $[2 + 1]$ and Diels-Alder $[4 + 2]$ cycloaddition. These direct reactions are generally used to introduce functional groups or polymers on the surface of CNTs [88]

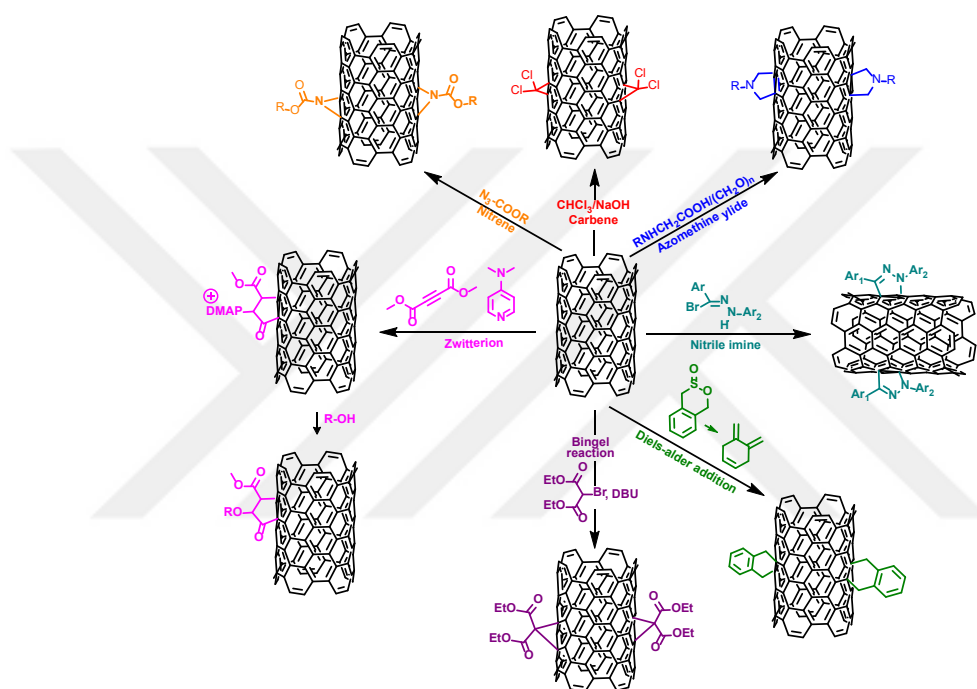


Figure 2.15 : Modification of carbon nanotubes by various cycloaddition reactions [89].

2.3.2.2 Diels-Alder reaction

The Diels–Alder (DA) cycloaddition reaction remains one of the most significant reactions in organic chemistry due to the $[4+2]$ cycloaddition formation between a dienophile and a conjugated diene (4 π electron system). At the end of the reaction, two σ and one new π bond are formed. Since the σ bonds are generally stronger than the π bonds, the reaction is supported in terms of energy. In Diels-Alder reactions, the presence of electron withdrawing groups on the dienophile and electron donor groups on the dienes accelerate the reaction. In addition, the use of temperature, pressure or Lewis acids accelerates the reaction.

It is known fact that spherical geometry and trigonal carbon atoms with a high bond strain of fullerenes can easily change into tetrahedral carbon atoms to give Diels-Alder cycloaddition reaction [90]. In addition, C60 performs as a dienophilic olefin during Diels-Alder reactions, due to its comparatively low-lying LUMO properties. The possibility of CNTs for reacting with dienes or dienophiles via Diels-Alder reaction has been argued since 2002, and some studies approved this experimentally [9]. Sidewalls of SWCNTs have a relatively lower degree of curvature, and their bond strain in the trigonal carbon atoms become lower than fullerene. Because of this, CNTs are less responsive for direct functionalization reactions than fullerenes, because CNTs do not have strongly curved regions. However, it has been proposed that cycloaddition may still occur on the regions of the CNTs that are more highly strained, such as tube bends or defect sites [90].

Baskaran and co-workers published a paper in which they described modification of MWCNTs via Diels-Alder reaction by using MWCNTs as a dienophile and benzocyclobutenes derivatives as diene [9] (Figure 2.16).

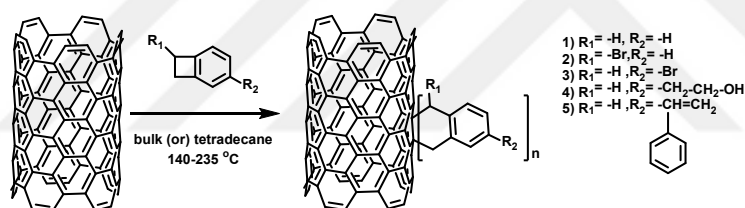


Figure 2.16 : Diels-Alder reaction between benzocyclobutene and MWCNTs.

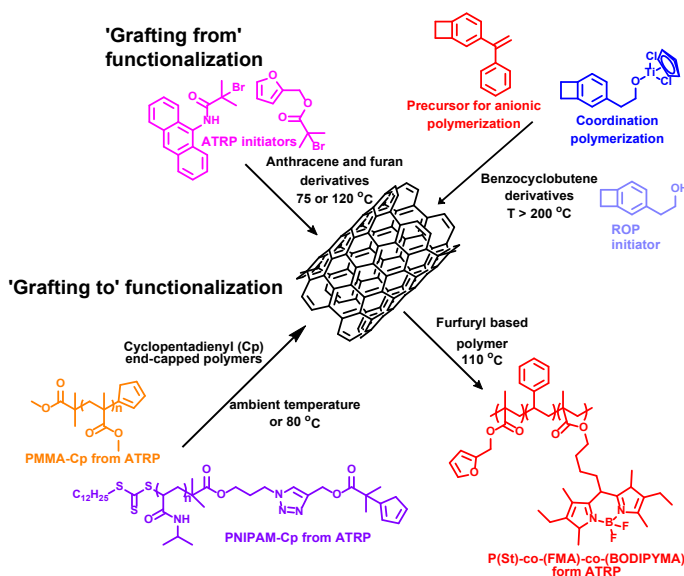


Figure 2.17 : Modification of CNTs via Diels-Alder cycloaddition reaction in the presence polymers performed via ‘grafting from’ and ‘grafting to’ methodologies [12].

In many review articles, methods for chemically functionalizing of carbon-based nanomaterials such as oxidation, fluorination, free radical incorporation, 1,3 cycloaddition, Bingel reaction are often atmospheric-sensitive (air, moisture) and require several synthetic steps before functionalization. However, Diels-Alder [4 + 2] cycloaddition reaction can be applied under moderate conditions to the surface of carbon nanotubes, fullerene, or graphene, in the presence of polymer having suitable end groups (Figure 2.17). Actions of CNTs as dienes or dienophiles have been of great interest for researchers since 2002 [10, 11]. Also Barner-Kowollik and co-workers succeeded in Diels-Alder [4+2] cycloaddition reaction of single-walled carbon nanotubes (SWCNTs) as dienophile with diene end-capped polymers without pre-modification [11]. Zydziak et al. reviewed the literature and reported that CNTs can behave as both diene [11] and dienophile [91] when proper reaction conditions are provided [12]. Figure 2.18 (a) and Figure 2.18 (b) provide the experimental data on these reaction conditions.

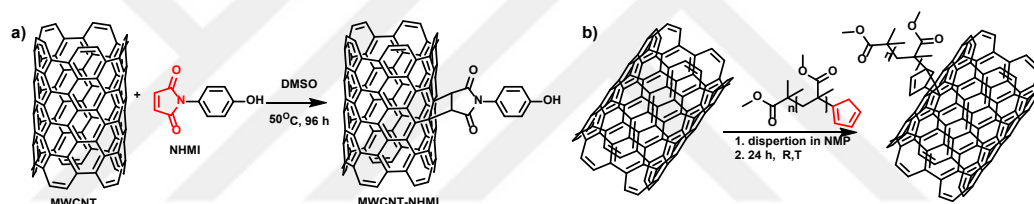


Figure 2.18 : Functionalization of **a)** MWCNTs with N-(4-hydroxyphenyl) maleimide [91] and **b)** SWCNTs with cyclopentadienyl end-capped PMMA[11] through Diels-Alder reaction.

2.3.2.3 Nitrene addition reaction

Molecules with azide function, starting with discovery of organic azides by Peter Griess in 1864, have been increasingly used for years in chemistry, biology and materials science [92]. Nitrene intermediate can be obtained by using thermal, photochemical or in the presence of some metal catalysts. N_2 molecules are obtained by the elimination of covalent decomposition of the azides. Aziridines are obtained by addition of thermally or photochemically produced nitriles to alkenes via intermolecular cycloaddition reaction. However, the statement of “nitrene addition” may not be the proper term, since addition of organic azides to alkenes is not a direct addition reaction. The mechanism of aziridine formation is divided into two steps following as formation of triazoline adduct and aziridine [93]. Figure 2.19 below illustrates the mechanism of aziridine formation/nitrene addition. In the proper reaction conditions, strained alkyl-

substituted alkenes and electronically weak/ rich alkenes (such as fullerenes, CNTs) can act as dipolarophile to give aziridines in the presence of organoazides [15].

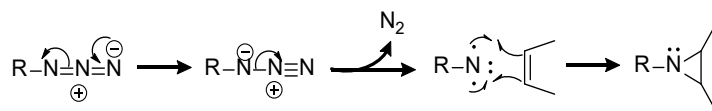


Figure 2.19 : The mechanism of nitrene addition steps.

Depending on nature of organic azide molecule, it can decompose between 25° C to 200 °C. It should be noted that some azides, such as *o*-substitute aryl azides, do not form nitrene thermally due to the releasing nitrogen from their substituents. Moreover, nitrene intermediates can not be formed from acyl and aroyl azides because of the Curtius rearrangement, they reorder instinctively to isocyanates with the elimination of nitrogen [94]. Molecules having not only azide but also second function such as -OH, -NH₂, -COOH, -Br are more favorable to modify of carbon nanomaterial via nitrene addition. The reason for this is while azides with second functional groups (*f*-azides) are bonding into the surface of carbon nanomaterials (carbon nanotubes, fullerenes, graphene), other functional group make carbon nanomaterial more soluble in the organic solvent [95].

Hirsch and co-workers first demonstrated this type of cycloaddition experimentally in 2001. In their seminal study, the [2+1] cycloaddition of nitrenes to SWCNTs surface achieved in the presence of 200-fold excess of alkyl azidoformate [16, 17] (Figure 2.20).

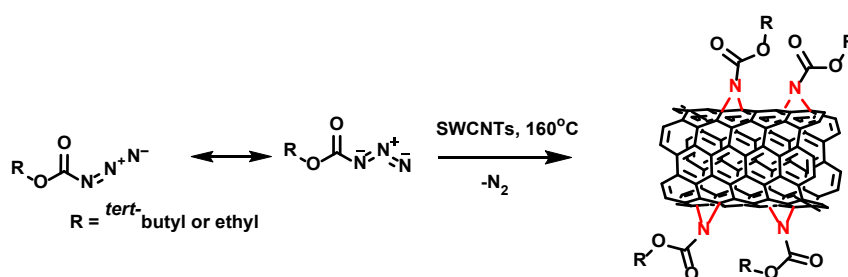


Figure 2.20 : Sidewall functionalization by [2+1] cycloaddition of nitrenes [16].

Two type of reactive intermediates that are singlet state nitrene (two loaded p-orbital) and triplet state nitrene (one loaded p-orbital and two unpaired electron) can take place during thermolysis of azide. Both types of nitrene can form the aziridine ring by the electrophilic [2 + 1] cycloaddition on the convex surface of the carbon nanotube. By way of illustration, Kar et. al. and Yilmaz et. al. showed how azide end-capped

polystyrene fused into the surface of SWCNTs and fullerene respectively (Figure 2.21) [96, 97].

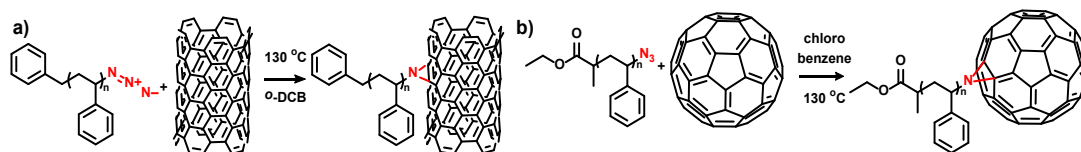


Figure 2.21 : Modification of SWCNTs with different azide end-capped PS.

In addition, Fréchet and coworkers accomplished an easy method for the surface modification of carbon nanotubes with perfluoroarylazides in 2008 (Figure 2.22). Particularly, perfluoroarylazide was chosen as a nitrene precursor owing to its high intermolecular insertion efficiency relative to other aryl- or alkylazides [98].

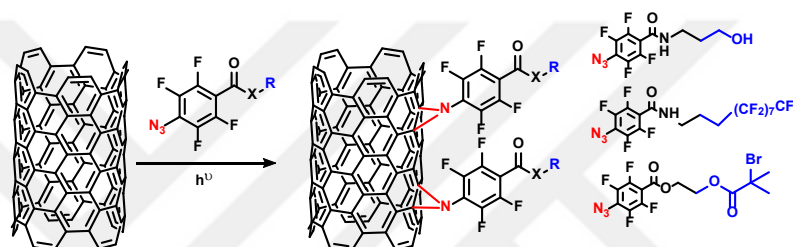


Figure 2.22 : Functionalization of CNTs forests by perfluoroazides via [2+1] cycloaddition [98].

Several advantages for nitrene addition are listed below as:

1. Materials with azide can be synthesized easily and under moderate conditions.
2. Since only nitrogen gas is released during the reaction, the reaction process is accepted as eco-friendly and suitable for green chemistry
3. Reaction conditions do not cause severe damage to the surface of carbon nanomaterials.
4. As a result of one reaction, various functional groups (-OH, -NH₂, -COOH, -Br) are grafted onto the carbon nanomaterial surface.
5. The reaction can take place both thermally and photochemically [99].

2.3.2.4 Thiol-ene click chemistry

Thiol-ene reactions have been established as an important alternative to CuAAC since the thiol-ene reactions do not require any toxic metals and explosive azides [100]. This provides a huge advantage over CuAAC. Besides, thiol-ene reactions are tolerant to oxygen and water [101]. Thiols can react with several reaction partners (Figure 2.23).

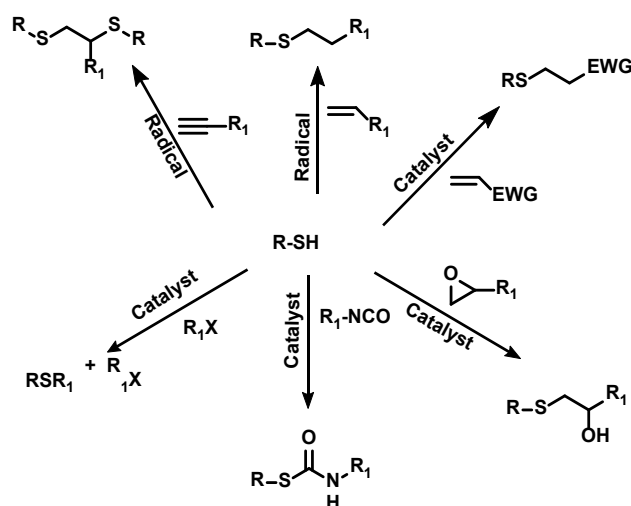


Figure 2.23 : Efficient and different thiol reactions. EWG: electron withdrawing group. X = Br, I and R₁ = aliphatic or aromatic organic groups.

One of the most attractive aspects of thiol-ene radical reactions is the high conversion rate and almost complete conversion of addition of thiol to an alkene is obtained in short reaction times [102]. Thiol-ene radical reaction proceeds via chain process: initiation, propagation and termination [103] (Figure 2.24).

Initiation can take place in two ways, either photochemically or thermally [104] (Figure 2.25). However, photo-induced initiation is most often used [105]. In both procedures, radical initiators are applied to promote the cleavage reaction. Yagci and co-workers have studied the different radical initiators and concluded that 2,2-dimethoxy-2-phenylacetophenon (DMPA) is by far the most efficient [106]. The thermal initiation proceeds via the addition of azobis(isobutyronitrile) (AIBN).

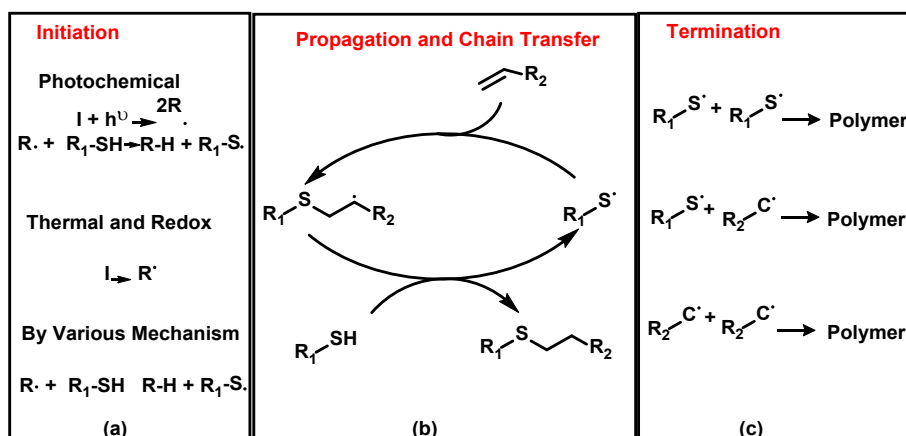


Figure 2.24 : Radical thiol-ene reaction mechanism; initiation, propagation, chain transfer and termination processes [107].

In both initiation procedures, the cleavage of the initiator yields an alkyl radical, which attacks on thiol and cleaves the hydrogen yielding thiyl radical.

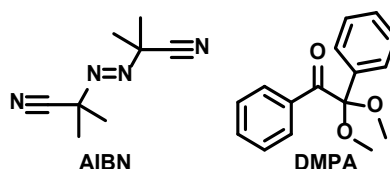


Figure 2.25 : Structure of radical thermal initiator AIBN and photo-initiator DMPA.

Propagation involves two steps. First, the generated thiyl radical attacks on the C=C double bond. The resulting carbon centered radical then cleaves another hydrogen from another thiol. Termination step involves the radical-radical coupling.

One very important feature of the thiol-ene radical reaction is that the reaction rate depends on the alkene structure [103] (Figure 2.26). Alkenes with high electron density give rapid reaction with thiyl radical compared to the electron poor enes, subsequently highly substituted alkenes give slower reaction rate than singly substituted alkenes.

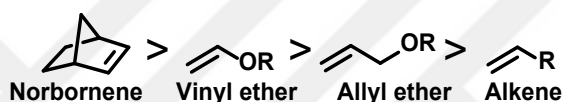


Figure 2.26 : Relative reactivity of ene structures used in radical thiol-ene reactions [103].

The effect of thiol structure on the rate of the thiol-ene conjugation has also been investigated by Hoyle et al [103]. Three thiol structures, alkyl thiols, thiol glycolate esters, and thiol propionate esters, have been tested in thiol-ene radical polymerization (Figure 2.27). Thiols containing weaker S-H bond (propionate ester and glycolate ester) have been found to give 6 times faster reactions than thiols with stronger S-H bond (1-pentanethiol).

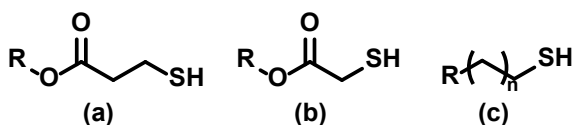


Figure 2.27 : a) Alkyl 3-mercaptopropionate b) alkylthiolglycolate c) alkyl thiol [103].

Seppälä and co-workers obtained chemical modification by using thiol-ene click reaction of graphene oxide (GO) in the presence of 2,2-azobis(2-methylpropanitrile) (AIBN) as a thermal initiator and cysteamine hydrochloride (HS-(CH₂)₂-NH₂.HCl) as a thiol source that is fused to graphene oxide surface upon reaction with the C=C bonds (Figure 2.28) [108].

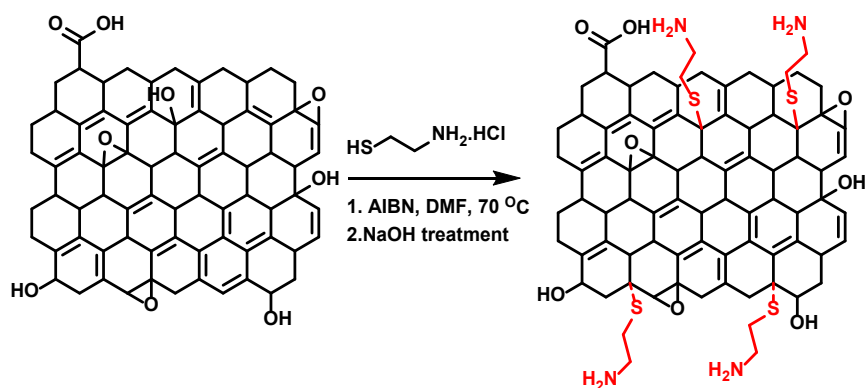


Figure 2.28 : A notable example of modification of GO surface with cysteamine hydrochloride via thiol-ene chemistry [108].

Another example of modification of multiwalled carbon nanotubes via thermal initiation method of thiol-ene click chemistry made by Arsu and co-workers (Figure 2.29). In this study, firstly thiol functional polystyrene was prepared and then grafted multiwall carbon nanotubes in the presence of AIBN thermal initiator [13].

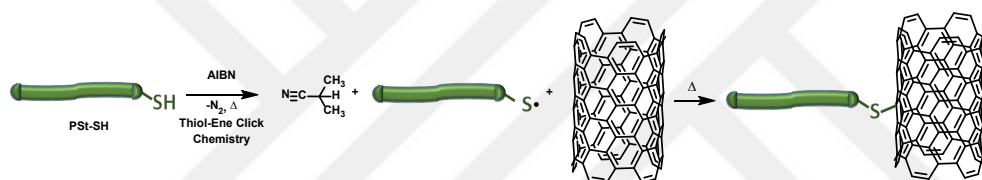


Figure 2.29 : Functionalization of MWCNTs with thiol end-capped polystyrene through thiol-ene click chemistry [13].

In the study published in 2012 by Yagci and co-workers, thiol-ene chemistry was applied to obtain a single modified-C60 product. In the first step of the work, polystyrene polymer carrying a ω -bromine chain-end functionality was obtained by atom-transfer radical polymerization (ATRP) technique and the bromine end group was converted to -SH function.

Then, resulted PS-SH polymer was grafted to C60 in favor of the thermal route, since there was less chance of side reaction in the presence of the radical initiator AIBN [14]. Figure 2.30 presents overall process schematically.

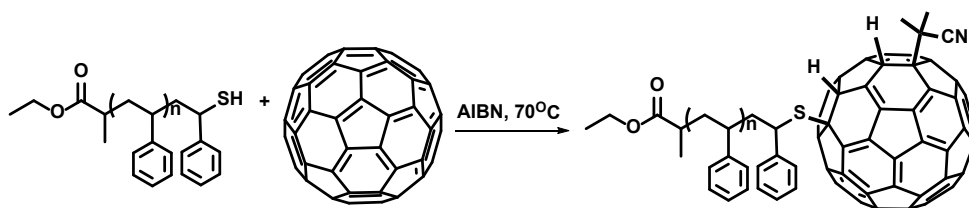


Figure 2.30 : Thermally initiated thiol-ene reaction between C60 and polystyrene with ω -thiol functionality in toluene solution with AIBN.

2.3.2.5 Amidation and esterification reactions of oxidized carbon nanotubes

The appropriate chemical modification of the surface of carbon nanotube can increase both the dispersion in the solvent and the thermophysical, mechanical and electrical properties.

For this purpose, many researchers used oxidized carbon nanotubes. Hydroxyl and carboxylic acid groups occur on the surface of the oxidized carbon nanotubes. These groups are well suited for post-functionalization by introducing acyl chloride or the active ester group on the surface of carbon nanotubes. The only disadvantage is that very severe reaction conditions are required, such as long mixing of the oxidation process in HNO_3 and H_2SO_4 .

The appropriate chemical modification of the surface of carbon nanotube can increase both the dispersion in the solvent and the thermos-physical, mechanical and electrical properties.

In the literature, different forms of use of oxidized carbon nanotubes are seen. Thim and co-workers have recently published paper in which they described oxidization of SWNTs after mixing SWCNTs with HNO_3 and H_2SO_4 for 6 hours. Subsequently, amidation between carboxylic acid groups on the surface of SWCNTs and dodecylamine was proceeded. Thus, nonpolar nature of dodecylamine reduces non-polar interactions between walls of SWCNTs and steric effect of dodecylamine prevents agglomeration of SWCNTs. Finally, in this work SWCNTs with alkyl groups are reinforced with high molecular density polyethylene glycol (HDPE). The properties of the obtained material were compared with the unmodified SWCNTs to which the same treatment was applied. As a result, a significant increase was found in the dispersion of modified with the alkyl groups of carbon nanotube in nonpolar polymer matrix. Detailed reaction conditions were illustrated briefly in Figure 2.31 [109].

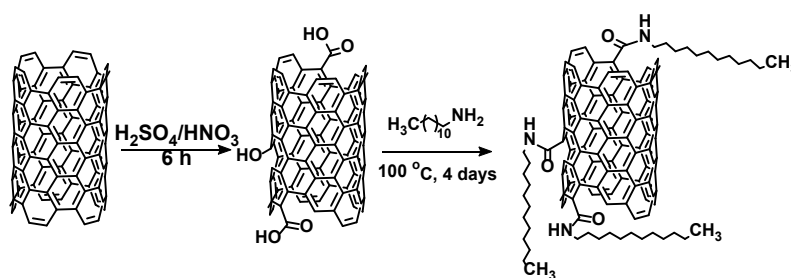


Figure 2.31 : Modification of surface of SWCNTs via amidation.

Moreover, Theato and co-workers pointed to a new way that is an active ester modification method to functionalize sidewalls of carbon nanotubes. In this research, carboxylic acid groups on the sidewalls of multiwalled carbon nanotubes were reacted with thionyl chloride to convert them into the acyl chlorides. Following this step, acyl chlorides reacted with pentafluorophenol to bring it into the active ester. Resulted active ester modified MWCNTs were exhibited air-stable and moisture resistant properties. In addition to this, they were highly reactive to react with primary or secondary amines resulting in amide bonds [26]. Figure 2.32 presents overall reactions.

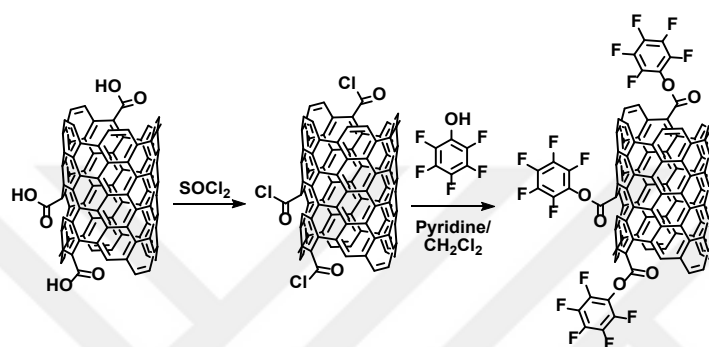


Figure 2.32 : Preparation of pentafluorophenyl ester modified MWCNTs.

In 2014, Borros and coworkers reported a successful surface functionalization for MWCNTs by the plasma polymerization of pentafluorophenyl methacrylate (PFM). Thiol-PEG-amine which is an important chemical linker to introduce thiol-terminated DNA onto sidewalls of CNTs, reacted with PFM functionalized carbon nanotubes by using the advantage of high reactivity of PFP to amine terminated molecules [110]. Detailed reaction conditions were illustrated briefly in Figure 2.33.

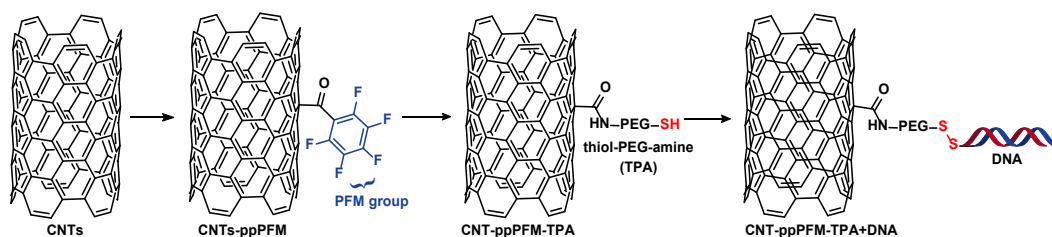


Figure 2.33 : Modification strategy for introducing DNA to sidewalls of CNTs.

3. DOUBLE SURFACE MODIFICATION OF VARIOUS CNTS

Double click modification strategy is one of the most preferred strategies for macromolecular architecture. The double modification strategies, which consist of a combination of different click reactions, permit the preparation of polymers in different topologies and the diversification of polymers that can not be achieved using only one type of reaction [27]. However, introducing new functional group into sidewalls of carbon nanotubes is a challenging matter. Therefore, organic synthesis methods and ‘click reaction’ strategies in polymer science have been started to be applied to this kind of “nano” materials to overcome solubility problems of carbon nanotubes.

The purpose of the first part of the thesis is the application of various double combinations of the Diels-Alder, nitrene addition and thiol-ene click reactions to perform double modification strategy to carbon nanotubes (MWCNTs, MWCNT-COOH, SWCNTs) for surface modification. For this purpose, first, well-defined anthracene, maleimide, furan, nitrene and thiol-terminated various polymers were prepared by using several controlled/ “living” radical polymerization methods. In addition to these polymers, some small molecules with anthracene, maleimide, furan, and azide functionality were used for modeling reactions. The unique aspect of this study is to obtain double surface modification of MWCNTs with covalent bonding and “grafting to” method sequentially by using reactions, such as Diels–Alder and thiol-ene. Figure 3.1 indicates the schematic illustration of double surface modification of CNTs.

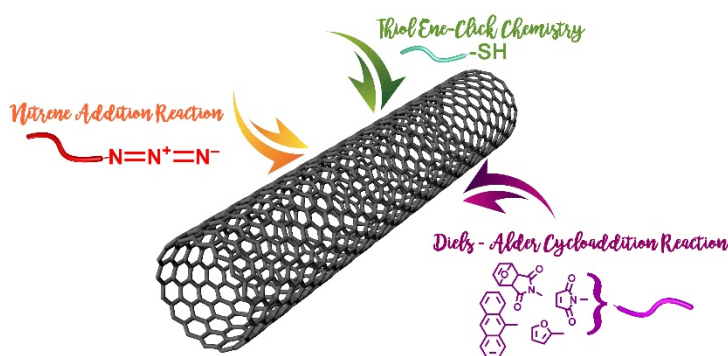


Figure 3.1 : Schematic illustration of double surface modification of CNTs.

3.1 Experimental Part

Materials

MWCNTs (3-15 walls, in average 14.5 nm wide and 1-10- μ m long) were kindly donated by Bayer Material Science AG (Baytubes C 150 P) and used as received.

-COOH Functionalized multi-walled nanotubes (MWNTs-COOH) and single-walled nanotubes (SWCNTs) were supplied by Nanostructured & Amorphous Materials, Inc. and used as received. Single-walled Carbon Nanotubes were supplied by Sigma-Aldrich with Lot number 704121.

Styrene (St, 99%, Merck), methyl metacrylate (MMA, 99%, Aldrich), *n*-Butyl acrylate (*n*BA, 99%, Aldrich), *tert*-butylacrylate (*t*BA, 99%, Aldrich) and *N*, *N*, *N'*, *N''*, *N'''*-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) were passed through basic alumina column to remove inhibitor prior to use.

ϵ -Caprolactone (ϵ -CL, 99%, Aldrich) was dried over CaH₂ and distilled in vacuum prior to use. Poly(ethylene glycol) monomethylether (Me-PEG-OH, M_n = 550, Acros, M_n = 2000 and 5000, Fluka) were dried by azeotropic distillation with anhydrous toluene.

Furan (99%, Aldrich), maleic anhydride (99%, Aldrich), ethanolamine (99.5%, Aldrich), succinic anhydride (97%, Aldrich), 9-anthracenemethanol (97%, Aldrich), α -bromoisobutryl bromide (98%, Aldrich), ethyl α -bromoisobutyrate (98%, Aldrich), triethylamine (Et₃N, 99.5%, Aldrich), *N,N'*-dicyclohexylcarbodiimide (DCC, 99%, Aldrich), 4-dimethylaminopyridine (DMAP, 99%, Aldrich), and CuCl (99.9%, Aldrich) were used as received.

Tetrahydrofuran (THF, [360589], Sigma-Aldrich), *N,N*-dimethylformamide (DMF, [319937] Sigma-Aldrich), dichloromethane (CH₂Cl₂, [24233], Sigma-Aldrich), toluene ([9351-02], J. T. Baker), *N*-Methyl-2-pyrrolidone (NMP, [443778], Sigma-Aldrich), 1,4-dioxane ([296309], Aldrich), dimethyl sulfoxide (DMSO, [472301], Sigma-Aldrich), anisole ([123226], Sigma-Aldrich), 1,2-dichlorobenzene (*o*-DCB, [D56802], Sigma-Aldrich), methanol ([106009], Merck), hydrochloric acid (HCl, [30721], Sigma-Aldrich) were used without purification. Ethyl acetate (EtOAc) and hexane were in technical grade and distilled prior to use.

Sodium azide (NaN_3 , [71290], Sigma-Aldrich), *p*-toluenesulfonyl chloride (tosyl chloride [240877], Sigma-Aldrich), sodium sulfate (Na_2SO_4 , [106649], Merck), DL-homocysteine thiolactone hydrochloride (TLA, [53530], Sigma-Aldrich), triethyl amine ([JW635-07], J. T. Baker), furfuryl alcohol ([185930], Sigma-Aldrich), ethylene carbonate ([E26258], Sigma-Aldrich), 2,6-di-*tert*-butyl-4-methylphenol (BHT, [34750], Sigma-Aldrich) and thiourea ([T8656], Sigma-Aldrich) used as received without further purification.

Instrumentation

^1H (500 MHz) and ^{13}C (125 MHz) spectra of samples were recorded in CDCl_3 using an Agilent VNMRS 500 instrument. The conventional gel permeation chromatography (GPC) measurements were carried out with an Agilent instrument (Model 1100) with a pump, refractive index and UV detectors and four Waters Styragel columns (HR 5E, HR 4E, HR 3, HR 2), (4.6 mm internal diameter, 300 mm length, packed with 5 μm particles). The effective molecular weight ranges of columns were 2000–4000000, 50–100000, 500–30000, and 500–20000 g mol^{-1} , respectively. THF was used as an eluent at a flow rate of 0.3 mL min^{-1} at 30 $^\circ\text{C}$ and toluene was used as an internal standard. The molecular weights of the polymers were calculated based on linear polystyrene (PS) standards (Polymer Laboratories). Thermogravimetric analyses (TGA) were performed Perkin Elmer Diamond TG/DTS at 10 $^\circ\text{C min}^{-1}$ heating rate under a flowing N_2 atmosphere. FT-IR spectra were recorded on an Agilent technologies Cary 630 FT-IR instrument over the range 4000–500 cm^{-1} .

4,10-dioxatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (*Adduct*), 4-(2-hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (*Adduct-OH*) [111], 4-(2-ethoxy)-4-oxabutanoic acid (*Adduct-COOH*) [112], 2-bromo-2-methyl propionic acid 2-(3,5-Dioxo-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl) ethyl ester (*Adduct-Br*) [111], 9-anthrylmethyl 2-bromo-2-methyl propanoate (*Anth-initiator*) [113], 4-(anthracen-9-ylmethoxy)-4-oxobutanoic acid (*Anth-COOH*) [114], 1-(2-oxotetrahydrothiophen-3-yl)-1H-pyrrole-2,5-dione (*MI-TLa*) [115], 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea (*TU*) [116], mono carboxylic acid end-functionalized PEG (*PEG-COOH*) [117], α -furan protected maleimide-terminated-poly(ethylene glycol) (*MI-PEG*) [118], thiol terminated polyethylene glycol (*PEG-SH*) [119], and RAFT polymerizations of *n*-butyl acrylate (*PnBA-SH*) and styrene (*PS-SH*) with DBTTC [120] were prepared according to published procedures.

3.1.1 Synthesis of furan-2-ylmethyl 2-bromo-2-methylpropanoate (Furan-Br)

Furfuryl alcohol (0.62 mL, 7.18 mmol) and DMAP (0.17 g, 1.44 mmol) were dissolved in 50 mL of CH₂Cl₂, and Et₃N (1.20 mL, 8.60 mmol) was added. The reaction mixture was then cooled to 0 °C. 2-bromo isobutyryl bromide (1.82 g, 7.89 mmol) was added dropwise within 30 minutes to this solution. The reaction mixture was stirred for 15 min. at 0 °C then for overnight at room temperature. The ammonium salt was filtered off and the solvent was evaporated under reduced pressure. The remaining residue was extracted with CH₂Cl₂, and saturated aqueous NaHCO₃. The aqueous phase again extracted with CH₂Cl₂, and combined organic phases dried over Na₂SO₄. The solution was concentrated, and the crude product was purified by column chromatography over silica gel eluting with hexane/EtOAc (10:1) to give Furan-Br as colourless oil. Yield: 1.05 g (60%).

¹H NMR (CDCl₃, δ) 7.43 (m, 1H, furan), 6.44 (dd, 1H, furan), 6.37 (dd, 1H, furan), 5.16 (s, 2H), 1.93 (s, 6H, C(CH₃)₂-Br).

3.1.2 Synthesis of *N*-(2-azidoacetyl) homocysteine-γ-thiolactone (TLa-N₃)

N-(2-azidoacetyl) homocysteine- γ -thiolactone was prepared in two steps. As a first step, *N*-(2-bromoacetyl) homocysteine- γ -thiolactone (*TLa-Br*) was synthesized as described in the literature procedure [121]. Secondly, obtained TLa-Br (2 g, 8.39 mmol) was dissolved in 10 mL acetonitrile and added into NaN₃ (0.81 g, 12.59 mmol) which was previously dissolved in 10 mL distilled water. The reaction mixture was stirred at room temperature for overnight. Then, mixture was diluted with EtOAc, and extracted twice with distilled water. The organics were dried over Na₂SO₄ and evaporated. The polymer was dried in a vacuum oven at 40 °C. (Yield = 1.5 g, 89 %).

¹H NMR (500 MHz, DMSO-*d*₆, δ): 8.67 (s, 1 H), 4.61 (m, 1 H), 3.90 (s, 2 H), 3.40-3.30 (m, 2 H), 2.44 (m, 1 H), 2.09 (m, 1 H).

3.1.3 General procedure for the synthesis of furan protected maleimide end-functionalized PMMA (MI-PMMA)

In a 25 mL of Schlenk tube, MMA (5.00 mL, 46.70 mmol), PMDETA (0.19 mL, 0.94 mmol), CuCl (0.093 g, 0.94 mmol), toluene (5 mL), and *Adduct-Br* (0.33 g, 0.94 mmol) were added, and the reaction mixture was degassed by FPT cycles, and left in argon. The tube was then placed in a thermostated oil bath at 40 °C for predetermined times. The polymerization mixture was diluted with THF, passed through a basic

alumina column to remove the catalyst, and precipitated into hexane. The polymer was dried for 24 h in a vacuum oven at 40 °C.

$([M]_0/[I]_0 = 50; [I]_0:[CuCl]_0:[PMDETA]_0=1:1:1, M_{n, GPC} = 3390 \text{ g/mol}, M_w/M_n = 1.18,$ relative to PMMA standards).

^1H NMR (500 MHz, $CDCl_3$, δ): 6.54 (s, 2H, $CH=CH$, bridge protons), 5.27 (s, 2H, -CHO, bridge-head protons), 4.20 - 4.15 (m, 4H, $NCH_2CH_2OC=O$), 3.59 (br, OCH_3 of PMMA), 2.92 (s, 2H, $CH-CH$, bridge protons), 2.20-0.65 (br, aliphatic protons of PMMA).

3.1.4 General procedure for the synthesis of anthracene end- functionalized PMMA (anth-PMMA)

MMA (20 mL, 175 mmol), PMDETA (0.18 mL, 0.87 mmol), CuCl (0.086 g, 0.87 mmol), and the initiator *Anth-Br* (0.31 g, 0.87 mmol) were added in a 25 mL of schlenk tube and the reaction mixture was degassed by three FPT cycles and left in vacuum. The tube was placed in a thermostated oil bath at 90 °C for 1 hour. After that time, dark-green polymerization mixture was diluted with THF, passed through a basic alumina column to remove the catalyst, and precipitated in hexane. The polymer was dried for 24 h in a vacuum oven at 40 °C.

$([M]_0/[I]_0 = 200; [I]_0:[CuCl]_0:[PMDETA]_0=1:1:1; M_{n, GPC} = 3400 \text{ g/mol}, M_w/M_n = 1.25,$ relative to PMMA standards).

^1H NMR (500 MHz, $CDCl_3$, δ): 8.5 (s, 1H, *ArH* of anthracene), 8.28 (d, 2H, *ArH* of anthracene), 8.02 (s, 2H, *ArH* of anthracene), 7.5 (m, 4H, *ArH* of anthracene), 6.05 (m, 2H, CH_2 -anthracene), 3.57 (OCH_3 of PMMA), 2.1-0.6 (aliphatic protons of PMMA).

3.1.5 General procedure for the preparation of azide-end functionalized PtBA (PtBA-N₃)

PtBA-N₃ was prepared in two steps. As a first step, bromo end-functionalized PtBA (PtBA-Br) was prepared by ATRP of *t*BA. To a 25 mL Schlenk tube, *t*BA (12 mL, 82 mmol), PMDETA (0.17 mL, 0.82 mmol), CuBr (0.12 g, 0.82 mmol), ethylene carbonate (1.05 g, 0.10 mmol), and ethyl 2-bromoisobutyrate (EiBr) (0.16 g, 0.82 mmol) were added, and the reaction mixture was degassed by three FPT cycles and left in *vacuo*. The tube was then placed in a thermostated oil bath at 80 °C for predetermined times. The polymerization mixture was diluted with THF, passed

through a neutral alumina column to remove the catalyst, and precipitated into the solution of water and methanol (1/4; v/v). After decantation, the polymer was dissolved in CH₂Cl₂, extracted with water and the water phase was again extracted with CH₂Cl₂ and combined organic phase was dried over Na₂SO₄ and evaporated. The polymer was dried in a vacuum oven at 40 °C.

¹H NMR (CDCl₃, δ): 4.1 (m, C=OOCH₂ and CHBr end group of PtBA), 2.2 (br, CH of PtBA), 2.0-1.0 (br, aliphatic protons of PtBA).

Secondly, previously obtained PtBA-Br (1g, 0.22 mmol, $M_{n, \text{NMR}} = 4500$ g/mol) was dissolved in 10 mL of DMF and NaN₃ (0.43 g, 6.67 mmol) was added. The reaction mixture was stirred at 50 °C for overnight, after which time it was cooled to room temperature and diluted with CH₂Cl₂ and extracted 2 times with water. The organics were dried over Na₂SO₄ and evaporated. The polymer was dried in a vacuum oven at 40 °C.

¹H NMR (CDCl₃): 4.1 (m, -C=OOCH₂-), 3.72 (bs, -CHN₃ end group of PtBA), 2.2 (br, -CH of PtBA), 2.0-1.0 (br, aliphatic protons of PtBA).

3.1.6 General procedure for the preparation of furan-end functionalized PS (Furan-PS)

St (10 mL, 0.10 mmol), PMDETA (0.10 mL, 0.52 mmol), CuBr (0.074 g, 0.52 mmol) and the initiator *Furan-Br* (0.13 g, 0.52 mmol) were added in a 25 mL of schlenk tube and the reaction mixture was degassed by three FPT cycles and left in vacuum. The tube was placed in a thermostated oil bath at 110 °C for 1 hour. After that time, dark-green polymerization mixture was diluted with THF, passed through a basic alumina column to remove the catalyst, and precipitated in hexane. The polymer was dried for 24 h in a vacuum oven at 40 °C.

$[M]_0/[I]_0 = 200$, $[I]_0:[CuBr]_0:[PMDETA]_0 = 1:1:1$. $M_{n, \text{GPC}} = 1950$; $\bar{D} = 1.13$, relative to PS standards. ¹H NMR (CDCl₃, δ): 7.5-6.2 (br, ArH of PS), 4.4 (br, 1H, CH(Ph)-Br end group of PS), 3.7-3.4 (br, 2H, CH₃CH₂O), 2.2-0.8 (m, aliphatic protons of PS and CH₃).

3.1.7 General procedure for the preparation of azide-end functionalized PS (PS-N₃)

Synthesis procedure of azide-end functionalized PS consisted of two steps. In the first step, ω-bromide terminated PS (PS-Br) was prepared by ATRP of Styrene at 110 °C.

St (10 mL, 87 mmol), PMDETA (0.09 mL, 0.43 mmol), CuBr (0.062 g, 0.43 mmol), and ethyl 2-bromoisobutyrate (EiBr) (0.064 mL, 0.43 mmol) were placed in a round bottom 25 mL Schlenk tube, respectively. Following this step, the reaction mixture was degassed by three FPT cycles and left in a vacuum. The tube was kept stirring (500 rpm) in a thermostated oil bath at 110 °C for 40 minutes. After that time, the dark-green polymerization mixture was diluted with THF, passed through a basic alumina column for removing the catalyst. Finally, the raw polymer intermediate was re-dissolved in THF and added dropwise into the methanol for purification. This precipitation step repeated twice and dried in a vacuum oven at 40 °C for 24h.

$[M]_0/[I]_0 = 200$, $[I]_0:[CuBr]_0:[PMDETA]_0 = 1:1:1$. $M_{n, GPC} = 1950$; $D = 1.13$, relative to PS standards. ^1H NMR ($CDCl_3$, δ): 7.5-6.2 (br, ArH of PS), 4.4 (br, 1H, $CH(Ph)$ -Br end group of PS), 3.7-3.4 (br, 2H, CH_3CH_2O), 2.2-0.8 (m, aliphatic protons of PS and CH_3).

Next, previously obtained PS-Br (0.40 g, 0.20 mmol, $M_{n, GPC} = 1950$ g/mol) and sodium azide (0.65 g, 10 mmol) were dissolved in DMF (20 mL). Then, the mixture stirred for overnight at ambient temperature. The product was precipitated in an excess amount of methanol. PS- N_3 was dried for 24 h in a vacuum oven at 40 °C.

$M_{n, GPC} = 2720$ g/mol; $D = 1.07$, relative to PS standards. ^1H NMR ($CDCl_3$, δ): 7.5-6.2 (br, ArH of PS), 3.9 (br, 1H, $CH(Ph)$ - N_3), 3.7-3.4 (br, 2H, CH_3CH_2O), 2.2-0.8 (m, aliphatic protons of PS and CH_3).

3.1.8 Synthesis of anthracene end-functionalized PEG (Anth-PEG)

Me-PEG-OH ($M_w = 2000$) (1 g, 0.50 mmol) was dissolved in 30 mL of dry CH_2Cl_2 . Anth-COOH (0.46 g, 1.50 mmol) and DMAP (0.006 g, 0.05 mmol) were added to the solution. DCC (0.30 g, 1.50 mmol) dissolved in 5 mL of CH_2Cl_2 was added to the reaction mixture and the solution was stirred at room temperature for overnight. After filtration off the urea byproduct, the mixture was precipitated into diethyl ether. The polymer was dissolved in THF and then precipitated into diethyl ether in order to give pure Anth-PEG as a pale-yellow solid. (Yield = 0.85 g, 74%).

^1H NMR (500 MHz, $CDCl_3$, δ): 8.52 - 7.51 (9H, ArH of anthracene), 6.17 (s, 2H, CH_2 -anthracene), 4.16 (t, 2H, PEG- $OCH_2CH_2OC=O$), 3.65 (2H, PEG-

OCH₂CH₂OC=O), 3.62 (m, 4H, -OCH₂CH₂ repeating unit of PEG), 3.38 (s, 3H, PEG-OCH₃), 2.65 (4H, C=OCH₂CH₂C=O).

3.1.9 Synthesis of furfuryl end-functionalized PEG (Furfuryl-PEG)

PEG-COOH (Me-PEG-OH M_w = 2000 g/mol) (2 g, 0.950 mmol) was dissolved in 30 mL of dry CH₂Cl₂. Furfuryl alcohol (0.240 mL, 2.850 mmol) and DMAP (0.011 g, 0.095 mmol) were added to the solution. DCC (0.580 g, 2.850 mmol) dissolved in 5 mL of CH₂Cl₂ was added to the reaction mixture and the solution was stirred at room temperature for overnight. After filtration off the urea byproduct, the mixture was precipitated into diethyl ether. The polymer was dissolved in THF and then precipitated into diethyl ether in order to give pure furfuryl-PEG as a light-yellow solid. (Yield = 1.46 g, 70%). ¹H NMR (CDCl₃, δ): 7.42 (s, 1H), 6.40-6.36 (d, 2H), 5.07 (s, 2H), 4.23 (t, 4H, PEG-OCH₂CH₂OC=O), 3.65 (m, 4H, -OCH₂CH₂ repeating unit of PEG), 3.37 (s, 3H, PEG-OCH₃), 2.66 (4H, C=OCH₂CH₂C=O).

3.1.10 Synthesis of azide end functional PEG (PEG-N₃)

Me-PEG-OH (M_n=2000 g/mol) (5 g, 2.50 mmol) was dissolved in 150 mL of CH₂Cl₂ and TEA (0.34 mL, 2.50 mmol) was added to this solution. The mixture was cooled to 0 °C and *p*-toluenesulfonyl chloride (tosyl chloride) (0.12 g, 0.62 mmol) in CH₂Cl₂ were added dropwise (30 min) to the reaction mixture. Then the reaction mixture was stirred overnight at room temperature. First, it was extracted with cold 4 M HCl, then with distilled water and dried over Na₂SO₄. The organic phase was evaporated, and white solid was further purified by column chromatography over silica gel eluting with firstly CH₂Cl₂ and secondly with MeOH/CH₂Cl₂ (1/6) to give tosylated PEG as colorless viscous liquid. (Yield = 4.3 g, 79 %). ¹H NMR (500 MHz, CDCl₃, δ): 7.80 - 7.34 (8H, PEG-OSO₂C₆H₄CH₃), 4.15 (2H, OCH₂CH₂-OSO₂C₆H₄CH₃), 3.63 (OCH₂CH₂ repeating unit of PEG), 3.37 (3H, CH₃-PEGOSO₂C₆H₄CH₃) 2.44 (3H, PEG-OSO₂C₆H₄CH₃).

Then, tosylated-PEG, (4.30 g, 1.99 mmol) was dissolved in DMF (20 mL) and NaN₃ (1.29 g, 19.95 mmol) was added to this solution. After stirring the reaction mixture overnight at room temperature, CH₂Cl₂ and water were added, and the organic layer was extracted three times with water and dried over Na₂SO₄. Solvent was removed under reduced pressure and PEG-N₃ afforded as colorless viscous liquid (Yield = 3.7

g, 91 %). ^1H NMR (500 MHz, CDCl_3 , δ): 3.63 (m, OCH_2CH_2 repeating unit of PEG), 3.36 (5H, $\text{CH}_3\text{-PEG-N}_3$ and $\text{CH}_2\text{O-N}_3$).

3.1.11 Preparation of furan-protected maleimide-end-functionalized PCL (MI-PCL)

PCL-MI was prepared by ROP of ϵ -CL (5.0 mL, 0.045 mol) using both DBU (0.16 mL, 1.13 mmol) and TU (0.41 g, 1.13 mmol) as catalyst and *adduct-OH* (0.23 g, 1.13 mmol) as an initiator at 40 °C for 4 h. The degassed monomer in CH_2Cl_2 (8 mL), catalyst, and initiator were added to a previously flamed schlenk tube equipped with a magnetic stirring bar in the order mentioned. The tube was degassed with three freeze-pump-thaw (FPT) and left in vacuum. After the polymerization, the mixture was diluted with THF, and precipitated into an excess amount of cold methanol. The purified polymer was isolated by filtration and dried at 40 °C in a vacuum oven for 24 h. Yield = 3.49 g, 67 %, $M_{n, \text{theo}} = 3100$ g/mol, $M_{n, \text{NMR}} = 3300$ g/mol, $M_{n, \text{GPC}} = 5750$ g/mol, $M_w/M_n = 1.08$, relative to PS standards. ^1H NMR (500 MHz, CDCl_3 , δ): 6.52 (s, 2H, CH=CH , vinyl protons), 5.26 (s, 2H, -CHO , bridge-head protons), 4.22 (t, 2H, $\text{NCH}_2\text{CH}_2\text{OC=O}$), 4.06 (t, $\text{CH}_2\text{OC=O}$ of PCL), 3.78-3.60 (m, 4H, $\text{NCH}_2\text{CH}_2\text{OC=O}$ and CH_2OH end-group of PCL), 2.86 (s, 2H, CH-CH , bridge protons), 2.30 (t, C=OCH_2 of PCL), 1.85-1.25 (m, CH_2 of PCL).

3.1.12 Mono modification of CNTs via Diels-alder cycloaddition reaction

3.1.12.1 Model reaction-1

50 mg of MWCNTs were dispersed in 50 mL of toluene in an ultrasonic bath. After 20 minutes of dispersion, 250 mg *MI-TLa* was added, and the mixture were stirred at 110 °C for 48 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 μm), to remove unreacted furan protected *MI-TLa*. Residual solid on the filter was sonicated with using excessive amount of fresh THF and filtered again until the unreacted *MI-TLa* was fully removed. The recovered black powder was dried under vacuum.

3.1.12.2 Model reaction-2

50 mg of MWCNTs were dispersed in 10 mL of toluene in an ultrasonic bath. After 20 minutes of dispersion, 250 mg 9-anthracenemethanol was added, and the mixture were stirred at 80 °C in dark for 48 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 μm), to remove 9-anthracenemethanol. Residual

solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until the unreacted 9-anthracenemethanol could not be detected in the solvent (monitored by UV-spectrophotometer). The recovered black powder was dried under vacuum.

3.1.12.3 Model reaction-3

50 mg of MWCNTs were dispersed in 20 mL of DMSO in an ultrasonic bath. After 20 minutes of dispersion, 1.33 mL (1.5 g) furfuryl alcohol was added, and the mixture were stirred at 50 °C for 96 hour [91]. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 μ m), to remove furfuryl alcohol.

Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until the unreacted furfuryl alcohol could not be detected in the solvent (monitored by FTIR). The recovered black powder was dried under vacuum.

3.1.12.4 CNT-1

50 mg of MWCNTs were dispersed in 30 mL of toluene in an ultrasonic bath. After 20 minutes of dispersion, 250 mg furan protected MI-PMMA was added, and the mixture were stirred at 110 °C for 48 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 μ m), to remove unreacted furan protected MI-PMMA.

Residual solid on the filter was sonicated with using excessive amount of fresh THF and filtered again until the unreacted furan protected MI-PMMA could not be detected in the solvent (monitored by GPC). The recovered black powder was dried under vacuum.

3.1.12.5 CNT-2

40 mg of MWCNTs were dispersed in 20 mL of toluene in an ultrasonic bath. After 20 minutes of dispersion, 200 mg *r*MI-PMMA and 1 mg BHT were added, and the mixture were stirred at 75 °C for 24 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 μ m), to remove unreacted *r*MI-PMMA.

Residual solid on the filter was sonicated with using excessive amount of fresh THF and filtered again until the unreacted *r*MI-PMMA could not be detected in the solvent (monitored by GPC). The recovered black powder was dried under vacuum.

3.1.12.6 CNT-3

25 mg of MWCNTs were dispersed in 50 mL of toluene in an ultrasonic bath. After 20 minutes of dispersion, 250 mg MI-PEG₂₀₀₀ was added, and the mixture were stirred at 110 °C for 48 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 µm), to remove MI-PEG₂₀₀₀.

Residual solid on the filter was sonicated with using excessive amount of fresh THF. Then, solid filtered again until the unreacted MI-PEG₂₀₀₀ could not be detected in the solvent (monitored by GPC). The recovered black powder was dried under vacuum.

3.1.12.7 CNT-4

25 mg of MWCNTs were dispersed in 50 mL of toluene in an ultrasonic bath. After 20 minutes of dispersion, 250 mg *r*-MI-PCL was added, and the mixture were stirred at 110 °C for 48 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 µm), to remove *r*-MI-PCL.

Residual solid on the filter was sonicated with using excessive amount of fresh THF. Then, solid filtered again until the unreacted *r*-MI-PCL could not be detected in the solvent (monitored by GPC). The recovered black powder was dried under vacuum.

3.1.12.8 CNT-5

25 mg of MWCNTs were dispersed in 20 mL of *N*-methyl-2-pyrrolidone in an ultrasonic bath. After 20 minutes of dispersion, 250 mg anth-PMMA was added, and the mixture were stirred at 80 °C for 48 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 µm), to remove anth-PMMA. Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until the unreacted anth-PMMA could not be detected in the solvent (monitored by UV-spectrophotometer). The recovered black powder was dried under vacuum.

3.1.12.9 CNT-6

25 mg of MWCNTs were dispersed in 20 mL of *N*-methyl-2-pyrrolidone in an ultrasonic bath. After 20 minutes of dispersion, 250 mg anth-PEG₂₀₀₀ was added, and the mixture were stirred at 80 °C in dark for 48 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 µm), to remove anth-PEG₂₀₀₀. Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until the unreacted anth-PEG₂₀₀₀ could not be detected in the

solvent (monitored by UV-spectrophotometer). The recovered black powder was dried under vacuum.

3.1.12.10 CNT-7

25 mg of MWCNTs-COOH were dispersed in 20 mL of toluene in an ultrasonic bath. After 20 minutes of dispersion, 250 mg anth-PMMA was added, and the mixture were stirred at 80 °C in dark for 48 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 µm), to remove anth-PMMA. Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until the unreacted anth-PMMA could not be detected in the solvent (monitored by UV-spectrophotometer). The recovered black powder was dried under vacuum.

3.1.12.11 CNT-8

50 mg of MWCNTs-COOH were dispersed in 10 mL of toluene in an ultrasonic bath. After 20 minutes of dispersion, 500 mg anth-PEG₂₀₀₀ was added, and the mixture were stirred at 80 °C in dark for 48 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 µm), to remove anth-PEG₂₀₀₀.

Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until the unreacted anth-PEG₂₀₀₀ could not be detected in the solvent (monitored by UV-spectrophotometer). The recovered black powder was dried under vacuum.

3.1.12.12 CNT-9

50 mg of MWCNTs were dispersed in 15 mL of toluene in an ultrasonic bath. After 20 minutes of dispersion, 250 mg furan-PEG₂₀₀₀ was added, and the mixture were stirred at 75°C for 48 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 µm), to remove furan-PEG₂₀₀₀.

Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until the unreacted furan-PEG₂₀₀₀ could not be detected in the solvent (monitored by GPC). The recovered black powder was dried under vacuum.

3.1.12.13 CNT-10

40 mg of MWCNTs-COOH were dispersed in 15 mL of anisole in an ultrasonic bath. After 20 minutes of dispersion, 200 mg furan-PEG₂₀₀₀ was added, and the mixture

were stirred at 75 °C for 48 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 µm), to remove furan-PEG₂₀₀₀.

Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until the unreacted furan-PEG₂₀₀₀ could not be detected in the solvent (monitored by GPC). The recovered black powder was dried under vacuum.

3.1.12.14 CNT-11

40 mg of MWCNTs-COOH were dispersed in 15 mL of toluene in an ultrasonic bath. After 20 minutes of dispersion, 200 mg furan-PEG₂₀₀₀ was added, and the mixture were stirred at 75 °C for 48 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 µm), to remove furan-PEG₂₀₀₀. Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until the unreacted furan-PEG₂₀₀₀ could not be detected in the solvent (monitored by GPC). The recovered black powder was dried under vacuum.

3.1.13 Mono modification of CNTs via Nitrene addition

3.1.13.1 Model reaction-4

25 mg of SWCNTs (Sigma-Aldrich) were dispersed in 50 mL of 1,2-dichlorobenzene in an ultrasonic bath. After 20 minutes of dispersion, 500 mg TLa-N₃ was added, and the mixture were stirred at 130 °C for 72 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 µm), to remove TLa-N₃. Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until the unreacted TLa-N₃ could not be detected in the solvent (monitored by FTIR). The recovered black powder was dried under vacuum.

3.1.13.2 CNT-12

20 mg of MWCNTs were dispersed in 20 mL of 1,2-dichlorobenzene in an ultrasonic bath. After 20 minutes of dispersion, 400 mg PEG₂₀₀₀-N₃ was added, and the mixture were stirred at 130 °C for 72 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 µm), to remove PEG₂₀₀₀-N₃. Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until the unreacted PEG₂₀₀₀-N₃ could not be detected in the solvent (monitored by FTIR). The recovered black powder was dried under vacuum.

3.1.13.3 CNT-13

25 mg of MWCNTs were dispersed in 20 mL of 1,2-dichlorobenzene in an ultrasonic bath. After 20 minutes of dispersion, 250 mg PEG₂₀₀₀-N₃ was added, and the mixture were stirred at 130 °C for 96 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 µm), to remove PEG₂₀₀₀-N₃. Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until the unreacted PEG₂₀₀₀-N₃ could not be detected in the solvent (monitored by FTIR). The recovered black powder was dried under vacuum.

3.1.13.4 CNT-14

25 mg of MWCNTs were dispersed in 20 mL of 1,2-dichlorobenzene in an ultrasonic bath. After 20 minutes of dispersion, 250 mg PS-N₃ was added, and the mixture were stirred at 130°C for 72 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 µm), to remove PS-N₃. Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until the unreacted PS-N₃ could not be detected in the solvent (monitored by FTIR). The recovered black powder was dried under vacuum.

3.1.13.5 CNT-15

40 mg of MWCNTs-COOH were dispersed in 40 mL of 1,2-dichlorobenzene in an ultrasonic bath. After 20 minutes of dispersion, 800 mg PtBA-N₃ was added, and the mixture were stirred at 130 °C for 72 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 µm), to remove PtBA-N₃. Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until the unreacted PtBA-N₃ could not be detected in the solvent (monitored by FTIR). The recovered black powder was dried under vacuum.

3.1.13.6 CNT-16

20 mg of MWCNTs-COOH were dispersed in 80 mL of 1,2-dichlorobenzene in an ultrasonic bath. After 20 minutes of dispersion, 400 mg PEG₂₀₀₀-N₃ was added, and the mixture were stirred at 130 °C for 72 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 µm), to remove PEG₂₀₀₀-N₃. Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until the unreacted PEG₂₀₀₀-N₃ could not be detected in the solvent (monitored by FTIR). The recovered black powder was dried under vacuum.

3.1.14 Mono modification of CNTs via Thiol-ene reaction

3.1.14.1 CNT-17

50 mg of MWCNTs were dispersed in 30 mL of DMF in an ultrasonic bath. After 20 minutes of dispersion, 150 mg PS-SH ($M_{n, \text{GPC}} = 4300 \text{ g/mol}$) and 3 mg AIBN were added, and the mixture were stirred at 80 °C for 24 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 μm), to remove PS-SH. Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until the unreacted PS-SH could not be detected in the solvent (monitored by GPC). The recovered black powder was dried under vacuum.

3.1.14.2 CNT-18

50 mg of MWCNTs were dispersed in 30 mL of DMF in an ultrasonic bath. After 20 minutes of dispersion, 150 mg PEG₂₀₀₀-SH and 3 mg AIBN were added, and the mixture were stirred at 80 °C for 24 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 μm), to remove PEG₂₀₀₀-SH.

Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until the unreacted PEG₂₀₀₀-SH could not be detected in the solvent (monitored by GPC). The recovered black powder was dried under vacuum.

3.1.14.3 CNT-19

20 mg of SWCNTs (Sigma Aldrich) were dispersed in 50 mL of DMF in an ultrasonic bath. After 20 minutes of dispersion, 100 mg PS-SH ($M_{n, \text{GPC}} = 4300 \text{ g/mol}$) and 3 mg AIBN were added, and the mixture were stirred at 80 °C for 24 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 μm), to remove PS-SH.

Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until the unreacted PS-SH could not be detected in the solvent (monitored by GPC). The recovered black powder was dried under vacuum.

3.1.14.4 CNT-20

50 mg of MWCNTs-COOH were dispersed in 30 mL of DMF in an ultrasonic bath. After 20 minutes of dispersion, 150 mg PS-SH and 3 mg AIBN were added, and the mixture were stirred at 80 °C for 24 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 μm), to remove PS-SH. Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until

the unreacted PS-SH could not be detected in the solvent (monitored by GPC). The recovered black powder was dried under vacuum.

3.1.15 Combination of Diels-Alder Cycloaddition, Thiol-ene Click reactions and Nitrene Addition on to CNTs' surface for modification

3.1.15.1 DB CNT-1

10 mg of CNT-13 were dispersed in 20 mL of DMF in an ultrasonic bath. After 10 minutes of dispersion, 150 mg PnBa-SH and 3 mg AIBN were added, and the mixture were stirred at 80 °C for 24 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 µm), to remove PnBa-SH.

Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until the unreacted PnBa-SH could not be detected in the solvent (monitored by GPC). The recovered black powder was dried under vacuum.

3.1.15.2 DB CNT-2

10 mg of CNT-13 were dispersed in 20 mL of DMF in an ultrasonic bath. After 10 minutes of dispersion, 150 mg PS-SH and 3 mg AIBN were added, and the mixture were stirred at 80 °C for 24 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 µm), to remove PS-SH.

Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until the unreacted PS-SH could not be detected in the solvent (monitored by GPC). The recovered black powder was dried under vacuum.

3.1.15.3 DB CNT-3

10 mg of CNT-15 were dispersed in 40 mL of DMF in an ultrasonic bath. After 10 minutes of dispersion, 150 mg PS-SH and 3 mg AIBN were added, and the mixture were stirred at 80 °C for 24 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 µm), to remove polymers.

Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until the unreacted polymers could not be detected in the solvent (monitored by FTIR). The recovered black powder was dried under vacuum.

3.1.15.4 DB CNT-4

20 mg of CNT-2 were dispersed in 20 mL of DMF in an ultrasonic bath. After 10 minutes of dispersion, 100 mg PS-SH and 3 mg AIBN were added, and the mixture

were stirred at 80 °C for 24 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 µm), to remove PS-SH. Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until the unreacted PS-SH could not be detected in the solvent (monitored by GPC). The recovered black powder was dried under vacuum.

3.1.15.5 DB CNT-5

20 mg of CNT-18 were dispersed in 50 mL of toluene in an ultrasonic bath. After 10 minutes of dispersion, 100 mg *r*-MI-PCL was added, and the mixture were stirred at 110 °C for 48 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 µm), to remove *r*-MI-PCL. Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until the unreacted *r*-MI-PCL could not be detected in the solvent (monitored by GPC). The recovered black powder was dried under vacuum.

3.1.15.6 DB CNT-6

20 mg of CNT-15 were dispersed in 50 mL of toluene in an ultrasonic bath. After 10 minutes of dispersion, 400 mg anth-PMMA was added, and the mixture were stirred at 80 °C in dark for 48 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 µm), to remove anth-PMMA.

Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until the unreacted anth-PMMA could not be detected in the solvent (monitored by UV-spectrophotometer). The recovered black powder was dried under vacuum.

3.1.15.7 DB CNT-7

20 mg of CNT-13 were dispersed in 50 mL of *N*-methyl-2-pyrrolidone in an ultrasonic bath. After 10 minutes of dispersion, 400 mg furan-PS was added, and the mixture were stirred at 80 °C for 48 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 µm), to remove furan-PS.

Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until the unreacted furan-PS could not be detected in the solvent (monitored by UV-spectrophotometer). The recovered black powder was dried under vacuum.

3.1.16 Surface reaction of carbon nanotubes via one-pot double modification sequentially

3.1.16.1 DB CNT-8

50 mg of SWCNTs (Nanostructured & Amorphous Materials, Inc.) were dispersed in 20 mL of 1,2-dichlorobenzene in an ultrasonic bath. After 10 minutes of dispersion, 200 mg PtBA-N₃ was added, and the mixture were stirred at 130 °C for 24 hours. 24 hours later, 200 mg MI-PMMA was also added into the mixture and leave to stir at 110 °C for more 48 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 µm), to remove polymers.

Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until the unreacted polymers could not be detected in the solvent (monitored by FTIR). The recovered black powder was dried under vacuum.

3.1.16.2 DB CNT-9

50 mg of SWCNTs (Sigma-Aldrich) were dispersed in 200 mL of DMF in an ultrasonic bath. After 10 minutes of dispersion, 250 mg PS-SH and 5 mg AIBN were added, and the mixture were stirred at 80 °C for 24 hours. 24 hours later, 250 mg PEG₂₀₀₀-N₃ was also added into the mixture and gradually heated up to 130 °C for more 72 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 µm), to remove polymers. Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until the unreacted polymers could not be detected in the solvent (monitored by FTIR). The recovered black powder was dried under vacuum.

3.1.16.3 DB CNT-10

50 mg of SWCNTs (Sigma-Aldrich) were dispersed in 200 mL of 1,2-dichlorobenzene in an ultrasonic bath. After 10 minutes of dispersion, 250 mg *r*MI-PMMA was added, and the mixture were stirred at 80 °C for 24 hours. 24 hours later, 250 mg PEG₂₀₀₀-N₃ was also added into the mixture, and gradually heated up to 130 °C for more 72 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 µm), to remove polymers. Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until the unreacted polymers could not be detected in the solvent (monitored by FTIR). The recovered black powder was dried under vacuum.

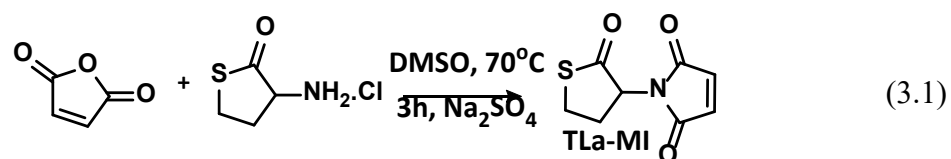
3.2 Results and Discussion

The strategy that have been followed during this chapter, is based on the combination of double “click” reactions such as Diels-Alder cycloaddition, nitrene addition and thiol-ene reaction with carbon nanotubes. First, furan, furan protected maleimide and anthracene end-functionalized polymers are prepared either by ATRP or esterification reaction. Secondly, azide end- functionalized polymers are prepared either by ATRP or esterification reaction. Lastly, thiol end- functionalized polymers are prepared either by RAFT polymerization or esterification reaction. These polymers are added irreversibly to carbon nanotubes (MWCNTs, MWCNTs-COOH, SWCNTs) in situ to undergo the Diels-Alder reaction, nitrene addition, thiol-ene reaction respectively in order to obtain a hybrid nanotube material. In addition to these mono modification reactions, the combination of double click reactions, DA, nitrene addition and thiol-ene reactions were utilized by our group for the first time and observed to be a suitable reaction for polymer-carbon nanotube conjugation as well. Based on the above explanation, last part includes the double click reactions approach, both one-pot and sequential.

3.2.1 Synthesis of organic compounds

Maleimides, a well-known structure in Diels-Alder and Michael-addition reactions, are frequently used in material and bioscience. In addition to maleimides, thialoactones are also quite important since the intermediate product formed by the ring opening reaction following the nucleophilic substitution of thiolactones with amines can give thiol-X reactions.

The synthesis that provided the combination of maleimide and thiolactone structures ((1-(2-oxotetrahydrothiophen-3-yl)-1H-pyrrole-2,5-dione, MI-TLa) was published by Rudolph et al. in 2015 [115]. In this study, MI-TLa was also synthesized same as defined in that publication (3.1). Introducing thiolactone function into the sidewalls of MWCNTs via Diels-Alder reaction is possible presence of maleimide moiety.



As shown in ^1H NMR spectrum, the maleimide signals can be found in 6.76 ppm while the CH_2 protons for the thiolactone are observed between 4.78, 3.35 and 2.81, 2.48 ppm as multiplet signals (Figure 3.2).

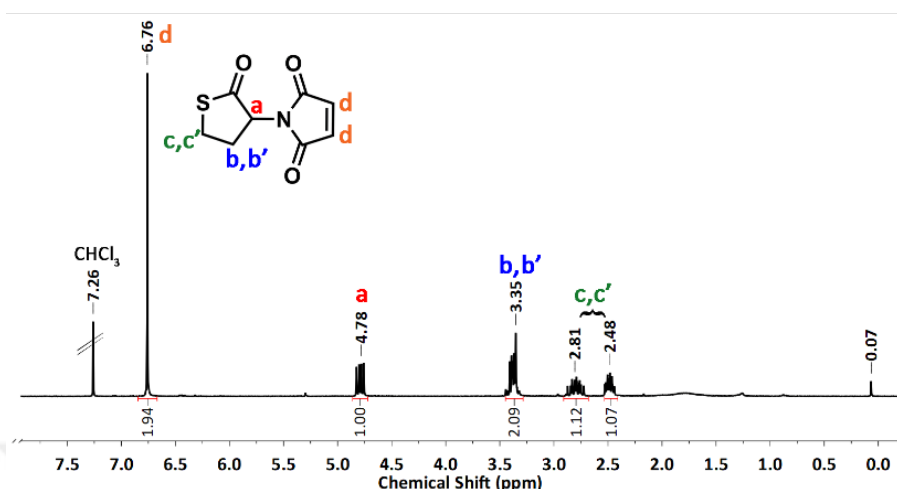


Figure 3.2 : ^1H NMR spectrum of *MI-TLa* in CDCl_3 (500 MHz).

Another approach for loading thiolactone unit onto MWCNTs' sidewalls is nitrene addition reaction. To do this, azide unit should be introduced to thiolactone. Therefore, after the reaction of DL-Homocysteine thiolactone hydrochloride with bromoacetyl bromide, bromide unit of obtained *N*-(2-bromoacetyl) homocysteine- γ -thiolactone (TLa-Br) was converted into azide via substitution reaction in the presence of NaN_3 in acetonitrile as an overnight reaction. As a result of this reaction *N*-(2-azidoacetyl) homocysteine- γ -thiolactone (TLa- N_3) was obtained (3.2).

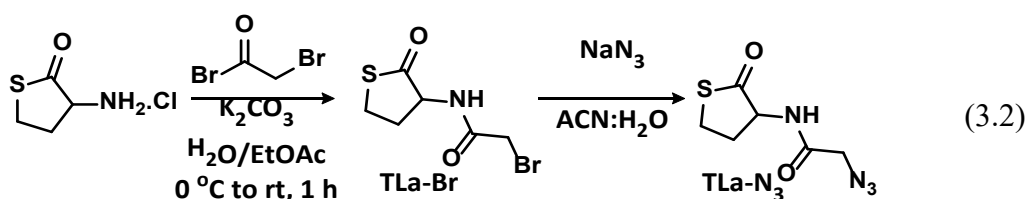


Figure 3.3 shows ^1H NMR spectra of TLa-Br and TLa- N_3 . Azidation was clearly proven by ^1H NMR spectrum of TLa- N_3 (Figure 3.3 (b)) on which chemical shifts of the amide protons are shifted from 8.67 to 8.50 ppm and from 4.68-4.59 to 4.65-4.56 ppm corresponding to $-\text{CHN}_3$.

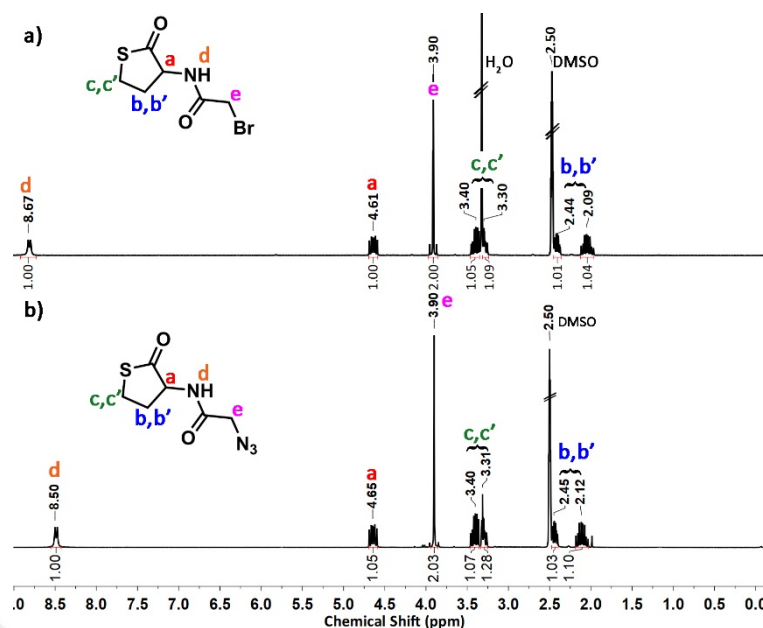


Figure 3.3 : ^1H NMR spectra of (a) *TLa-Br* and (b) *TLa-N₃* in $\text{DMSO-}d_6$ (500 MHz).

Furthermore, observing azide-stretching band at FTIR spectrum have also confirmed the structure of *TLa-N₃* (Figure 3.4) which have been observed by ^1H NMR spectrum.

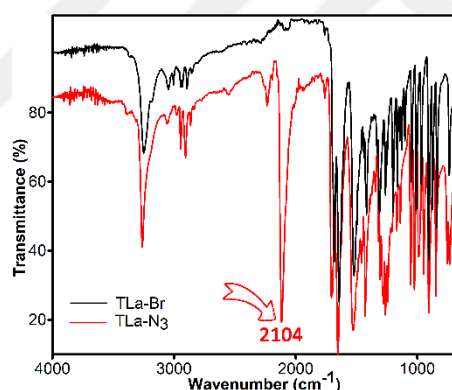
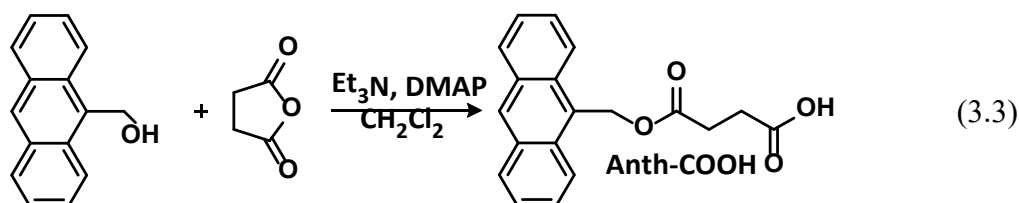


Figure 3.4 : Infrared spectra overlay of *TLa-Br* and *TLa-N₃*.

9-anthracene methanol was used as a starting material. The hydroxyl functionality was converted to carboxylic acid by a reaction with succinic anhydride in the presence of Et_3N /DMAP catalyst system and CH_2Cl_2 as solvent to give 4-(anthracen-9-ylmethoxy)-4-oxobutanoic acid (*anth-COOH*) (3.3).



The structure was confirmed by ^1H NMR spectrum (Figure 3.5). A shift of methylene protons linked to anthracene ring due to esterification reaction from 5.6 ppm to 6.21

ppm and multiplet peaks around 2.68-2.62 ppm assigned to $C=OCH_2CH_2C=O$ clearly indicates that *anth-COOH* was achieved.

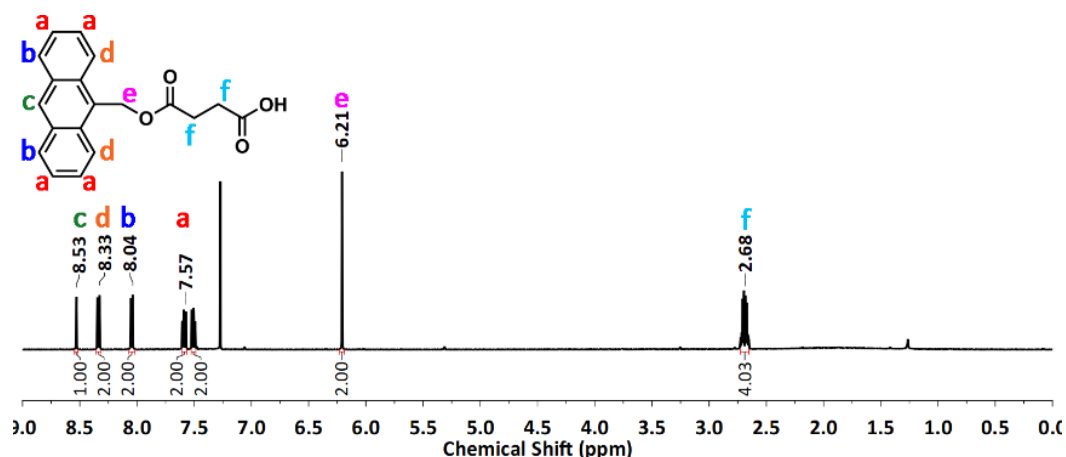
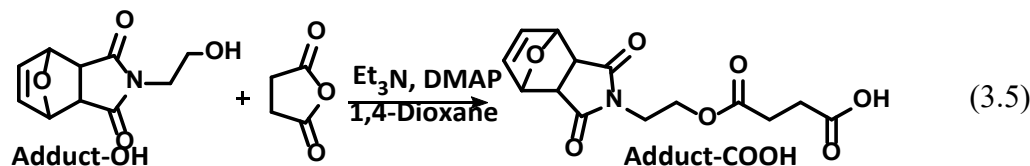
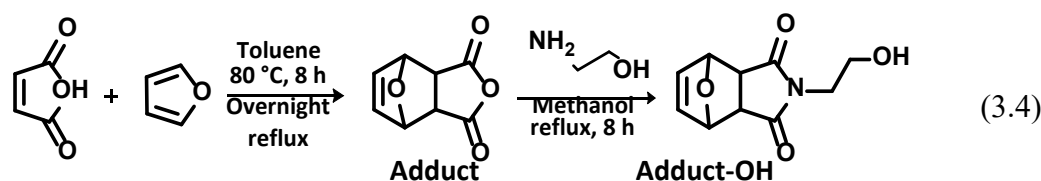


Figure 3.5 : ^1H NMR spectrum of 4-(anthracen-9-ylmethoxy)-4-oxobutanoic acid (*anth-COOH*) in CDCl_3 (500 MHz).

The initiator with proper functionalities for Diels-Alder reaction was first prepared. 4-(2-hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione, (*adduct-OH*) was first synthesized in two steps. Furan and maleic anhydride were reacted in toluene at 80 °C, then the formed 3 α ,4,7,7 α -tetrahydro-4,7-epoxyisobenzofuran-1,3-dione (*adduct*) (3.4), was utilized for the synthesis of *Adduct-OH* by adding the solution 2-amino ethanol in methanol into dispersion of *Adduct* in methanol (3.4).



By overlaying the ^1H NMR spectra of *Adduct-OH* and *Adduct-COOH* onto each other, it can clearly be seen that the methylene protons next to OH were present at 3.69-3.74 ppm. Moreover, the characteristic protons of the adduct were also present at 6.51 ppm (bridge vinyl protons), 5.27 ppm (bridge-head protons) and 2.88 ppm (bridge protons) respectively. These results confirmed that the synthesis of *adduct-OH* was accomplished (Figure 3.6 (a)).

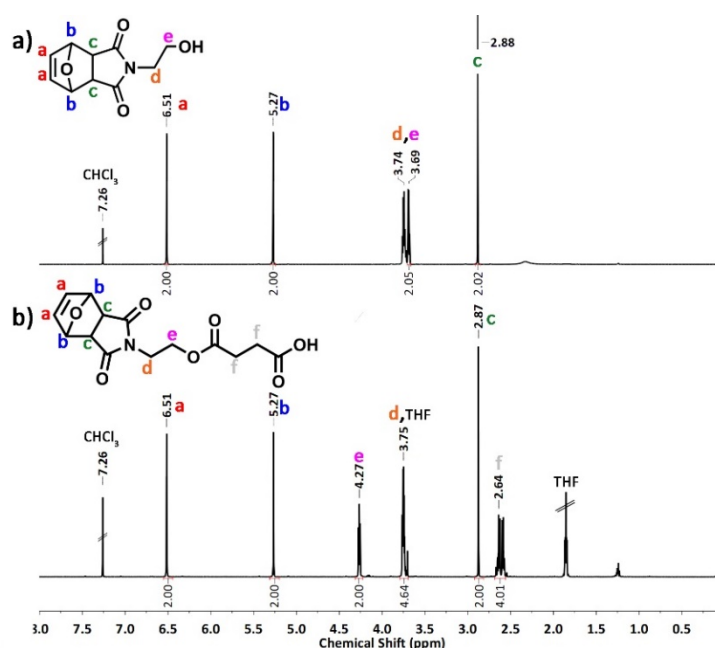
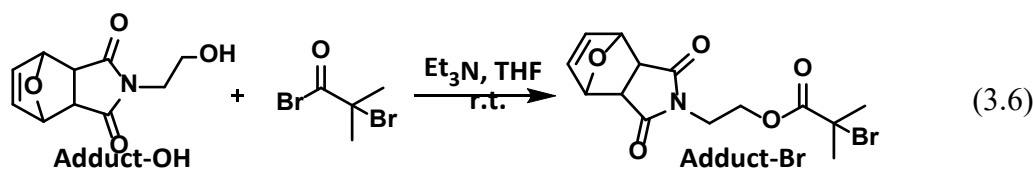


Figure 3.6 : ¹H NMR spectra of (a) 4-(2-hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione (*adduct-OH*) and (b) 1,4-dioxane as solvent in order to give 4-(2-ethoxy)-4-oxobutanoic acid (*adduct-COOH*) in CDCl₃ (500 MHz).

In oncoming case, Adduct-COOH was used as a starting material to introduce furan protected maleimide function into polymers. The hydroxyl functionality of Adduct-OH was converted to carboxylic acid by a reaction with succinic anhydride in the presence of Et₃N/DMAP catalyst system and 1,4-dioxane as solvent in order to give 4-(2-ethoxy)-4-oxobutanoic acid (*adduct-COOH*) (3.5).

From ¹H NMR spectrum (Figure 3.6 (b)) of *adduct-COOH*, methylene protons next to the ester (NCH₂CH₂OC=O) and methylene protons adjacent to nitrogen (NCH₂CH₂OC=O) appeared at 4.27 ppm and 3.75 ppm respectively. Moreover, there were multipled peaks around 2.64-2.53 ppm, which confirmed successful conversion of hydroxyl group to carboxylic acid.

First, the initiators with proper functionalities for Diels-Alder reaction were prepared. 2-bromo-2-methyl-propionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo[5.2.1.02,6]dec-8-en-4-yl) ethyl ester (*adduct-Br*) was first synthesized in three steps. Following synthesis of Adduct-OH in two aforementioned steps (3.4), the last synthesis step of Adduct-Br was obtained by an esterification reaction between Adduct-OH and 2-bromoisobutryl bromide in THF at room temperature (3.6).



From ^1H NMR spectrum (Figure 3.7) of *Adduct-Br*, it can clearly be seen that the methyl protons next to Br were present at 1.88 ppm and the methylene protons next to the ester unit were present at 4.31 ppm. Moreover, the characteristic protons of adduct were also detected at 6.50 ppm (bridge vinyl protons), 5.25 ppm (bridge-head protons) and 2.85 ppm (bridge protons) respectively. These results confirmed that the synthesis of *Adduct-Br* was achieved.

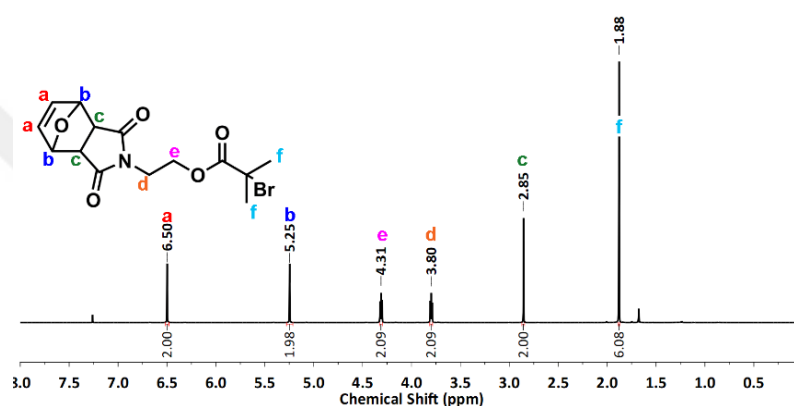
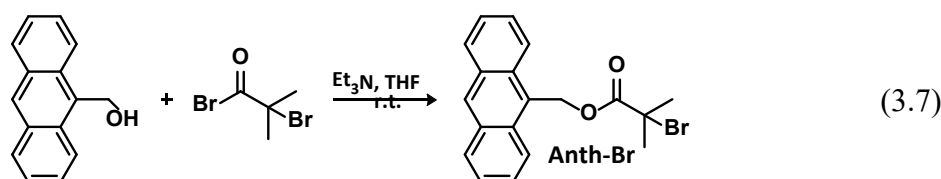


Figure 3.7 : ^1H NMR spectrum of 2-bromo-2-methyl-propionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl) ethyl ester (*Adduct-Br*) in CDCl_3 (500 MHz).

Another initiator with anthracene functionality for Diels-Alder reaction was prepared. 9-anthrylmethyl 2-bromo-2-methyl propanoate (*Anth-Br*) was first synthesized as an ATRP initiator by an esterification reaction between 9-anthracene methanol and 2-bromoisobutryl bromide in THF at room temperature (3.7).



Anth-Br was characterized by ^1H NMR from which anthracene protons were detected between 8.53 and 7.50 ppm, along with methylene protons adjacent to the anthracene and methyl protons next to Br were detected at 6.23 and 1.86 ppm, respectively (Figure 3.8). These results confirmed the structure of *Anth-Br*.

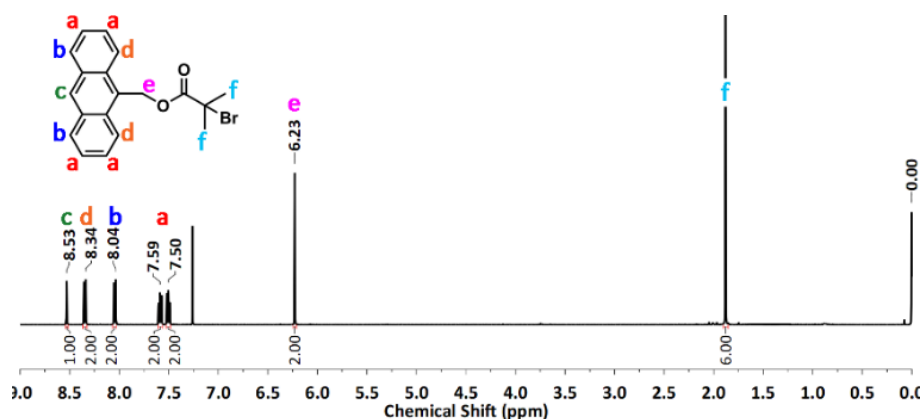
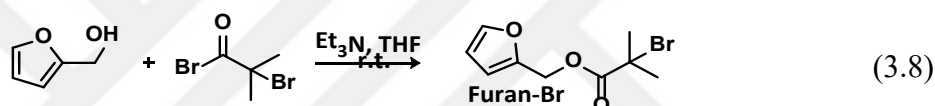


Figure 3.8 : ¹H NMR spectrum of anthracen-9-ylmethyl 2-bromo-2-methylpropanoate (*Anth-Br*) in CDCl₃ (500 MHz).

Lastly, initiator with furan functionality for Diels-Alder reaction was prepared. furan-2-ylmethyl 2-bromo-2-methylpropanoate (*Furan-Br*) was first synthesized as an ATRP initiator by an esterification reaction between furfuryl alcohol and 2-bromoisobutryl bromide in THF at room temperature (3.8).



Furan-Br was characterized by ¹H NMR from which furan protons were detected between 7.43, 6.44 and 6.37 ppm, along with methylene protons adjacent to the furan and methyl protons next to Br were detected at 5.15 and 1.92 ppm, respectively (Figure 3.9). These results confirmed the structure of *Furan-Br*.

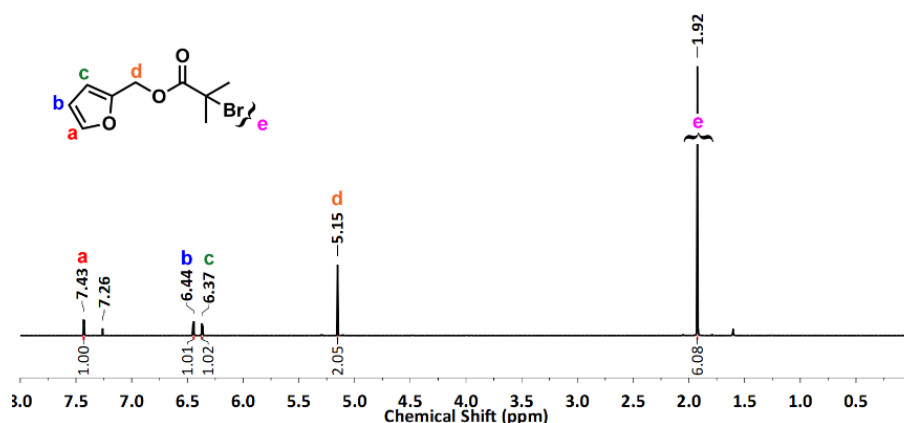
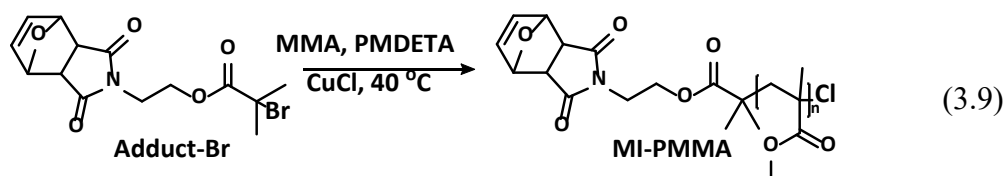


Figure 3.9 : ¹H NMR spectrum of furan-2-ylmethyl 2-bromo-2-methylpropanoate (*Furan-Br*) in CDCl₃ (500 MHz).

3.2.2 Synthesis of end-functional polymers

The experimental conditions of all polymers and results are given in Table 3.1 and Table 3.2.

Adduct-Br was used as an initiator in ATRP of MMA in the presence of CuCl/PMDETA as a catalyst system at 40 °C to obtain MI-PMMA (3.9). The maleimide functional group of the adduct-Br was protected with furan in order to prevent radical copolymerization of maleimide with MMA during polymerization. The polymerization temperature was deliberately kept low to avoid furan deprotection at elevated temperatures.



The $M_{n,NMR}$ of MI-PMMA (Figure 3.10) was determined from a ratio of integrated peaks at 3.59 ppm (OCH_3 protons of MMA) and $N-CH_2$ (δ 3.8 -3.4) which have signal 6.54 ppm as vinylic two protons, while being included the molecular weight of initiator (358 g/mol). The number-average molecular weight obtained by GPC ($M_{n, GPC} = 3390$ g/mol, relative to linear PMMA standards) is consistent with $M_{n,NMR}$, which indicates that the quantitative maleimide end-group functionalization of the PMMA was successful. Moreover, $M_w/M_n = 1.18$ calculated from GPC displays narrow molecular weight distribution.

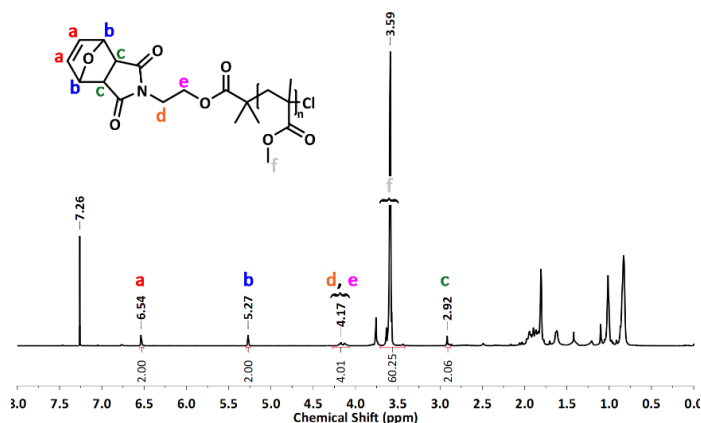
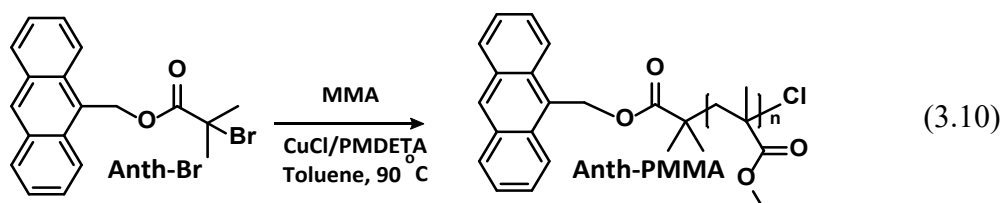


Figure 3.10 : ^1H NMR spectrum of MI-PMMA in $CDCl_3$ (500 MHz).

Linear α -anthracene-PMMA (Anth-PMMA) was prepared by ATRP of MMA using anth-Br as an initiator and CuCl/PMDETA as catalyst at 90 °C for 25 min (3.10).



$DP_n = 45$ and $M_{n, \text{NMR}} = 4800$ were determined from an integration ratio of a broad signal at 3.59 ppm which indicates $-\text{OCH}_3$ protons of MMA and a signal at 6.05 ppm which can be assigned to methylene protons adjacent to the anthracene, by including the molecular weight of initiator (357 g/mol) (Figure 3.11).

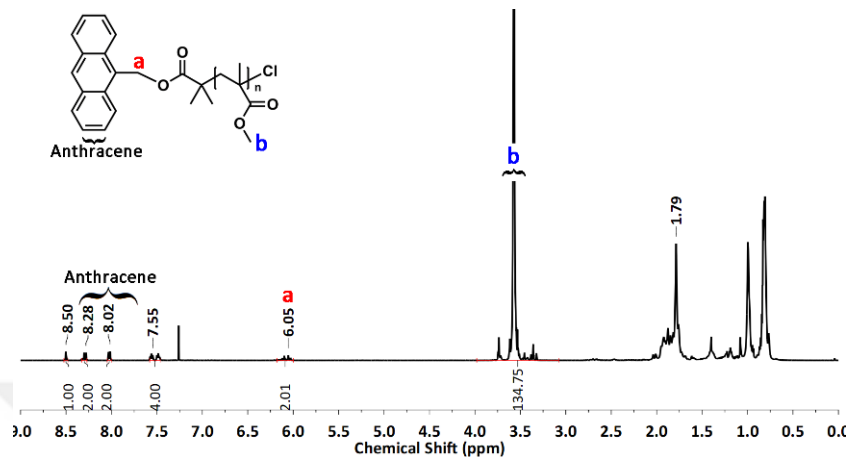
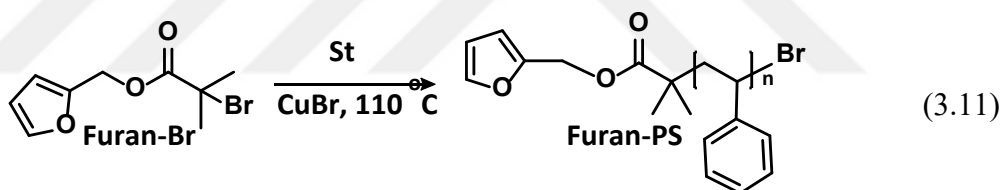


Figure 3.11 : ^1H NMR spectrum of *anth-PMMA* in CDCl_3 (500 MHz).

Linear α -furan-PS (Furan-PS) was prepared by ATRP of PS using Furan-Br as an initiator and $\text{CuBr}/\text{PMDETA}$ as catalyst at 110°C for 25 min (3.11).



The GPC and ^1H NMR spectroscopy (Figure 3.12) confirmed that functionalized polystyrene was properly prepared with controlled molecular weight ($M_{n, \text{GPC}} = 8870$ g/mol), low molecular weight distribution ($M_w/M_n = 1.07$) and desired functionalities (5.06 ppm, 2H, methylene protons adjacent to the furan).

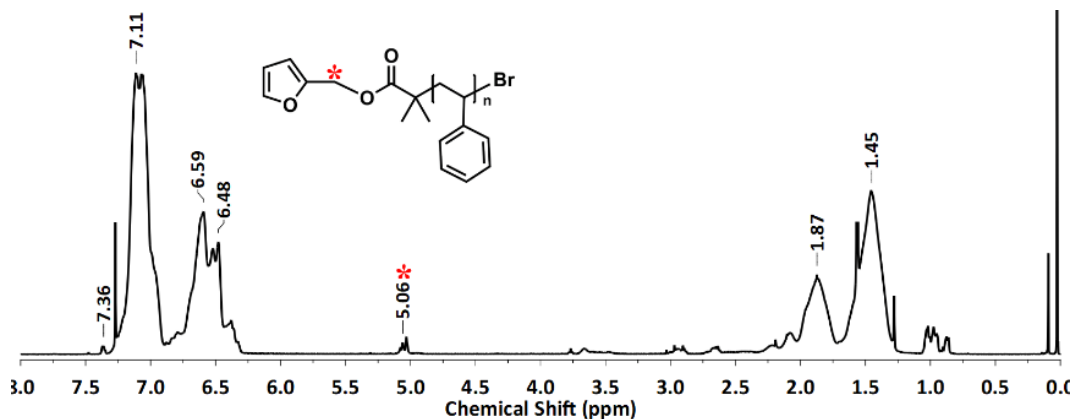
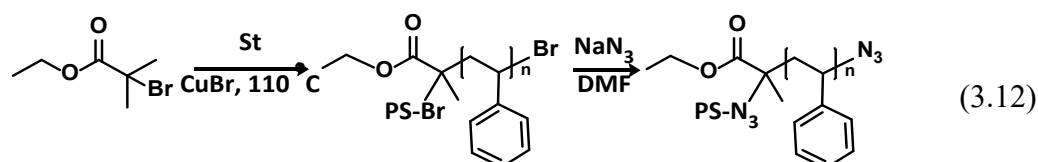


Figure 3.12 : ^1H NMR spectrum of *furan-PS* in CDCl_3 (500 MHz).

Azide-end functionalized polystyrene was produced in two steps. Firstly, PS-Br was obtained by ATRP of Styrene using ethyl α -bromoisobutyrate (EiBr) initiator. In the second step, the dried product was dissolved in DMF and NaN_3 was added to the mixture. Then it was stirred overnight at room temperature. Finally, PS- N_3 was obtained (3.12).



The GPC and ^1H NMR spectroscopy (Figure 3.13) confirmed that functionalized polystyrene was properly prepared with controlled molecular weight ($M_{n, \text{GPC}} = 2720$ g/mol), low molecular weight distribution ($M_w/M_n = 1.07$) and desired end-group functionalities (3.93 ppm (br, 2H, $\text{CH}(\text{Ph})\text{-N}_3$ end group of PS).

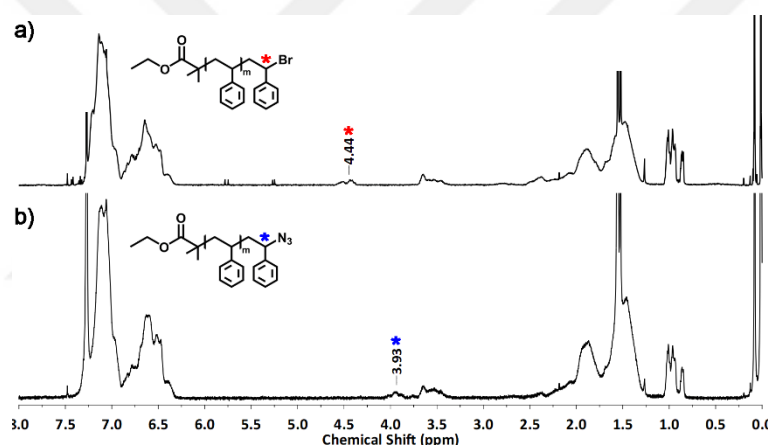
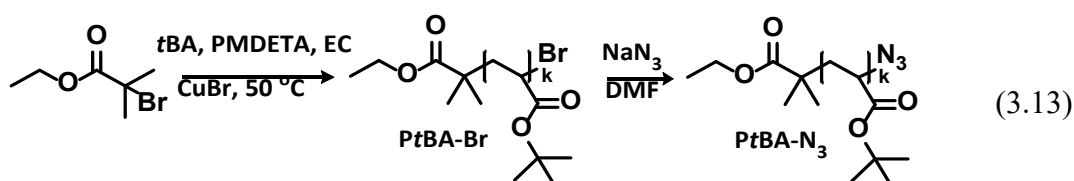


Figure 3.13 : ^1H NMR spectra of (a) PS-Br and (b) PS- N_3 in CDCl_3 (500 MHz).

The outer precursor PtBA-N_3 was also prepared in two steps (3.13). First PtBA-Br was efficiently synthesized by ATRP of $t\text{BA}$ using ethyl α -bromoisobutyrate as initiator. $M_{n, \text{NMR}}$ was calculated as 4500 g/mol by an integration area ratio of $-\text{CH}_2\text{OC}=\text{O}$ and $-\text{CHBr}$ end groups at 4.1 ppm and $-\text{CH}$ on the PtBA backbone at 2.2 ppm.



The results from NMR and GPC displayed that a successful living polymerization reaction occurred (Table 3.1). As a second step, the terminal Br functionality of linear PtBA-Br was facilely converted to the azide moiety by reacting with NaN_3 in DMF at 50 °C in order to give PtBA-N_3 .

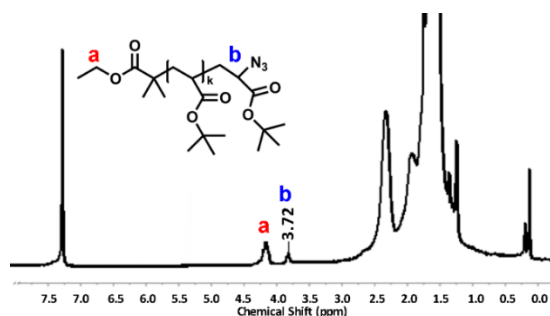


Figure 3.14 : ^1H NMR spectrum of PtBA-N₃ in CDCl₃ (500 MHz).

Azidation was clearly evidenced by ^1H NMR spectrum of PtBA-N₃ that a new signal corresponding to $-\text{CHN}_3$ at 3.72 ppm emerged (Figure 3.14).

Table 3.1: The experimental conditions and results of polymers that synthesized via ATRP.

Polymer	Initiator	Time	Temp. (°C)	M_n , GPC ^g	$\bar{D}$
MI-PMMA ^a	Adduct-Br	30 min	40	3390 ^h	1.18
Anth-PMMA ^b	Anth-Br	1 hour	90	3400 ^h	1.25
Furan-PS ^c	Furan-Br	1 hour	110	8870	1.07
PS-Br ^d	EiBr	1 hour	110	1950	1.13
PS-N ₃ ^e	-	overnight	r.t.	2720	1.07
PtBA-Br ^f	EiBr	45 min	50	3950	1.15
PtBA-N ₃ ^e	-	overnight	50	4500	1.10

^a [M]₀: [I]₀: [CuCl]: [PMDETA] = 50:1:1:1; polymerization was carried out at 40 °C. MMA/toluene = 1 (v/v).

^b [M]₀: [I]₀: [CuCl]: [PMDETA] = 200:1:1:1; polymerization was carried out at 90 °C. MMA / toluene = 1 (v/v).

^c [M]₀: [I]₀: [CuBr]: [PMDETA] = 200:1:1:1; polymerization was carried out at 110 °C.

^d [M]₀: [I]₀: [CuBr]: [PMDETA] = 200:1:1:1; polymerization was carried out at 110 °C.

^e Polymer (PS-Br or PtBA-Br) and NaN₃ in DMF stirred at room temperature for overnight.

^f [M]₀: [I]₀: [CuBr]: [PMDETA] = 100:1:1:1; polymerization was carried out at 50 °C. tBA/EC = 10 (w/w).

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

^h Determined by using GPC in THF at 30 °C relative to PMMA standards.

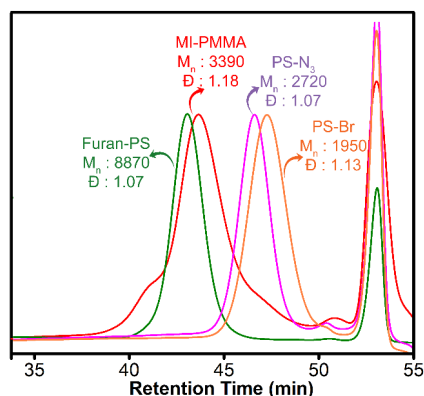
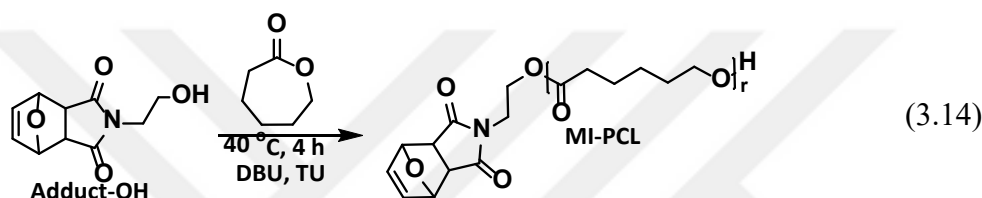


Figure 3.15 : Overlay GPC traces of MI-PMMA (red), anth-PMMA (blue), Furan-PS (green), PS-Br (orange), PS-N₃ (pink).

Moreover, the absolute molecular weights of polymers synthesized by ATRP collected in Table 3.1 and the corresponding GPC overlay traces are given in Figure 3.15. GPC traces of the all ATRP polymers were monomodal and had a low polydispersity index between 1.18 - 1.05 (Table 3.1).

Then compound adduct-OH was used as an initiator in ROP of ϵ -CL in the presence of both DBU and TU as a catalyst system at 40 °C, 4hours to obtain PCL-MI (3.14). The maleimide functional group of the adduct-OH was protected with furan in order to prevent radical copolymerization of maleimide with ϵ -CL during polymerization. The polymerization temperature was deliberately kept low to avoid furan deprotection at elevated temperatures.



Polymer was determined accordingly from the integration of the peaks at 4.05 ppm as PCL repeating unit protons and N-CH₂ (δ 3.8 -3.4) which have signal at 6.51 ppm as vinylic two protons (Figure 3.16).

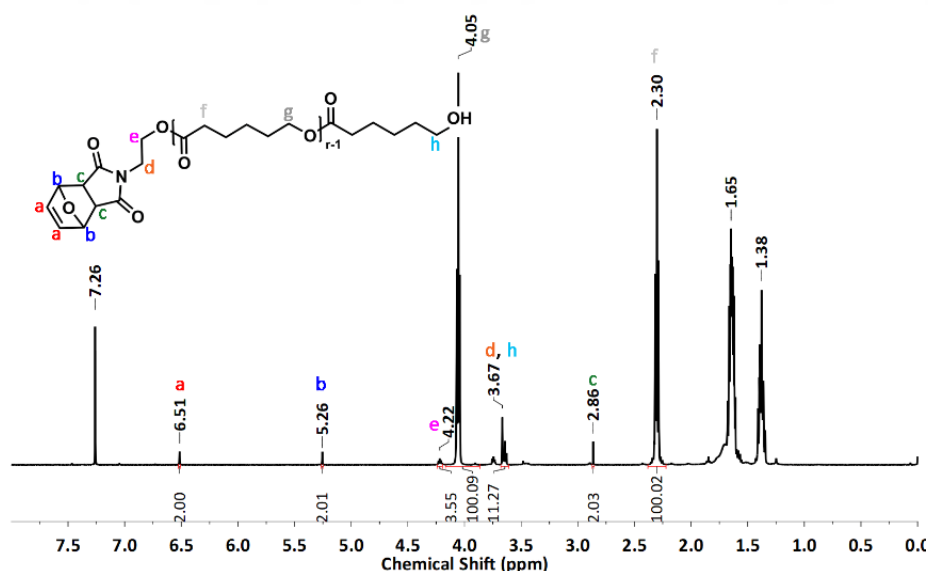
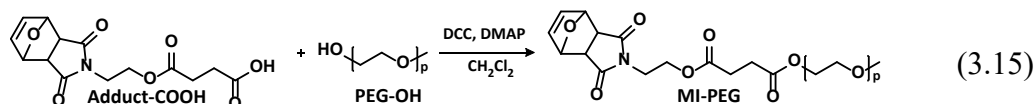


Figure 3.16 : ¹H NMR spectrum of *MI-PCL* in CDCl₃ (500 MHz).

After ATRP of the precursor polymers, esterification reaction of PEG precursors was carried out.

First, MI-PEG was synthesized in two steps. In this case, adduct-OH was used as a starting material (3.4). The hydroxyl functionality of adduct-OH was converted to the

carboxylic acid by a reaction with succinic anhydride in the presence of Et₃N/DMAP as catalyst system and 1,4-dioxane as solvent in order to give adduct-COOH (3.5). Then, the commercially available Me-PEG-OH (*M*_n = 2000 g/mol) was reacted with adduct-COOH to obtain MI-PEG (3.15).



The structure of the desired MI-PEG could be fully identified by ¹H NMR (Figure 3.17). The characteristic protons of MI-PEG, such as vinyl (*CH=CH*), bridge-head (*CHCH=CHCH*), repeating unit of PEG (*OCH₂CH₂*) and bridge *CH₂N(C=O)CH-CH*) have signals at 6.50, 5.25, 3.90 - 3.54 and 2.86 ppm, respectively. The *M*_n, NMR was determined by comparing the integral of vinyl end group signal (δ 6.50) as repeating unit of PEG and N-CH₂ (δ 3.9-3.54), while including the MW of adduct-COOH.

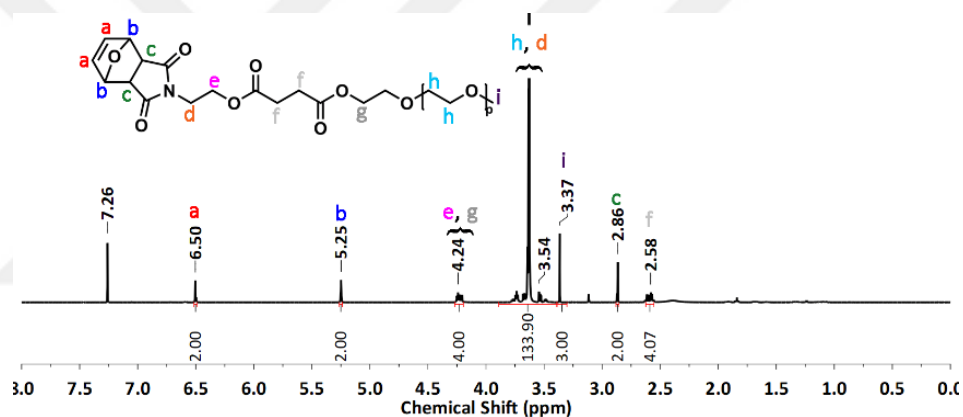
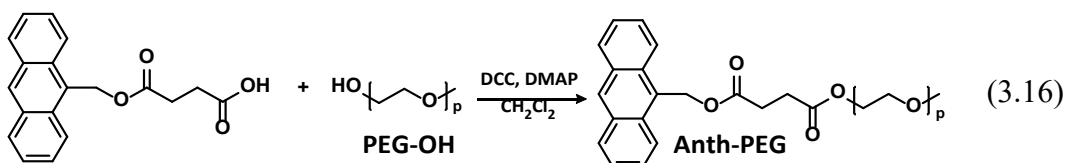


Figure 3.17 : ¹H NMR spectrum of *MI-PEG* in CDCl₃ (500 MHz).

In order to obtain the other precursors of PEG polymers, anth-PEG was synthesized in two steps. In this case, 9-anthracene methanol was used as a starting material. The hydroxyl functionality of 9-anthracene methanol was converted to the carboxylic acid by a reaction with succinic anhydride in the presence of Et₃N/DMAP as catalyst system and 1,4-dioxane as solvent in order to give 4-(anthracen-9-ylmethoxy)-4-oxobutanoic acid (anth-COOH) (3.5).

Then, the commercially available Me-PEG-OH (*M*_n = 2000 g/mol) was reacted with anth-COOH to obtain anth-PEG.



Anth-PEG was obtained by an esterification reaction between Me-PEG-OH ($M_n=2000$ g/mol) and excess amount of anth-COOH in the presence of DCC as a coupling agent and DMAP as a catalyst (3.16).

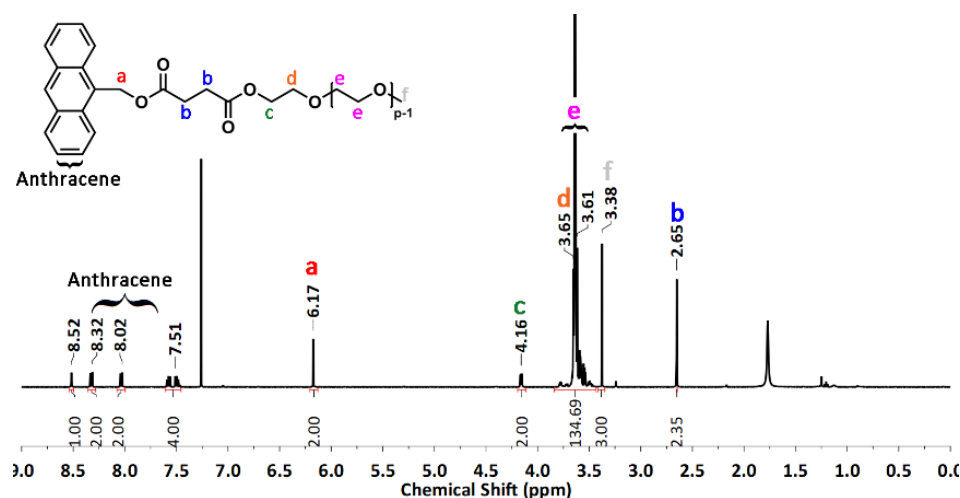
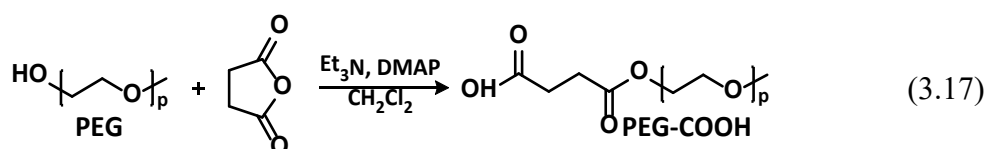


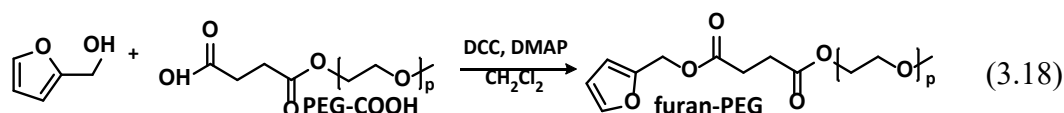
Figure 3.18 : ^1H NMR spectrum of *anth-PEG* in CDCl_3 (500 MHz).

From ^1H -NMR spectrum of Anth-PEG, the ring protons at 8.52-7.51 ppm, methylene protons linked to the ring at 6.17 ppm and the end group methylene protons of PEG (PEG- $\text{OCH}_2\text{CH}_2\text{OC}=\text{O}$) at 4.16 ppm were primarily detected (Figure 3.18). Number-average molecular weight ($M_{n, \text{NMR}} = 2000$) of Anth-PEG which is obtained by the NMR was determined by a ratio of integrated peaks at 3.62 ppm (OCH_2CH_2 protons of PEG) to 6.17 ppm (CH_2 -anthracene).

Thirdly, furan-PEG was synthesized in two steps. First of all, the hydroxyl functionality of the commercially available Me-PEG-OH ($M_n = 2000$ g/mol) was converted to carboxylic acid by a reaction with succinic anhydride in the presence of Et_3N /DMAP as catalyst system and 1,4-dioxane as solvent in order to give PEG-COOH (3.17).



Secondly, furfuryl-alcohol could react with PEG-COOH to give furan-PEG. Furan-PEG was obtained by an esterification reaction between Me-PEG-OH ($M_n=2000$ g/mol) and excess amount of furfuryl-alcohol in the presence of DCC as a coupling agent and DMAP as a catalyst (3.18). The raw product was precipitated in cold diethyl ether and further purified by two times dissolution-precipitation cycle.



^1H NMR spectrum of *Furan-PEG* clearly shows the characteristic signal of PEG units at 3.63 ppm together with furan at 7.42, 6.40 and 6.36 ppm thus strongly confirming the target structure was obtained (Figure 3.19). Thus, the number-average molecular weight of *Furan-PEG* which is obtained by NMR ($M_{n, \text{NMR}}$) is determined to be 53 ($\text{DP}_n \times 44 + \text{molecular weight (M}_w\text{) of furfuryl-alcohol} \approx 2430$).

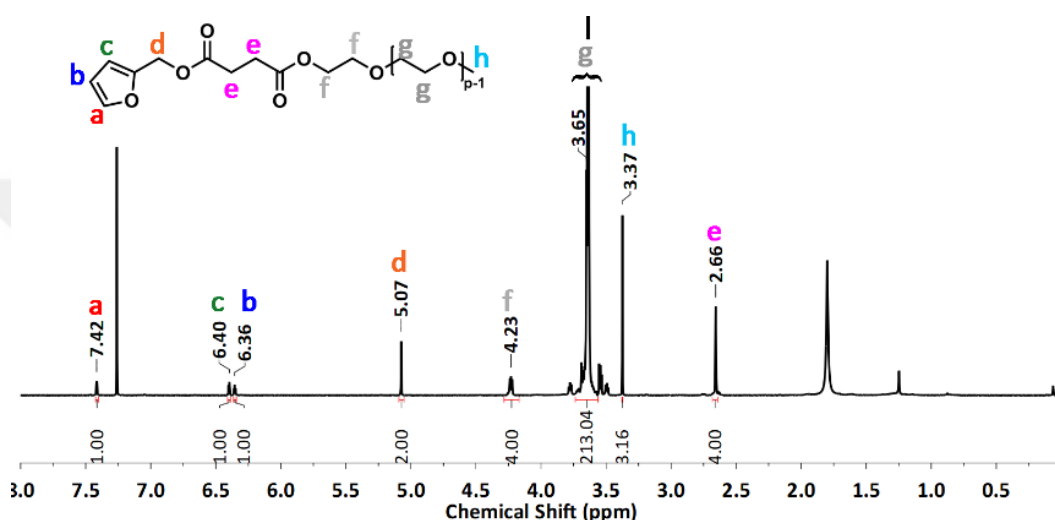
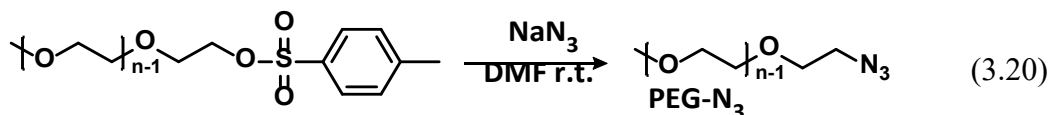
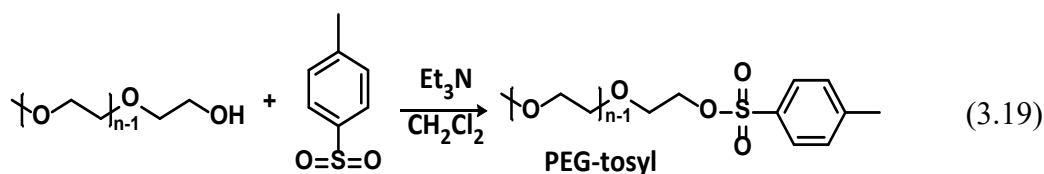


Figure 3.19 : ^1H NMR spectrum of *furan-PEG* in CDCl_3 (500 MHz).

Moreover, hydroxyl terminated PEG was first tosylated using tosyl chloride and then converted to azide form by reacting NaN_3 in DMF at room temperature. (3.19 and 3.20).



The structure of PEG-N_3 was confirmed by ^1H NMR spectroscopy. The signals of CH_2O end group of the PEG was shifted from 4.17 to main peak of PEG which is present at 3.65 ppm after the azide formation. Additionally, the ArH (7.80-7.34 ppm) and CH_3 (2.57 ppm) of the tosyl group disappeared from the spectrum (Figure 3.20).

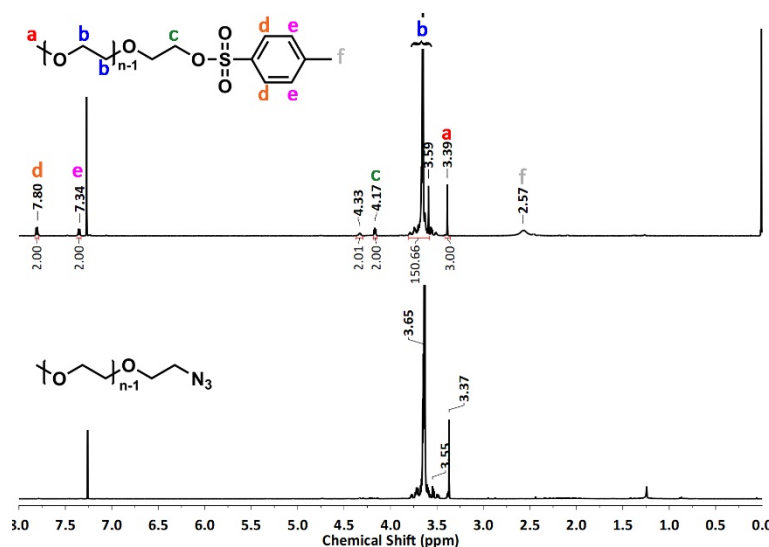


Figure 3.20 : ¹H NMR spectra of (a) PEG-tosyl and (b) PEG-N₃ in CDCl₃ (500 MHz).

Further evidence for PEG-N₃ formation was obtained by FT-IR spectroscopy. Although azidation can not be followed by ¹H NMR for this case, in the FT-IR spectrum a weak band for azide group was detected at 2094 cm⁻¹ (Figure 3.21).

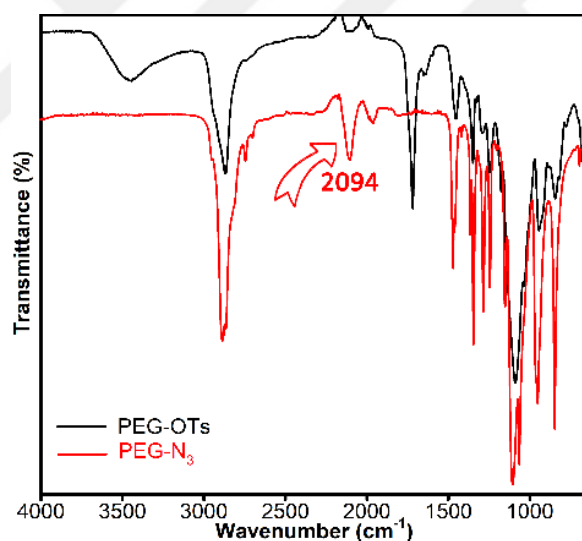
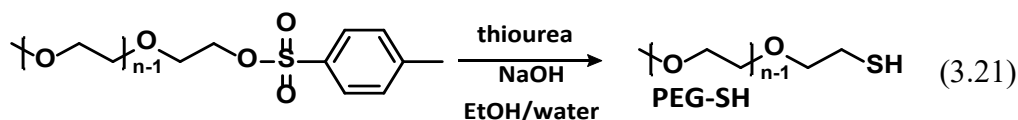


Figure 3.21 : FT-IR spectra of PEG-tosyl and PEG-N₃.

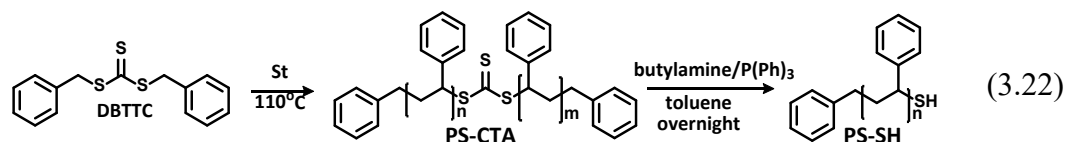
Hydroxyl terminated PEG was first tosylated using tosyl chloride and then converted to thiol form by reacting thiourea and NaOH in ethanol/H₂O mixture at reflux temperature under nitrogen. (3.21).



After purification, a clear shift to higher molecular weight region was observed from GPC measurement proved the formation of PEG-SH (Figure 3.24).

Thiol-terminated polymers which were synthesized by RAFT polymerization were kindly donated by Dr. Özcan Altıntaş.

A welldefined thiocarbonylthio terminated polystyrene (PS-CTA) was obtained by RAFT polymerization of styrene in toluene using DBTTC as chain transfer agent. Subsequently, PS-CTA was aminolysized using *n*-butylamine and then treated by P(Ph)₃ (3.22).



¹H NMR spectra of α-thiol PS and PS-CTA are shown in Figure 3.22. The singlet of the methine proton (red asterisk) (–SC(=S)S–CH(Ph)–) of PS-CTA was shifted from 4.51 to 3.50 ppm which indicates the presence of methine proton (blue asterisk) (HS–CH(Ph)–).

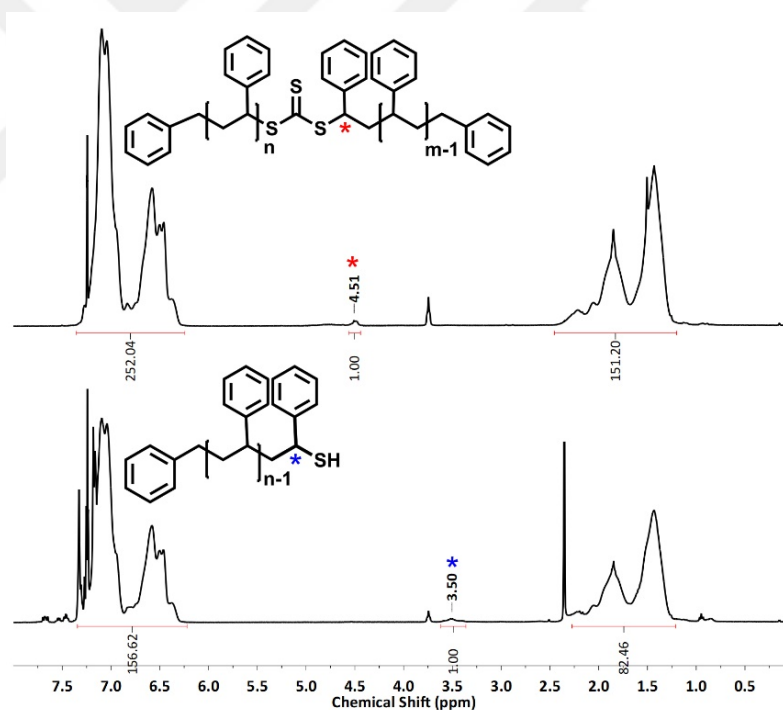


Figure 3.22 : ¹H NMR spectra of (a) PS-CTA and (b) PS-SH in CDCl₃ (500 MHz).

Another welldefined thiocarbonylthio terminated polymer, poly(butylacrylate) (PnBA-CTA) was obtained by RAFT polymerization of *n*-butylacrylate in toluene using DBTTC as chain transfer agent. Subsequently, PS-CTA was aminolysized using *n*-butylamine and then treated by P(Ph)₃ (3.23, Figure 3.23).

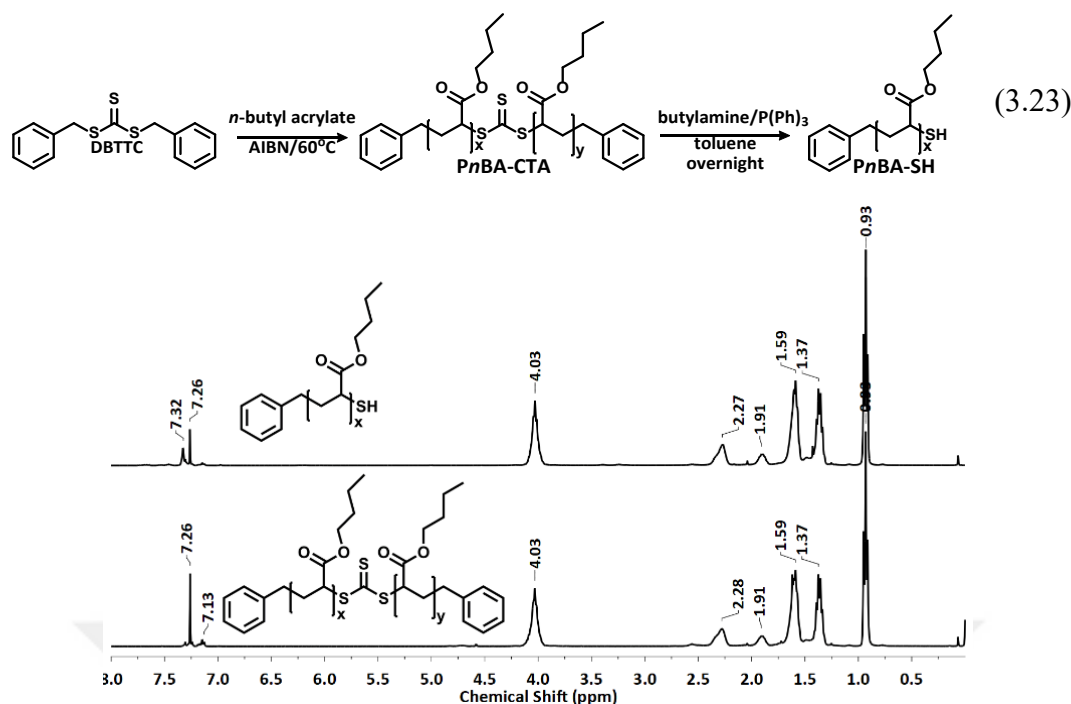


Figure 3.23 : ^1H NMR spectra of (a) PnBA-CTA and (b) PnBA-SH in CDCl_3 (500 MHz).

Table 3.2: Summarizes the experimental conditions and results of the polymers used for the modification of carbon nanotubes.

Polymer	Time	Temp ($^{\circ}\text{C}$)	M_n , GPC ^f	$\bar{D}$ ^f
MI-PCL ^a	4 h	40	5190	1.30
MI-PEG ^b	overnight	RT	2100	1.12
Anth-PEG ^c	overnight	RT	2360	1.05
Furan-PEG ^d	overnight	RT	2600	1.10
PEG-Tosyl	overnight	RT	3650	1.07
PEG-N ₃	overnight	RT	3740	1.14
PEG-SH	6 h	70	4080	1.18
PS-CTA	1 h	110	6415	1.25
PS-SH ^e	overnight		4290	1.24
PnBA-CTA	4 h	60	25900	1.12
PnBA-SH ^e	overnight		14090	1.29

^a Synthesized by ROP of ϵ -CL in CH_2Cl_2 using DBU/TU as a catalyst and Adduct-OH as an initiator at 40°C . $[\text{M}]_0:[\text{I}]_0 = 40$.

^b Obtained by an esterification reaction between compound Adduct-COOH and Me-PEG-OH (2000).

^c Obtained by an esterification reaction between compound Anth-COOH and Me-PEG-OH (2000).

^d Obtained by an esterification reaction between compound Furfuryl alcohol and Me-PEG-COOH.

^e Obtained by RAFT polymerization in the presence of DBTTC chain transfer agent.

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

Moreover, the absolute molecular weights of other polymers collected in Table 3.2 and the corresponding GPC overlay traces are given in Figure 3.24.

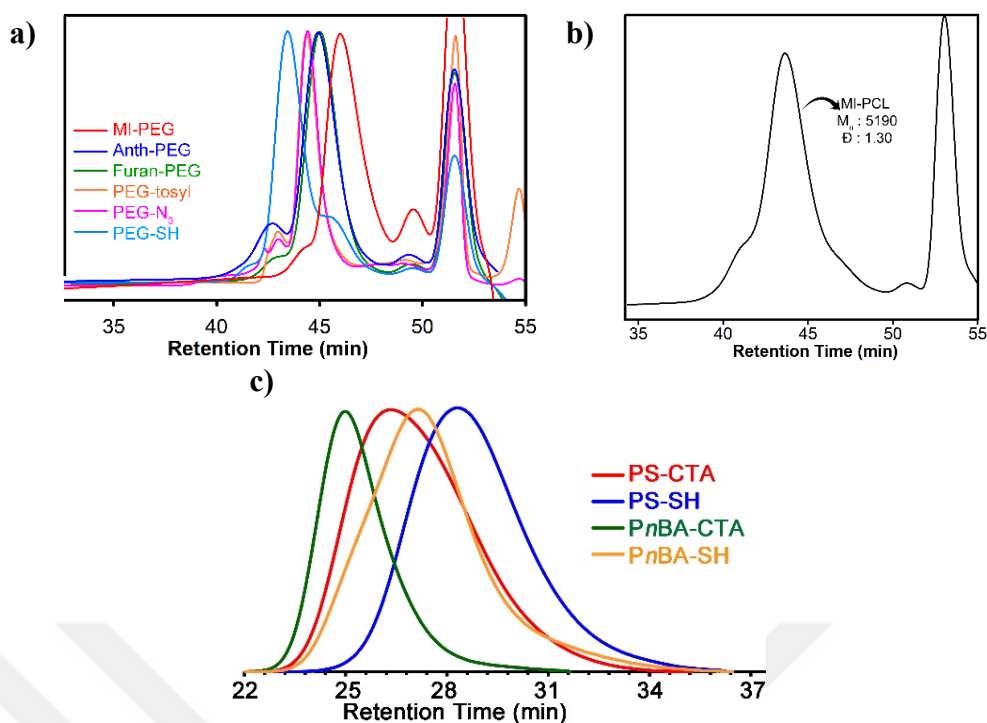


Figure 3.24 : Overlay GPC traces of (a) MI-PEG (red), anth-PEG (blue), furan-PEG (green), PEG-tosyl (orange), PEG-N₃ (pink), PEG-SH (light blue), and (b) MI-PCL (black) (c) PS-CTA (red), PS-SH (blue), PnBA-CTA (green) and PnBA-SH (orange).

GPC traces of the all polymers was monomodal and had a low polydispersity index between 1.30 - 1.05 (Figure 3.24).

3.2.3 Model reactions with CNTs

Before starting the double modification reactions of carbon nanotubes, four model experiments were designed in order to prove and evaluate the efficiency of these reactions. For this purpose, model reactions were arranged by using MI-TLa, 9-anthracenemethanol, furfuryl alcohol, TLa-N₃ and they reacted with carbon nanotubes to give previously designed reactions such as Diels-Alder cycloaddition, nitrene addition and thiol-ene reaction (Figure 3.25). The obtained products are named as MR-1 to MR-4.

The formation of the model reactions was further confirmed by FT-IR spectroscopy and TGA. Change in the weight loss of the MWCNTs samples functionalized with small molecules which have been measured between 250-650 °C, indicated that effective reactions were achieved. Subsequently, mono modification of various carbon nanotubes with polymers were carried out using similar conditions as described for model reaction. Then, double modification test reactions were carried out.

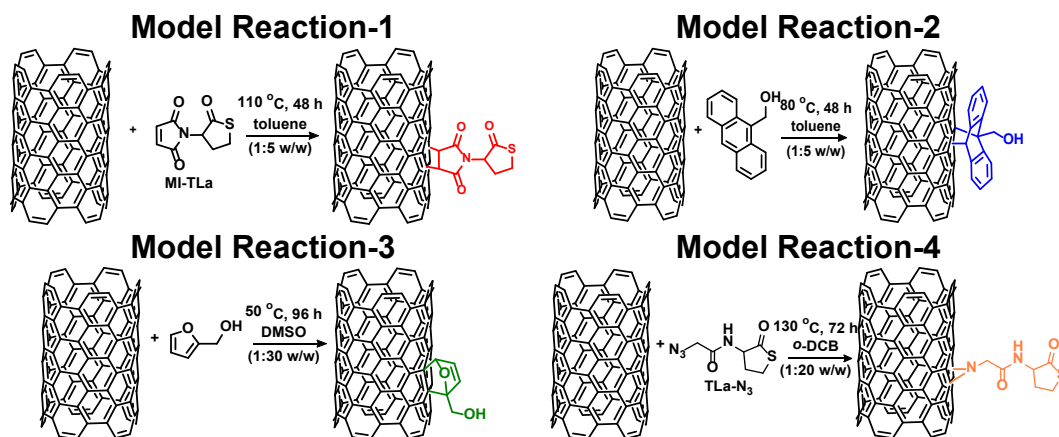


Figure 3.25 : Schematic illustration of model reactions.

FT-IR and TGA techniques have been utilized to characterize the model reaction samples. Figure 3.26 and Figure 3.27 show the infrared spectra of the pristine carbon nanotubes and Model Reaction-1 and 4. The transmission spectra of all carbon nanotubes were taken in a spectral range of $400 - 4000 \text{ cm}^{-1}$ with a resolution of 4 cm^{-1} and average of 64 scans. Moreover, the carbon nanotube samples were pressed with KBr into a pellet before measuring the infrared absorption spectra.

As described in the literature, FTIR spectra of pure CNTs do not exhibit any of the characteristic peaks of organic or inorganic chemical groups. Peaks at around 980 and 3430 cm^{-1} are assumed as OH groups, due to the adsorption of atmospheric moisture or remains of some purification processes[122]. Moreover, bands at 2920 and 2850 cm^{-1} are matching with asymmetric ($\nu_a \text{ CH}_2$) and symmetric ($\nu_s \text{ CH}_2$) stretching vibrations of the methylene group, which generally corresponds to defects in rings of CNTs [109]. Figure 3.26 shows the infrared spectra of the MI-TLa, pristine MWCNTs and MI-TLa grafted MWCNTs. Characteristic IR peaks for MI-TLa located at 1683 cm^{-1} (C=O), 1410 cm^{-1} (C-N-C), peaks between 1300 and 900 cm^{-1} correspond to the thiolactone ring, whereas the peaks between $830\text{-}690 \text{ cm}^{-1}$ corresponds to maleimide double bonds [115]. For model reaction-1, the FTIR spectroscopy confirms Diels-Alder cycloaddition reaction between maleimide bearing TLa and MWCNTs. Characteristic IR peaks located at 1631 , 1386 cm^{-1} is the proof of that the functional groups such as carbonyl stretching vibrations (C=O) and C-N-C are existed in Model Reaction-1.

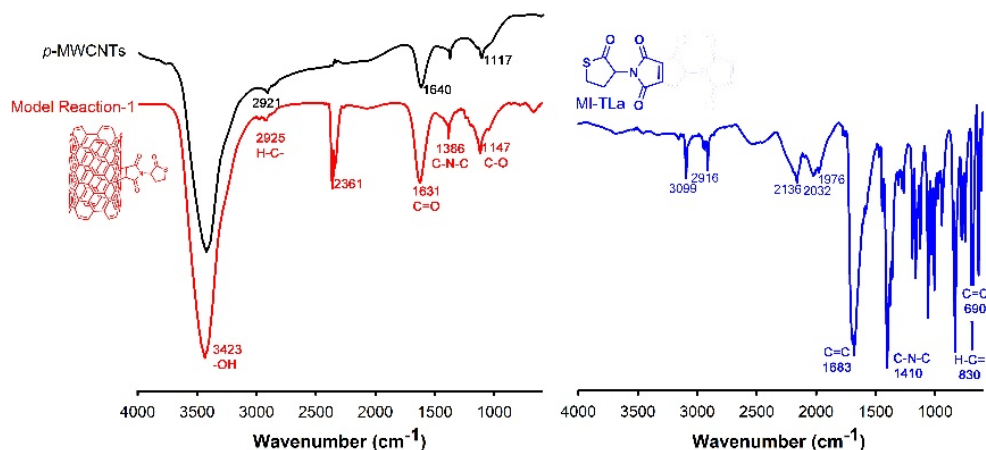


Figure 3.26 : FT-IR spectra of *p*-MWCNTs, Model Reaction-1 and MI-TLa.

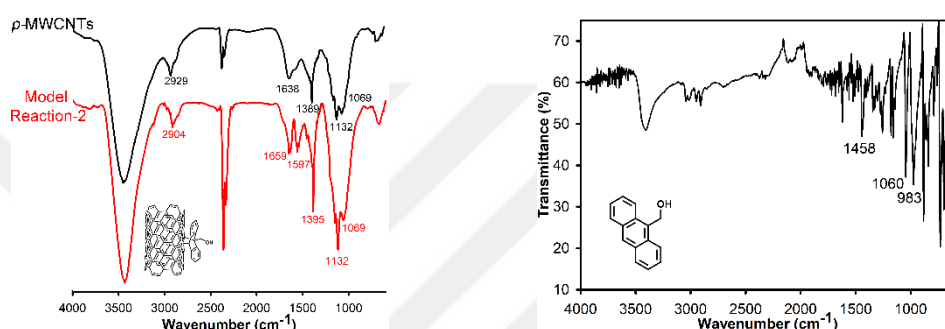


Figure 3.27 : FT-IR spectra of *p*-MWCNTs, Model Reaction-2 and 9-anthracenemethanol.

Figure 3.27 shows the infrared spectra of the 9-anthracenemethanol, pristine MWCNTs and Model Reaction-2. Characteristic IR peaks for 9-anthracenemethanol located at 1458 cm^{-1} (C-C stretching vibration of all phenyl rings which are weakly coupled with the rings C-H in-plane wagging vibration), C-O out-plane bending vibration at 1046 cm^{-1} and 986 cm^{-1} correspond to the skeleton vibration of phenyl ring [123]. The new broad peak around 1597 cm^{-1} which can be seen from the FTIR spectrum of Model Reaction-2 as a proof that Diels-Alder cycloaddition reaction between 9-anthracenemethanol and MWCNTs was succesful.

Additionally, FT-IR spectroscopy was used to evaluate the changes produced by functional groups on the surface of Model Reaction-4; (Figure 3.28) was used. For Model Reaction-4, the FTIR spectroscopy confirms the success of nitrene addition reaction between TLa- N_3 and SWCNTs. Characteristic IR peaks located at 1634 and 1384 cm^{-1} are the proof that the functional groups such as carbonyl stretching vibrations (C=O) and C-N-C are existed in Model Reaction-4.

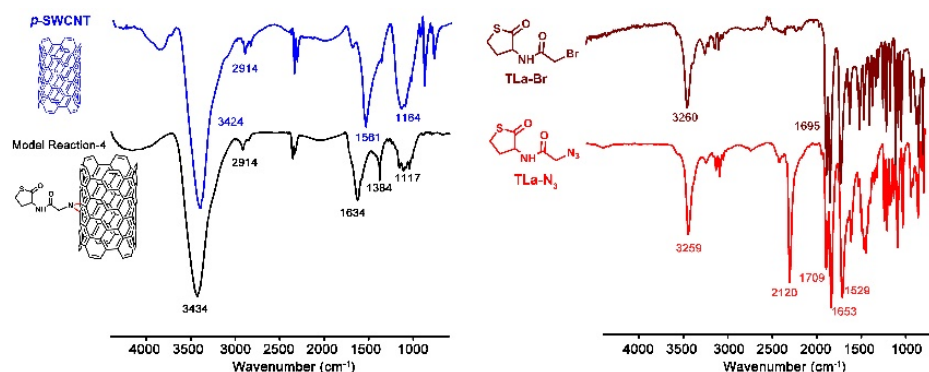


Figure 3.28 : FT-IR spectra of *p*-SWCNTs, Model Reaction-4, TLa-Br and TLa-N₃.

Thermal gravimetric analysis (TGA) gives valuable understanding of functionalized carbon nanotubes, in specific since most of the functionalizing moieties are thermally labile. Hence, TGA measurements had been done to evaluate weight changes and thermal properties of model reactions of carbon nanotubes.

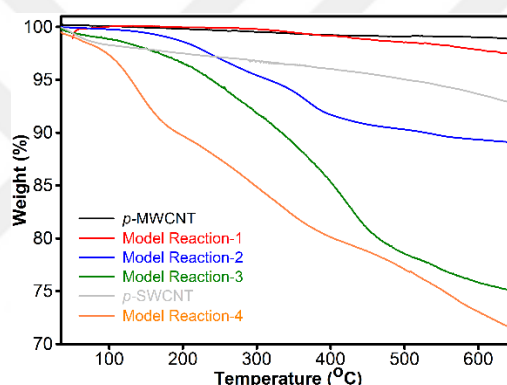


Figure 3.29 : Thermal gravimetric analysis curves of pristine carbon nanotubes and model reactions (#1-4) at a heating rate of 10 °C/min under nitrogen atmosphere.

As a result of these analysis that have been performed between 30-650 °C, the weight loss of pristine MWCNTs and SWCNTs were found 1 wt% and 4 wt% between 250-650 °C, respectively. The reason of these weight losses is thought to be impurities. On the same analysis, Model Reactions #1-4 exhibited uniform thermal degradation behavior with 2%, 10%, 23%, and 21% decrease in weight respectively (Figure 3.29).

Table 3.3 Thermogravimetric profiles of Model Reactions #1-4.

Entry	Molecule used for modification	Weight ^a (%)
<i>p</i> -MWCNTs	-	~ 1 %
<i>p</i> -SWCNTs	-	~ 4 %
MR-1	MI-TLa	2 %
MR-2	9-anthracenemethanol	10 %
MR-3	furfuryl alcohol	23 %
MR-4	TLa-N ₃	21 %

^a The weight loss from the *f*-CNTs samples at 650 °C is used to estimate the amount of polymer that is covalently attached to the CNTs surface and measured by TGA. A weight loss, due to polymer decomposition, was observed to occur between temperatures of 250-650 °C for *f*-CNTs.

Table 3.3 summarizes thermogravimetric profiles of model reactions #1-4 between 250-600 °C under nitrogen with a heat flow of 10 °C/min.

The positive results from the TGA and FT-IR based on the model reactions #1-4, motivated the study to move to a further step that was mono and double modifications of various carbon nanotubes (MWCNTs, MWCNTs-COOH and SWCNTs) with end-functional polymers.

The samples for UV measurements were prepared by dissolving 1 mg of CNTs in 4 mL of DMSO in a vial. The mixtures were dispersed using ultrasonic treatment for 15 min and a 3 mL of aliquot was placed in a UV cell, still in small quantities of precipitation observed because of the unreacted MWCNTs, SWCNTs.

Therefore, UV measurements were carried out after precipitation of particles within 1-2 min. It can easily be detected that *p*-MWCNTs and *p*-SWCNTs displayed no signals between 200-400 nm.

However, the modified CNTs (Model Reaction-1 and Model Reaction-4) displayed increasing absorbance because of the thiolactone and maleimide moieties, respectively (Figure 3.30).

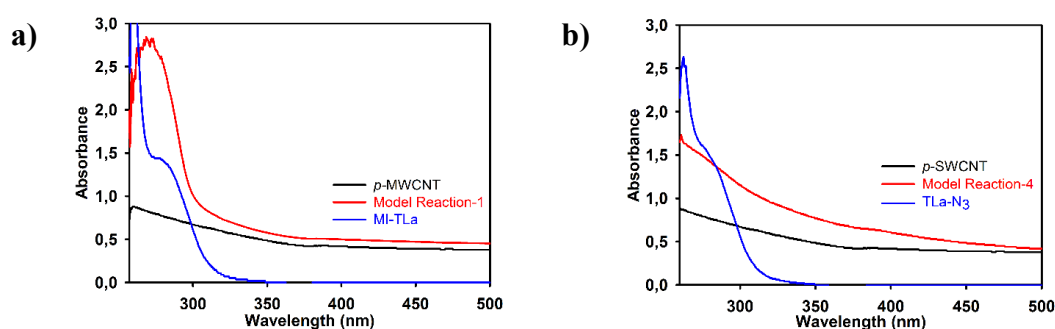


Figure 3.30 : UV absorption spectra of pristine carbon nanotubes, Model Reaction #1 and 4, and their precursors in DMSO.

3.2.4 Mono modification of carbon nanotubes with end-functionalized polymers

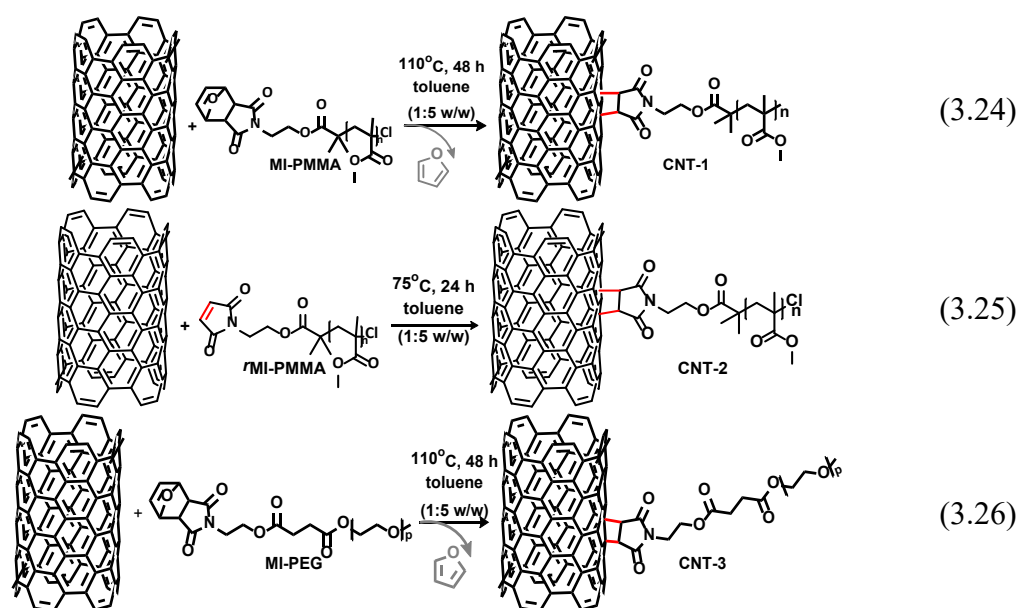
Polymers having reactive α - or ω - groups were directly used to functionalize CNTs to obtain CNT-hybrid materials since they are reactive towards CNTs. The objective of this part of the study was to design and synthesis of polymer-functionalized various carbon nanotubes with highly efficient click reactions such as Diels-Alder

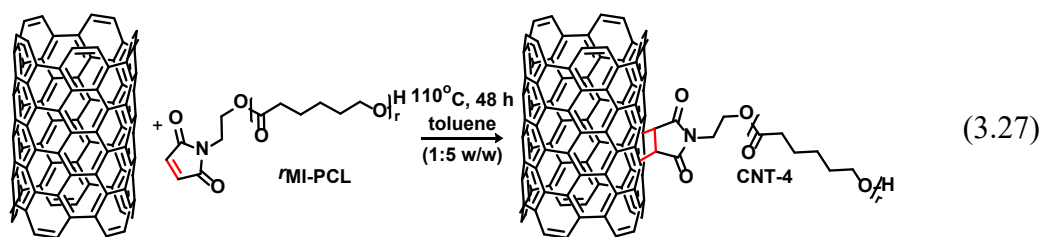
cycloaddition, nitrene addition and thiol-ene click reaction. The obtained products are named as CNT-1 to CNT-20.

3.2.4.1 Diels-Alder cycloaddition reaction

Usage of Diels-Alder cycloaddition reaction have many advantages both in polymer and material science since they do not generate any byproducts, they can be performed under mild conditions and there is no need to use any catalyst. As a result of these advantages, Diels-Alder reactions are chosen to work in the first part of this study. Thanks to their both diene and dienophile nature, CNTs can react with small molecules or polymers that have suitable functional groups. In order to do this, three different functional groups have been taken into consideration which are; maleimide, anthracene and furan. Polymers that includes these groups were synthesized by ATRP or esterification reactions as previously explained, and their characterization have been checked.

First, furan protected maleimide end-functionalized polymers are prepared by ATRP, esterification and ROP. Then furan protected maleimide end-functionalized polymers are deprotected by *retro* Diels-Alder (*r*-DA) by heating at 110 °C in toluene. The recovered maleimide groups are added irreversibly to carbon nanotubes to undergo the Diels-Alder reaction in order to obtain polymer-carbon nanotube hybrid materials. For this purpose, MI-PMMA, MI-PEG and MI-PCL are used. Reaction conditions and schematic illustration of reactions can be found on schemes 3.24 to 3.27.





The efficiency of the reactions was monitored by TGA following the decrease in the thermal degradation of polymer between 250 and 650 °C. In addition, these results confirmed that the synthesis of hybrid carbon nanotubes with maleimide end-functionalized polymers were achieved (Figure 3.31).

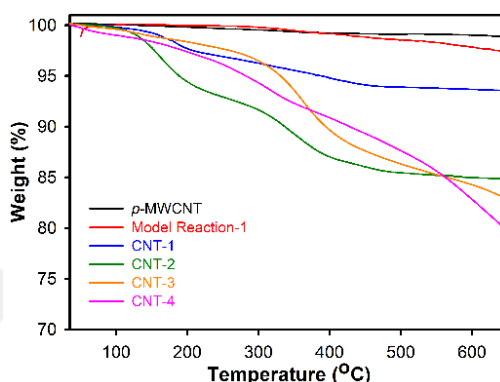


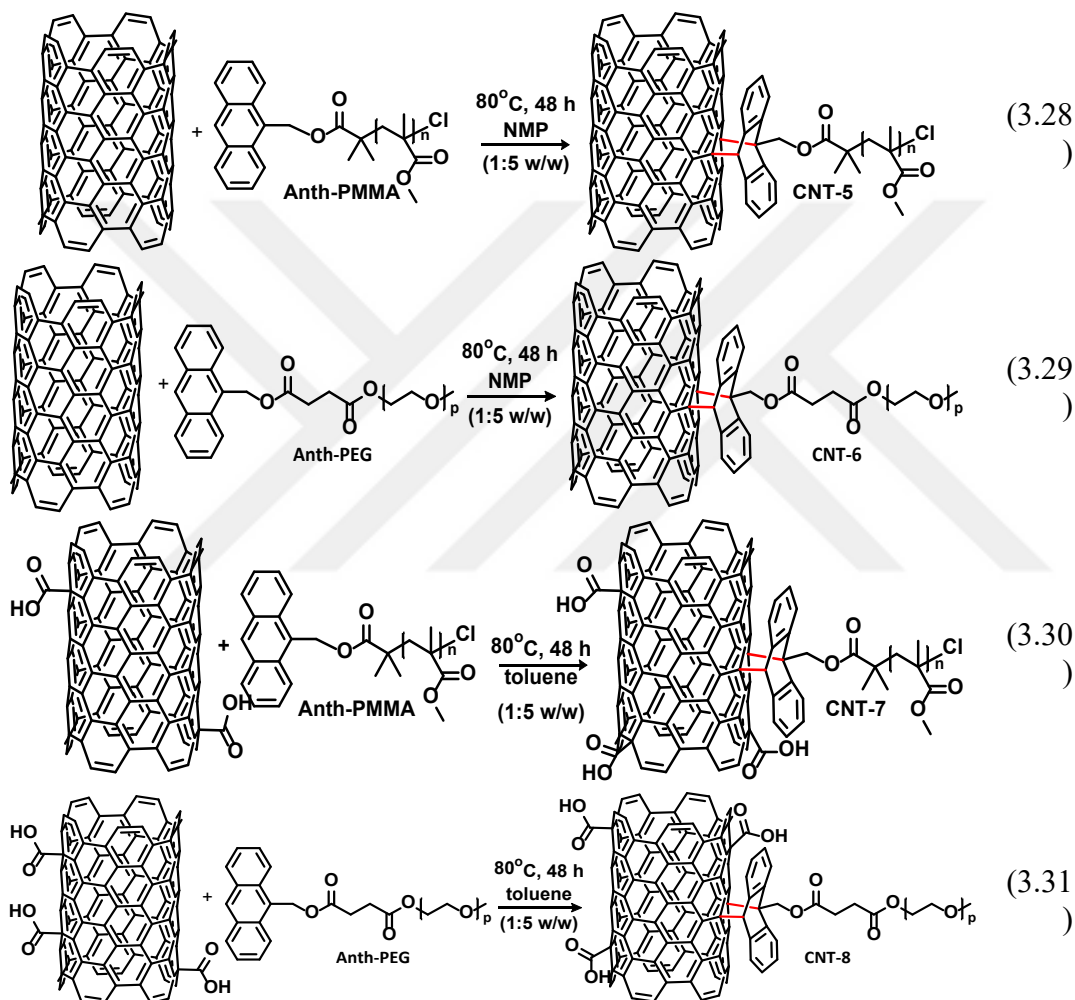
Figure 3.31 : Thermal gravimetric analysis curves of *p*-MWCNTs, Model Reaction-1, and CNTs (#1-4) at a heating rate of 10 °C/min under nitrogen atmosphere.

When compared to other results, small amount of weight loss for furan protected MI-PMMA modified MWCNTs (CNT-1) was observed in TGA measurement. Following the deprotection of MI-PMMA by *retro* Diels-Alder (*r*-DA), weight loss of CNT-2 was recorded increasingly as 14 % in the temperature range of 250-600 °C. For the same temperature range, CNT-3 showed about 15 % weight loss due to polymer decomposition. Moreover, 17.6 % weight loss was calculated from thermal gravimetric analysis of CNT-4, after the deprotection of MI-PCL ($M_n = 5190$ g/mol) by *r*-DA.

Quite a number of studies have reported the results of thermal analysis in order to prove efficiency of Diels-Alder reaction between maleimide containing small molecules/polymers and walls of carbon nanotubes or carbon based nanomaterials [91, 124, 125]. In the literature, the amount of weight loss caused by thermal analysis is within the range of 8% to 10%. So, the results obtained from the present study is better than the literature. This might be correlated with using higher temperature (110 °C) than the literature.

In the second set of experiments, the polymers (anth-PMMA, anth-PEG) with anthracene functionality for Diels-Alder reaction were prepared by ATRP and esterification reactions as previously explained. By a Diels-Alder reaction between these polymers and commercially available acid bearing MWCNTs (MWCNT-COOH) or unfunctionalized MWCNTs, modification efficiency of changing carbon nanotubes has been examined.

Reaction conditions and schematic illustration of reactions can be found 3.28-3.31.



The efficiency of the reactions was monitored by TGA following the decrease in the thermal degradation of polymer between 250 and 650 °C. In addition, these results confirmed that the synthesis of hybrid carbon nanotubes with anthracene end-functionalized polymers were achieved (Figure 3.32).

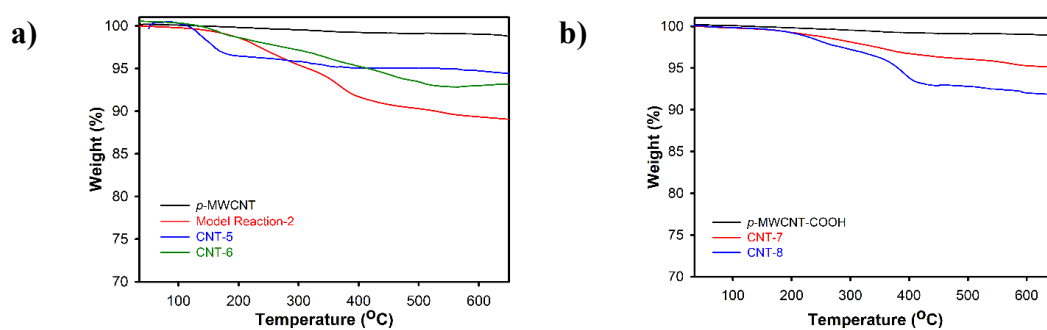


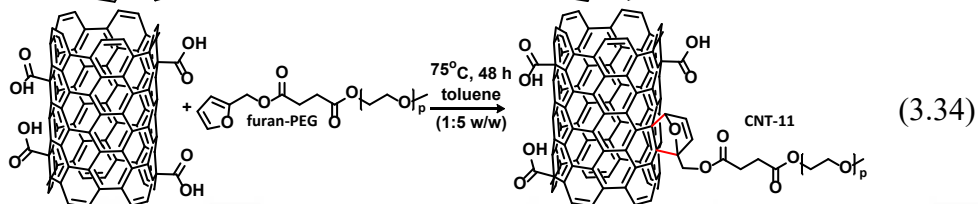
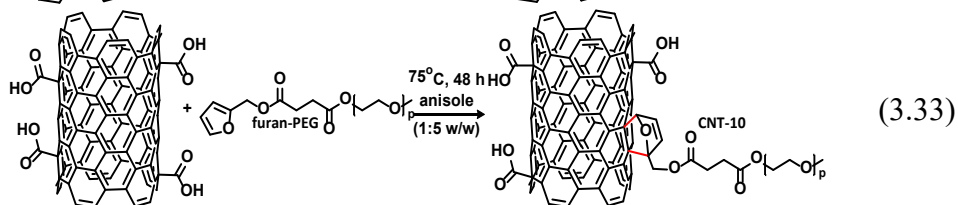
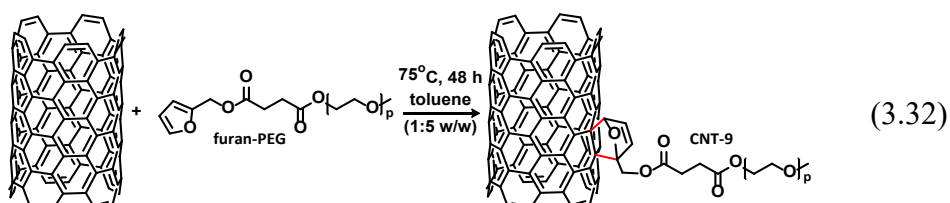
Figure 3.32 : Thermal gravimetric analysis curves of (a) *p*-MWCNTs, model reaction-2, and CNTs (#5-6), (b) *p*-MWCNT-COOH and CNTs (#7-8) at a heating rate of 10 °C/min under nitrogen atmosphere.

TGA measurement of CNT-5 showed 4.2 % weight loss which is correlated with low amount of anth-PMMA on MWCNTs. This may happen due to relatively higher molecular weight of anthracene end-functionalized PMMA or solvent (*N*-methyl-2-pyrrolidinone) which was chosen based on the literature [126]. Although there was no big difference between anth-PMMA and anth-PEG in terms of molecular weight, anth-PEG grafted MWCNTs (CNT-6) also showed low weight loss ratio (6%) in the temperature range of 250-600 °C. Therefore, type of the carbon nanotubes and solvent, which is commonly used for Diels-Alder reaction changed into acid bearing MWCNTs (MWCNT-COOH) and toluene, respectively. CNT-7 showed 4 % weight loss, which is same as CNT-5 in thermal gravimetric analysis. In addition, 7 % weight loss was calculated for CNT-7.

So far, there have been little discussions about modification of carbon nanotubes via Diels-Alder reaction in the presence of anthracene containing small molecules or polymers [127]. The most well-known approach for this modification is a high-speed vibration milling technique, which is used to modify fullerene C60 [128, 129]. In addition, to prove efficiency of Diels-Alder reaction between anthracene containing small molecules and CNTs some computational studies had been carried out.

In the third set of experiments, furan end-functionalized PEG was prepared using esterification strategy. By the Diels-Alder reaction between furan-PEG and either with commercially available acid bearing MWCNTs (MWCNT-COOH) or unfunctionalized MWCNTs, modification efficiency of changing carbon nanotubes has been examined.

Reaction conditions and schematic illustration of reactions can be found schemes 3.32 to 3.34.



The efficiency of the reactions was monitored by TGA following the decrease in the thermal degradation of polymer between 250 and 650 °C. Moreover, these results confirmed that the synthesis of hybrid carbon nanotubes with furan end-functionalized polymers were achieved (Figure 3.33).

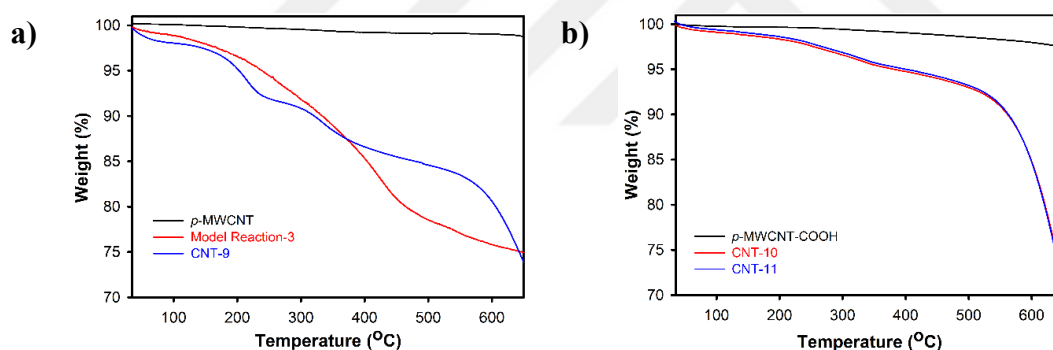


Figure 3.33 : Thermal gravimetric analysis curves of (a) *p*-MWCNTs, model reaction-3, and CNT-9, (b) *p*-MWCNT-COOH and CNTs (#10-11) at a heating rate of 10 °C/min under nitrogen atmosphere.

The analysis of Furan-PEG grafted MWCNTs (CNT-9) showed 20 % of weight loss in TGA measurement (Figure 3.33 (a)). Furthermore, two additional Diels-Alder reactions of MWCNT-COOH with furan-PEG had been done by using different solvents, which were anisole and toluene.

As a result, there was no difference in thermal analysis of CNT#10-11 and displayed 25 % of weight loss till 650 °C (Figure 3.33 (b)).

Quite a number of studies have reported the results of thermal analysis in order to prove efficiency of Diels-Alder reaction between furan (furfuryl) containing small

molecules/polymers and walls of carbon nanotubes or carbon-based nanomaterials. In the literature, the amount of weight loss caused by thermal analysis are within the range of 3% to 18%. This change might be correlated with the structure of furfuryl containing small molecules or polymers (poly(furfuryl methacrylate) etc.) that are used for modification [10, 88, 130]. So the present study gives slightly better results than the literature, which might be correlated with the preference of different solvent (toluene or anisole) than the literature.

Table 3.4: Thermogravimetric profiles and reaction conditions of *f*-carbon nanotubes via Diels-Alder Reaction.

Entry	Type of Carbon Nanotubes	Polymer Used For Modification ^a	Solvent	Temp (°C)	Weight (%) ^b
<i>p</i> -MWCNTs	-	-	-	-	~ 1 %
<i>p</i> -MWCNT-COOH	-	-	-	-	~ 2.5 %
CNT-1	MWCNTs	MI-PMMA	toluene	110	5.5 %
CNT-2	MWCNTs	<i>r</i> MI-PMMA	toluene	75	14 %
CNT-3	MWCNTs	MI-PEG	toluene	110	15 %
CNT-4	MWCNTs	<i>r</i> MI-PCL	toluene	110	17.6 %
CNT-5	MWCNTs	anth-PMMA	NMP	80	4.2 %
CNT-6	MWCNTs	anth-PEG	NMP	80	6 %
CNT-7	MWCNTs-COOH	anth-PMMA	toluene	80	4 %
CNT-8	MWCNTs-COOH	anth-PEG	toluene	80	7 %
CNT-9	MWCNTs	Furan-PEG	toluene	110	20 %
CNT-10	MWCNTs-COOH	Furan-PEG	anisole	75	25 %
CNT-11	MWCNTs-COOH	Furan-PEG	toluene	75	25 %

^a In all cases, polymers were employed with 5 fold-excess with respect to that carbon nanotubes in weight.

^b The weight loss from the *f*-CNTs samples at 650 °C is used to estimate the amount of polymer that is covalently attached to the CNTs surface and measured by TGA. A weight loss, due to polymer decomposition, was observed to occur between temperatures of 250-650 °C for *f*-CNTs.

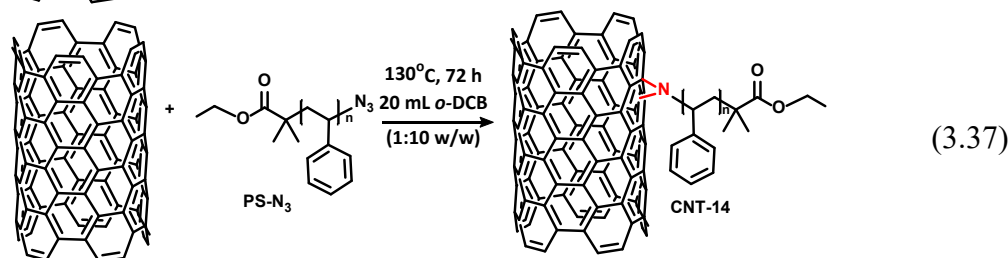
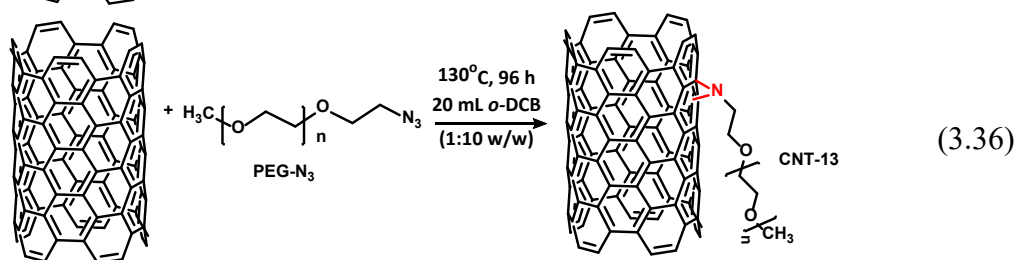
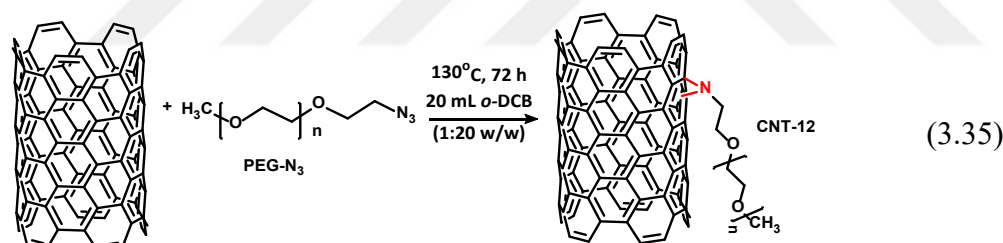
Table 3.4 summarizes thermogravimetric profiles of CNT#1-11 between 250-650 °C under nitrogen with a heat flow of 10 °C/min. These results proved the conclusion that the synthesis of CNT-polymer hybrid materials could be efficiently achieved by DA cycloaddition reaction. CNT-10 and CNT-11 provide the best efficiency results on the thermal gravimetric analysis, since the electron withdrawing groups (-COOH) are increasing the efficiency of dienophile (MWCNTs-COOH) against diene (furan) during DA cycloaddition reaction.

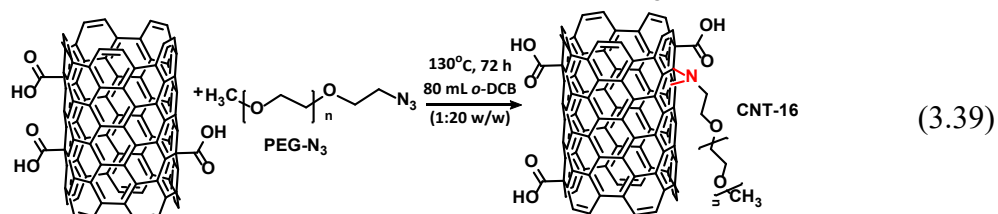
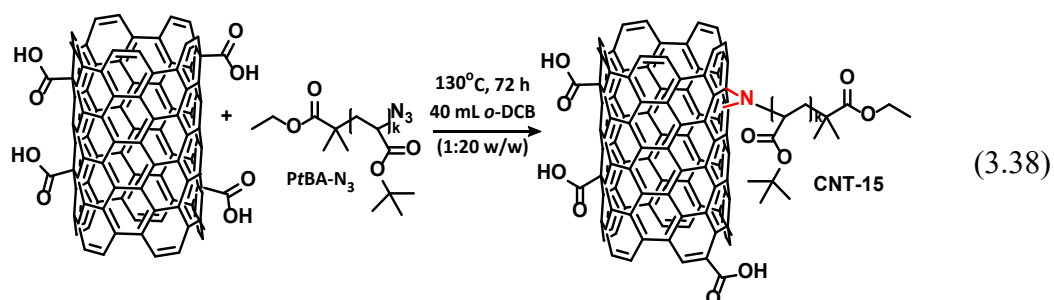
Overall results supported that efficiency of DA cycloaddition reaction between carbon nanotubes and end-functionalized polymers are listed furan, naked maleimide, furan protected maleimide and anthracene end-functionalized polymers by ascending sort.

3.2.4.2 Nitrene addition reaction

A series of azide-terminated polymers bearing an azide group at the end were synthesized either by esterification or ATRP reactions. Polymers with azide moiety have been taken into consideration for modifying MWCNTs and MWCNT-COOH by nitrene addition reaction. Polymers with azide were synthesized either by ATRP or esterification reactions as previously explained, and their characterization have been checked.

Organic azides thermally decompose in different temperature range from 25 to 200 °C depending on the substituents [16]. First, carbon nanotubes are dispersed in 1,2-dichlorobenzene (*o*-DCB) in an ultrasonic bath. Then, the [2+1] cycloaddition reaction between azide end-functionalized polymers and CNTs was performed in 1,2-dichlorobenzene (*o*-DCB) at 130 °C between 72 and 96 hours as shown in schemes from 3.35 to 3.39. For this purpose, PS-N₃ and PEG-N₃ are used.





The efficiency of the nitrene addition reactions were monitored by TGA following the decrease in the thermal degradation of polymer between 250 and 650 °C. These results confirmed that the synthesis of hybrid carbon nanotubes with azide end-functionalized polymers were achieved (Figure 3.34).

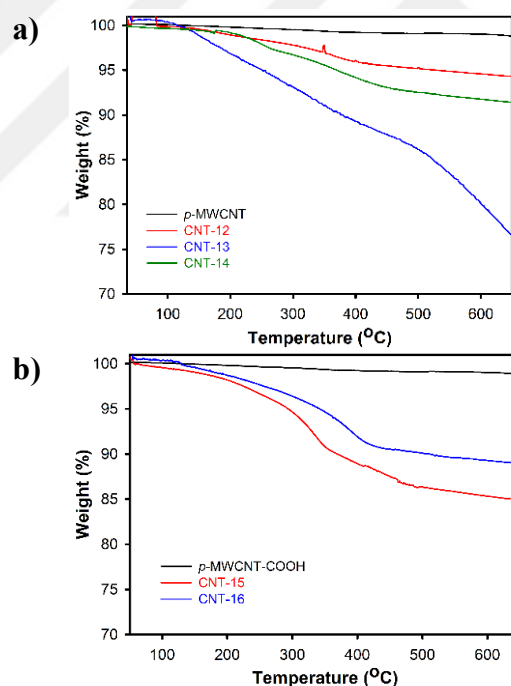


Figure 3.34 : Thermal gravimetric analysis curves of (a) *p*-MWCNTs, CNTs (#12-14) and (b) *p*-MWCNT-COOH, CNTs (#15-16) at a heating rate of 10 °C/min under nitrogen atmosphere.

The analysis of PEG- N_3 grafted MWCNTs (CNT-12) showed 4.5 % of weight loss in TGA measurement (Figure 3.34 (a)). However, thermal analysis of CNT-13, even if weight ratio between carbon nanotubes and polymer cut in half, shows a weight loss

as 19.5% once the reaction time extended to 96 hours. Also, the analysis of PS-N₃ grafted MWCNTs (CNT-14) showed 7 % of weight loss in TGA measurement.

Moreover, acid functionalized multiwalled carbon nanotubes were used to evaluate nitrene addition efficiency. The thermal gravimetric analysis results showed more weight loss in a dilute environment once to weight ratio is 1/20 and reaction time is 72 hours. Therefore, thermal analysis of CNT#15 and 16 displayed 13 % and 9 % of weight loss respectively, until 650 °C (Figure 3.34 (b)).

Table 3.5: Thermogravimetric profiles of *f*-carbon nanotubes via nitrene addition reaction.

Entry	Type of CNTs	Polymer used for modification	Time	Weight Ratio (CNTs:Polymer)	Weight (%) ^c
<i>p</i> -MWCNTs	-	-	-	-	~ 1 %
<i>p</i> -MWCNT-COOH	-	-	-	-	~ 2 %
CNT-12^a	MWCNTs	PEG-N ₃	72 h	20	4.5 %
CNT-13^b	MWCNTs	PEG-N ₃	96 h	10	19.5 %
CNT-14^b	MWCNTs	PS-N ₃	72 h	10	7 %
CNT-15^a	MWCNTs-COOH	PtBA-N ₃	72 h	20	13 %
CNT-16^a	MWCNTs-COOH	PEG-N ₃	72 h	20	9 %

^a In this case, polymers were employed with 20 fold-excess with respect to that carbon nanotubes in weight.

^b In this case, polymers were employed with 10 fold-excess with respect to that carbon nanotubes in weight.

^c The weight loss from the *f*-CNTs samples at 650 °C is used to estimate the amount of polymer that is covalently attached to the CNTs surface and measured by TGA. A weight loss, due to polymer decomposition, was observed to occur between temperatures of 250-650 °C for *f*-CNTs.

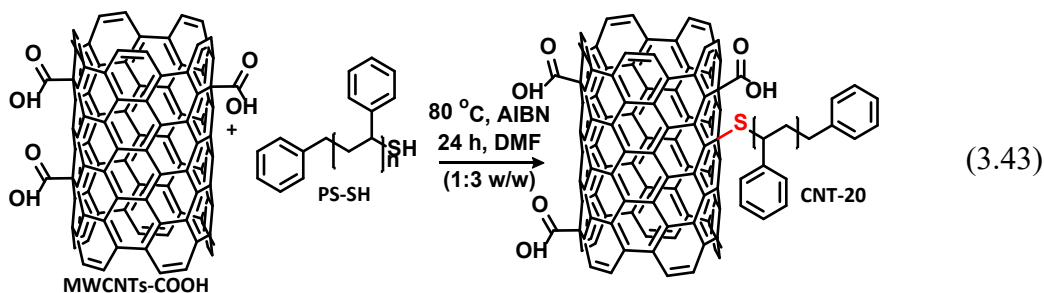
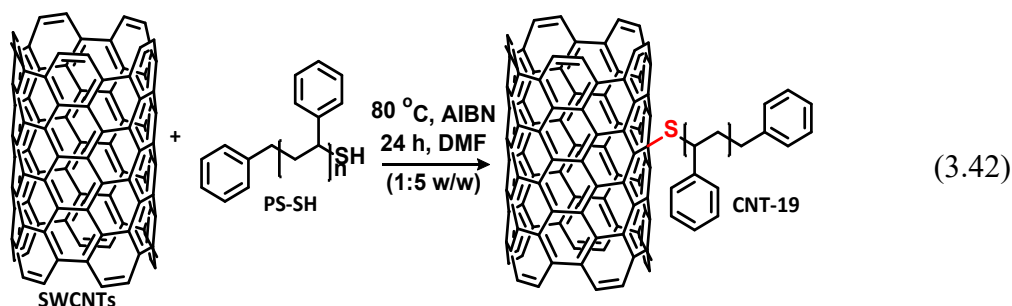
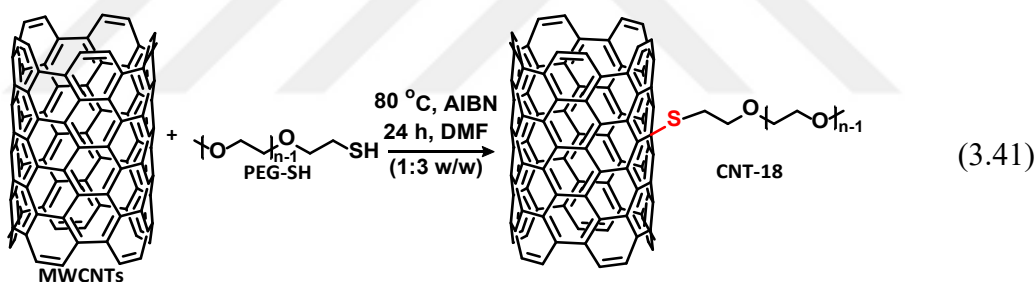
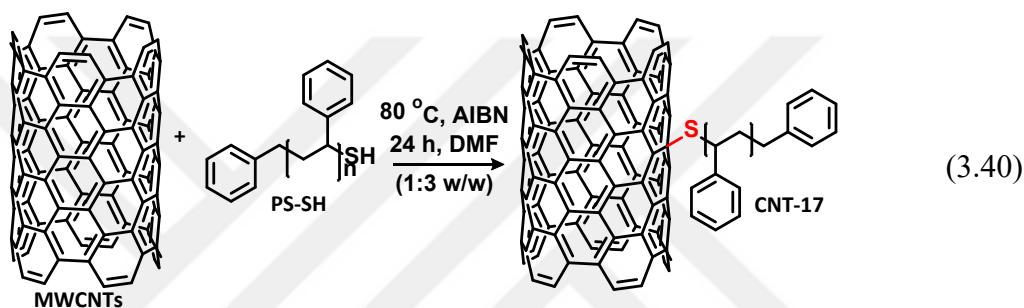
Thermogravimetric profiles of CNT#12-16 between 250-650 °C under nitrogen with a heat flow of 10 °C/min were tabulated in Table 3.5. These results proved that the synthesis of CNT-polymer hybrid materials could be efficiently achieved by nitrene addition reaction.

Quite a number of studies have reported the results of thermal analysis in order to prove efficiency of nitrene addition reaction between azide containing small molecules/polymers and walls of carbon nanotubes. In the literature, the amount of weight loss caused by thermal analysis are within the range of 5% to 70% [96, 131, 132]. So, the results obtained from the present study can accepted as compatible with the literature. Difference in the results might be correlated with usage of relatively lower temperature (130 °C) and difference in the polymer/CNTs weight ratio than the literature.

3.2.4.3 Thiol-ene click reaction

The last part of the mono modification has been taken into consideration for modifying variable CNTs by thiol-ene click reaction. A series of thiol-terminated polymers were synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization of the corresponding monomers (styrene and *n*-butylacrylate) in toluene at either 110 °C or 60 °C using dibenzyl trithiocarbonate (DBTTC) as RAFT agent and AIBN as the free radical initiator or by esterification reactions as previously explained and their characterization have been checked.

Reaction conditions and schematic illustration of reactions can be found on schemes 3.40 to 3.43.



Where the analysis of PS-SH grafted MWCNTs (CNT-17) showed 14 % of weight loss, PEG-SH grafted MWCNTs (CNT-18) showed 4 % of weight loss in TGA measurement (Figure 3.35 (a)). Furthermore, two additional thiol-ene reactions of SWCNTs and MWCNT-COOH with PEG-SH and PS-SH had been done by the same reaction conditions. Moreover, there is little difference in thermal analysis of CNT#19-20 which displayed 27-24 % of weight loss until 650 °C (Figure 3.35 (b), Figure 3.36).

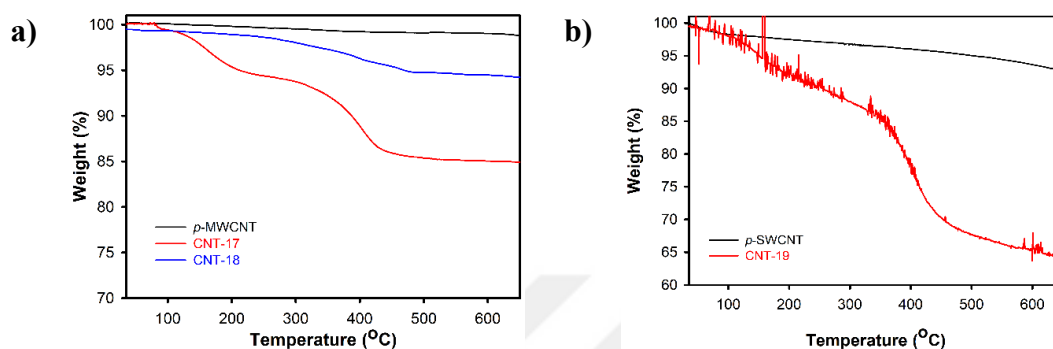


Figure 3.35 : Thermal gravimetric analysis curves of (a) *p*-MWCNTs, CNT (#17-18) and (b) *p*-SWCNT, CNT-19 at a heating rate of 10 °C/min under nitrogen atmosphere.

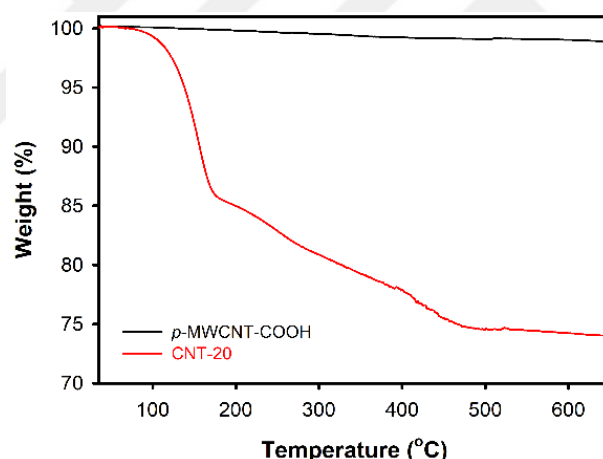


Figure 3.36 : Thermal gravimetric analysis curves of *p*-MWCNT-COOH, CNT-20 at a heating rate of 10 °C/min under nitrogen atmosphere.

Table 3.6 summarizes thermogravimetric profiles of CNT#17-20 between 250-650 °C under nitrogen with a heat flow of 10 °C/min. These results proved that the synthesis of CNT-polymer hybrid materials could be efficiently achieved by thiol-ene click reaction.

Table 3.6: Thermogravimetric profiles of *f*-carbon nanotubes via thiol-ene click reaction.

Entry	Type of carbon nanotubes	Polymer used for modification	Weight (%) ^c
<i>p</i> -MWCNTs	-	-	~ 1 %
<i>p</i> -MWCNT-COOH	-	-	~ 2 %
<i>p</i> -SWCNTs	-	-	~ 4 %
CNT-17 ^a	MWCNTs	PS-SH	14 %
CNT-18 ^a	MWCNTs	PEG-SH	4 %
CNT-19 ^b	SWCNTs	PS-SH	27 %
CNT-20 ^a	MWCNTs-COOH	PS-SH	24 %

^a In this case, polymers were employed with 3 fold-excess with respect to that carbon nanotubes in weight.

^b In this case, polymers were employed with 5 fold-excess with respect to that carbon nanotubes in weight.

^c The weight loss from the *f*-CNTs samples at 650 °C is used to estimate the amount of polymer that is covalently attached to the CNTs surface and measured by TGA. A weight loss, due to polymer decomposition, was observed to occur between temperatures of 250-650 °C for *f*-CNTs.

3.2.5 Double modification of carbon nanotubes with end-functionalized polymers

In this part of the study, a facile method for the double covalent functionalization of carbon nanotubes with polymers is presented. So, we turned our attention to “double modification strategy” to obtain polymer grafted carbon nanotubes. The success of mono-functionalization of various carbon nanotubes has motivated us to make a double modification on carbon nanotubes.

Using the results obtained from mono modifications of CNTs with different wall numbers and functional groups, it was decided to work on double modification of CNTs by below mentioned pairs:

- Nitrene Addition – Thiol-ene Click Reaction
- Diels-Alder Cycloaddition – Thiol-ene Click Reaction
- Thiol-ene Click Reaction – Diels-Alder Cycloaddition
- Nitrene Addition – Diels-Alder Cycloaddition Reaction

The whole synthetic pathways during this thesis can be summarized as in Figure 3.37.

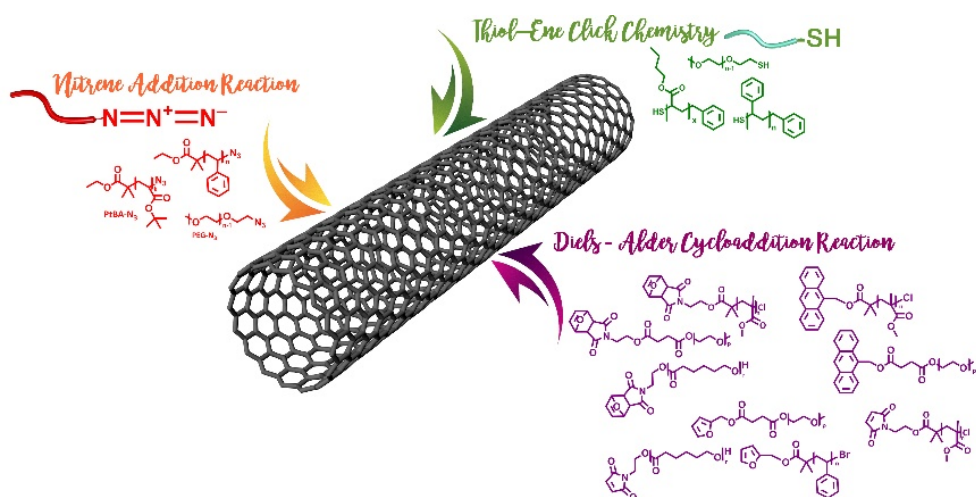


Figure 3.37 : Schematic pathways of double surface modification of CNTs.

In addition, our group was the first to utilize the combination of double modification strategy to carbon nanotubes and proved a partially suitable reaction for polymer-nanomaterials conjugation as well.

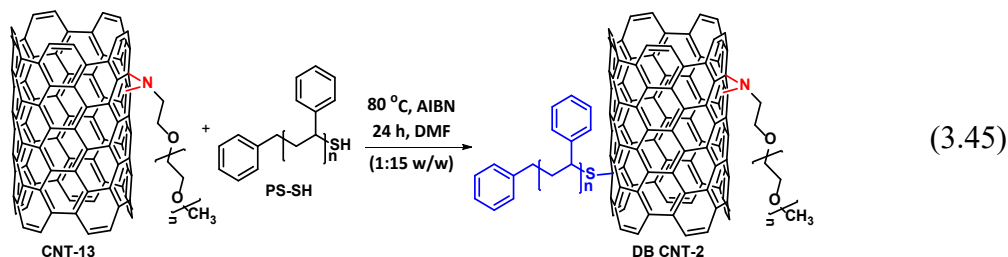
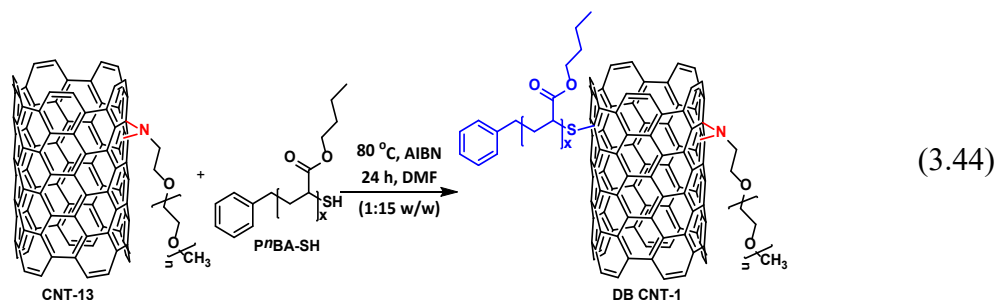
The obtained products are named as DB CNT-1 to DB CNT-10.

3.2.5.1 Double modification of carbon nanotubes with end-functionalized polymers: Nitrene addition – thiol-ene click reaction, Diels-Alder cycloaddition – thiol-ene click reaction, thiol-ene click reaction – Diels-Alder cycloaddition, and nitrene addition – Diels-Alder cycloaddition reaction

In this part of the study, the combination of nitrene chemistry and thiol-ene click reactions were chosen for the functionalization of carbon nanotubes with polymers as a first approach.

Previously obtained PEG-N₃ grafted MWCNTs (CNT-13) via nitrene addition was used for applying second modification, which was thiol-ene click chemistry with the polymers; PnBA-SH and PS-SH, respectively

For this purpose, CNT-13 reacted with 15-fold excess amount of thiol end-functionalized polymers (PnBA-SH and PS-SH) to yield DB CNT-1 and DB CNT-2 by preparing a similar experimental setup to mono modification of carbon nanotubes by thiol-ene click reaction (3.44-3.45).



Thermal gravimetric analysis of DB CNT-1, which was modified with PnBA-SH, showed no clear difference with respect to its previous step CNT-13 (Figure 3.38 (a)). However, DB CNT-2, which was modified with PS-SH, showed notable difference with respect to its previous step CNT-13 (Figure 3.38 (b)).

Thermal analysis of DB CNT-2 displayed 39.5 % total weight loss until 650 °C after second modification. The reason for this increase can be explained by the aromatic interactions between polystyrene polymer and sidewalls of carbon nanotubes.

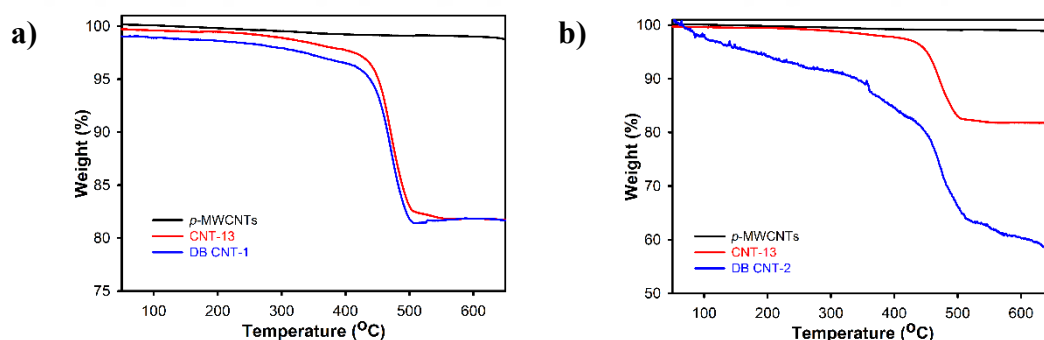
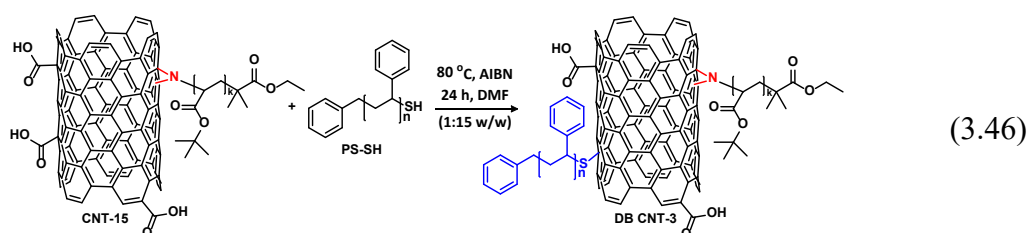


Figure 3.38 : Thermal gravimetric analysis curves of **a)** CNT-13 and DB CNT-1, **b)** CNT-13 and DB CNT-2 at a heating rate of 10 °C/min under nitrogen atmosphere.

Another azide end-functionalized polymer (PtBA-N₃) was grafted into sidewalls of the MWCNTs (CNT-15) by nitrene addition. Following this step, as a second modification thiol-ene click chemistry was chosen (3.46).



Thermal analysis of DB CNT-3 displayed 17 % total weight loss until 650 °C after second modification (Figure 3.39).

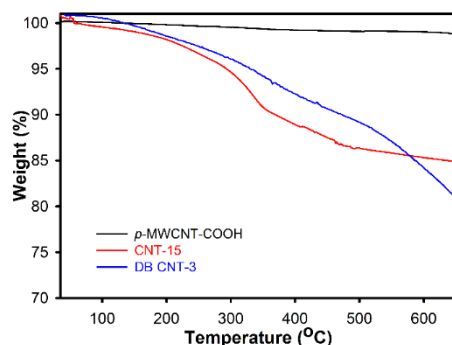
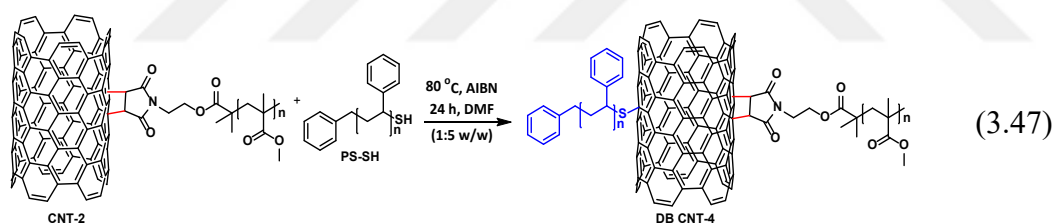


Figure 3.39 : Thermal gravimetric analysis curves of CNT-15 and DB CNT-3 at a heating rate of 10 °C/min under nitrogen atmosphere.

Another double modification approach was made by the combination of Diels-Alder cycloaddition and thiol-ene click reaction (DB CNT-4).

In this case, firstly DA cycloaddition reaction occurred between MWCNTs and deprotected maleimide end-functionalized PMMA (*r*MI-PMMA). Following that step, PMMA grafted MWCNTs (CNT-2) was reacted with PS-SH in the presence of AIBN in DMF at 80 °C to give double grafted MWCNTs (3.47).



Based on the thermal gravimetric analysis of DB CNT-4, grafting yield decreased by 7 % compared to its precursor step (Figure 3.40). This result is related to unexpected *retro* Diels-Alder reaction which could happen during the second step of modification due to the temperature (80 °C).

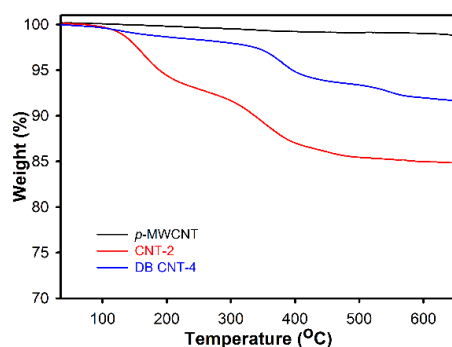
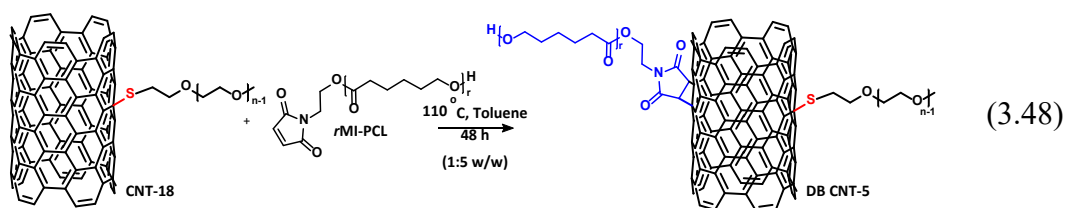


Figure 3.40 : Thermal gravimetric analysis curves of CNT-2 and DB CNT-4 a heating rate of 10 °C/min under nitrogen atmosphere.



To overcome unwanted *retro* Diels-Alder reaction during second modification, the strategy has changed into vice versa. Hence, MWCNTs were reacted with PS-SH in the presence of AIBN at 80 °C (CNT-18), and then the second modification was made with *r*MI-PCL in toluene at 110 °C for 48 hours (3.48). The results were satisfying, since grafted efficiency based on the thermal analysis increased from 4 % to 27 % (Figure 3.41).

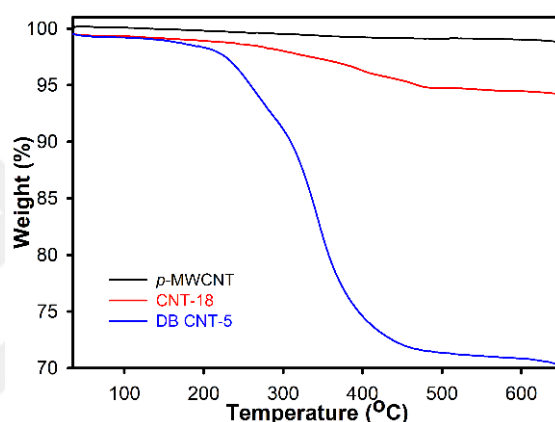
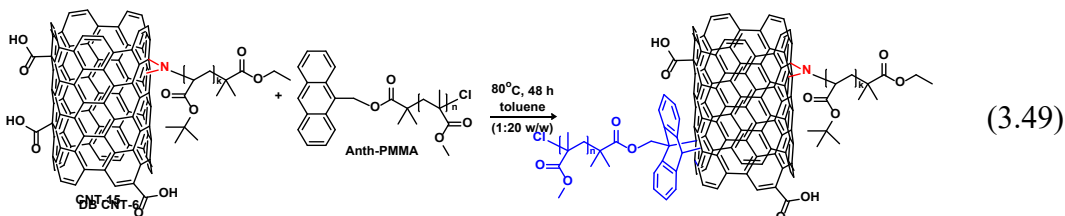


Figure 3.41 : Overlay of thermal gravimetric analysis curves of CNT-18 and DB CNT-5 a heating rate of 10 °C/min under nitrogen atmosphere.

In this part of the study, the combination of nitrene chemistry and Diels-Alder reaction were chosen for the functionalization of carbon nanotubes with polymers.

For this purpose, first, acid-bearing MWCNTs were grafted with PtBA- N_3 polymer and then anth-PMMA (3.49).



Surprisingly, this double modification strategy gave the best grafting efficiency results on the thermal gravimetric analysis, which increased from 13 % to 87 % (Figure 3.42).

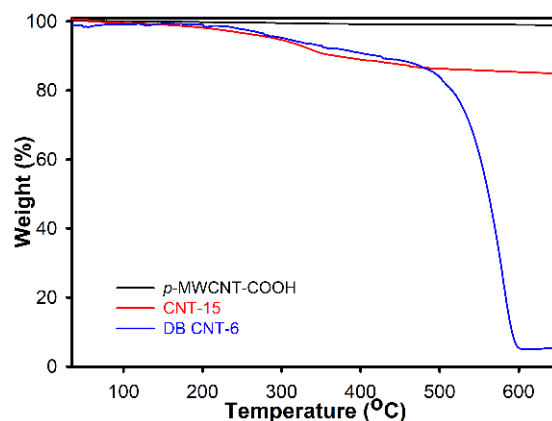
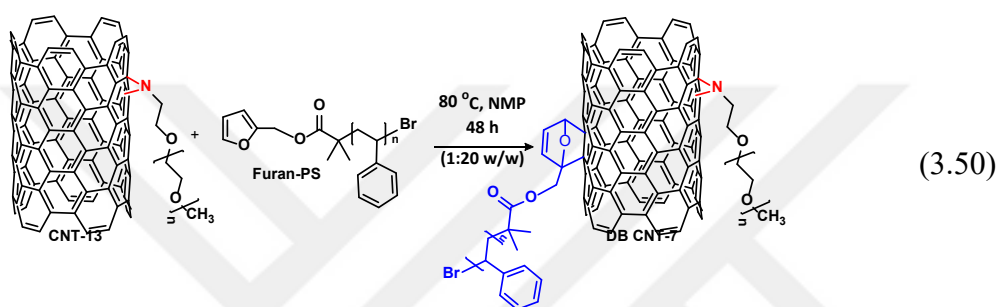


Figure 3.42 : Overlay of thermal gravimetric analysis curves of CNT-15 and DB CNT-6 a heating rate of 10 °C/min under nitrogen atmosphere.



Unfortunately, there was no change in the thermal analysis when previously obtained PEG-N₃ grafted MWCNTs (CNT-13) was used for applying second modification as Diels-Alder reaction with PS-Furan (3.50). Weight loss of DB CNT-7 stayed the same as its precursor step CNT-13 (Figure 3.43).

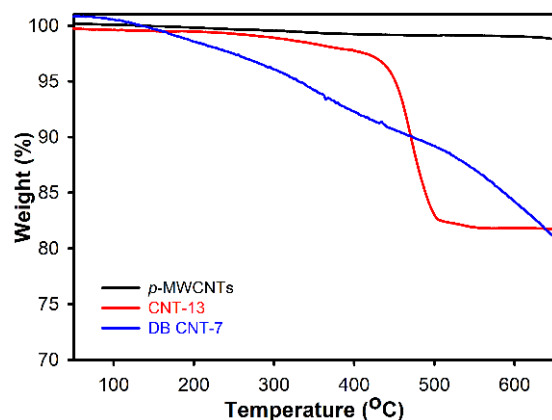


Figure 3.43 : Overlay of thermal gravimetric analysis curves of CNT-13 and DB CNT-7 a heating rate of 10 °C/min under nitrogen atmosphere.

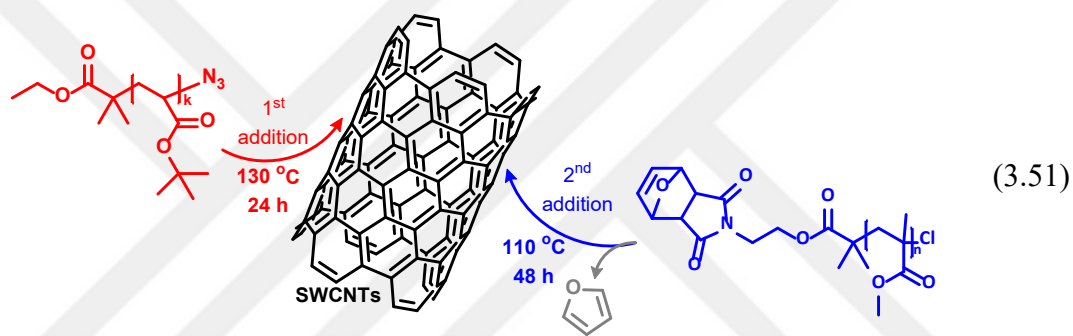
Table 3.7 summarizes thermogravimetric profiles of double modified carbon nanotubes between 250-650 °C under nitrogen with a heat flow of 10 °C/min. These results proved the conclusion that the synthesis of CNT-polymer hybrid materials

could be efficiently achieved by nitrene addition-thiol-ene, thiol-ene – Diels-Alder and nitrene addition – Diels-Alder reaction strategies.

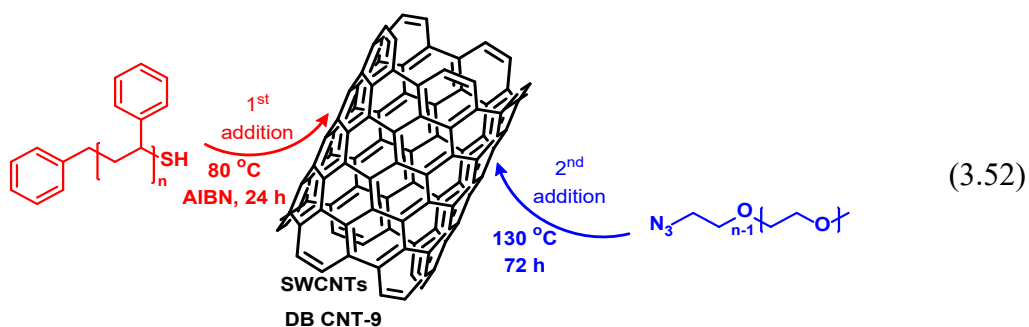
3.2.5.2 Surface modification of carbon nanotubes by one-pot double modification by sequential approach

In the last part of the study, sequential double modification reactions involving nitrene addition and Diels-Alder, thiol-ene and nitrene addition, Diels-Alder and nitrene addition were used for the preparation of polymer grafted SWCNTs.

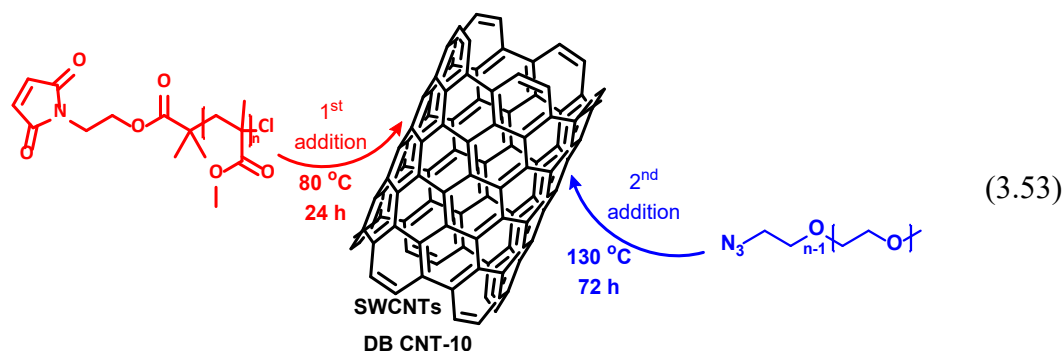
In the first strategy, SWCNTs were reacted with 4-fold excess *PtBA-N₃* in *o*-DCB at 110 °C. 24 hour later, 4-fold excess amount of *MI-PMMA* was added into the reaction mixture and let to stir for more 48 hours resulting in the formation of target double modified carbon nanotubes (3.51).



In the second strategy, SWCNTs were reacted with 5-fold excess *PS-SH* in the presence of *AIBN* in *DMF* at 80 °C. 24 hour later, 5-fold excess amount of *PEG-N₃* was added into the reaction mixture and let to stir for more 72 hours resulting in the formation of target double modified carbon nanotubes (3.52).



In the last strategy, SWCNTs were reacted with 5-fold excess *rMI-PMMA* in *o*-DCB at 80 °C. 24 hour later, 5-fold excess amount of *PEG-N₃* was added into the reaction mixture and let to stir for more 72 hours resulting in the formation of target double modified carbon nanotubes (3.53).



The analysis of DB CNT-8 showed 14 %, DB CNT-9 showed 19 % and DB CNT-10 showed 13 % of weight loss in TGA measurement (Figure 3.44 (a, b, c)).

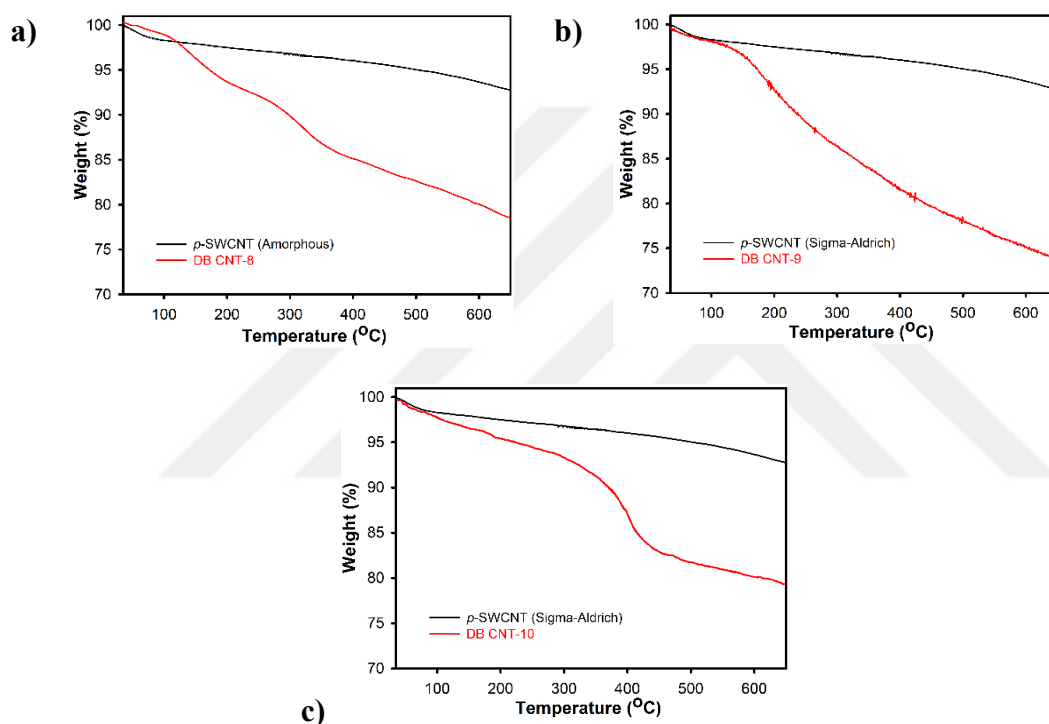


Figure 3.44 : Thermal gravimetric analysis curves of DB CNT-8, DB CNT-9 and DB CNT-10 a heating rate of 10 °C/min under nitrogen atmosphere.

Table 3.8 summarizes thermogravimetric profiles of carbon nanotubes double modified by sequential approach between 250-650 °C under nitrogen with a heat flow of 10 °C/min.

Table 3.7: Whole thermogravimetric profiles of *f*-carbon nanotubes after double modification

Type of the CNTs used in first modification	Polymer used in first modification	Entry of first modification	Weight loss (%) after first modification ^a	Polymer used in second modification	Entry of second modification	Total weight loss (%) after second modification ^a
MWCNTs	PEG-N ₃	CNT-13	19.5	PnBA-SH	DB CNT-1	19
MWCNTs	PEG-N ₃	CNT-13	19.5	PS-SH	DB CNT-2	39.5
MWCNT-COOH	PtBA-N ₃	CNT-15	13	PS-SH	DB CNT-3	17
MWCNTs	<i>r</i> MI-PMMA	CNT-2	14	PS-SH	DB CNT-4	7
MWCNTs	PEG-SH	CNT-18	4	<i>r</i> MI-PCL	DB CNT-5	27
MWCNT-COOH	PtBA-N ₃	CNT-15	9	anth-PMMA	DB CNT-6	87
MWCNTs	PEG-N ₃	CNT-13	19.5	furan-PS	DB CNT-7	19.5

^a The weight loss from the *f*-CNTs samples at 650 °C is used to estimate the amount of polymer that is covalently attached to the CNTs surface and measured by TGA. A weight loss, due to polymer decomposition, was observed to occur between temperatures of 250-650 °C for *f*-CNTs.

Table 3.8: Whole thermogravimetric profiles of *f*-carbon nanotubes by double modification and sequential approach

Type of the carbon nanotubes used in first modification	Entry of second modification	Polymer used in first modification	Polymer used in second modification	Total weight loss (%) after one-pot double modification ^a
SWCNTs (Amorphous)	DB CNT-8	PtBA-N ₃	MI-PMMA	14
SWCNTs (Sigma-Aldrich)	DB CNT-9	PS-SH	PEG-N ₃	19
SWCNTs (Sigma-Aldrich)	DB CNT-10	<i>r</i> MI-PMMA	PEG-N ₃	13

^a The weight loss from the *f*-CNTs samples at 650 °C is used to estimate the amount of polymer that is covalently attached to the CNTs surface and measured by TGA. A weight loss, due to polymer decomposition, was observed to occur between temperatures of 250-650 °C for *f*-CNTs.



4. ACTIVE ESTER SUBSTITUTION AND NITRENE ADDITION REACTIONS ON TO MULTIWALLED CARBON NANOTUBES FOR DOUBLE MODIFICATION

Here we suggest using polyethylene glycol (PEG) and polystyrene (PS) for double modification. PEG is an adequate polymer due to its biocompatibility, low toxicity, great solubility properties in water or other common solvents. PS is a hydrophobic vinyl polymer having a long hydrocarbon chain with a phenyl group attached to every other carbon atom. Different chemical methods have been applied to MWCNTs' surface and different polymers have been chosen in order to diversify the functionalities. Hence, active ester substitution and nitrene addition reactions have been chosen, and their combination was suggested as a new route for double modification of sidewalls of MWCNTs. The present study concerns with the synthesis of amine terminated PEG and azido terminated styrene polymers for the application of double modification strategy (active ester substitution and nitrene addition) in sequential process.

In summary, active ester substitution and nitrene addition reactions have been chosen, and their combination was suggested as a new route for double modification of sidewalls of MWCNTs. For this purpose, firstly commercially available acid bearing MWCNTs treated with thionyl chloride or oxalyl chloride and in the presence of catalytic amount of DMF for activation.

Secondly, PFP activated ester MWCNTs were prepared. For this step, pentafluorophenol was chosen to obtain activated ester derivative of MWCNTs, since the product (MWCNT-COOC₅F₆) is air-stable, has humidity resistance and has high reactivity to amines (primary and secondary) [26]. Then, previously synthesized amine-terminated PEG (M_n = 2000 g/mol) coupled with MWCNT-COOC₅F₆. Following this, synthesized PS-N₃ was coupled to MWCNT-CONHPEG at high temperature (130 °C) via nitrene addition reaction to obtain PS-g-MWCNT-CONHPEG. Figure 4.1 presents the schematic illustration of the study.

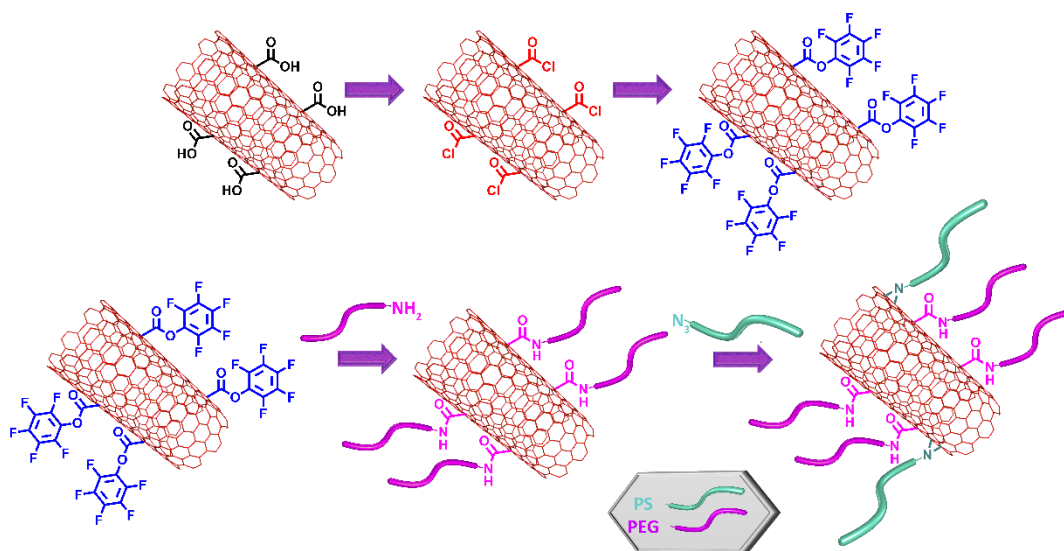


Figure 4.1 : Schematic illustration of functionalization process.

4.1 Experimental Part

4.1.1 Materials

-COOH Functionalized multi-walled nanotubes (MWCNTs-COOH) and were supplied by Nanostructured & Amorphous Materials, Inc. and used as received. Styrene (St, 99%, Sigma-Aldrich) and *N, N, N', N'', N''*-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) was passed through basic alumina column to remove inhibitor. Poly(ethylene glycol) monomethylether (Me-PEG-OH, $M_n = 2000$ g/mol, Fluka) were dried by azeotropic distillation with anhydrous toluene. *N,N*-dimethylformamide (DMF, 99.8%, Aldrich), tetrahydrofuran (THF, 99.8%, J.T. Baker), thionyl chloride (99%, Merck), oxalyl chloride (98%, Aldrich), thio-ethanol-amine hydrochloride (cysteamine hydrochloride) (98%, Aldrich), CuBr (99.9%, Aldrich), ethyl α -bromoisobutyrate (98%, Aldrich), sodium azide (99.5%, Aldrich), pentafluorophenol (99+ %, ACROS Organics), acryloyl chloride (96%, Aldrich) were used as received.

4.1.2 Instrumentation

^1H (500 MHz) and ^{13}C (125 MHz) spectra were recorded using an Agilent VNMR 500 instrument in CDCl_3 . The conventional gel permeation chromatography (GPC) measurements were carried out with an Agilent instrument (Model 1100) with a pump, refractive index and UV detectors and four Waters Styragel columns (HR 5E, HR 4E, HR 3, HR 2), (4.6 mm internal diameter, 300 mm length, packed with 5 μm particles).

The effective molecular weight ranges of columns were 2000–4000000, 50–100000, 500–30000, and 500–20000 g mol⁻¹, respectively. THF was used as an eluent at a flow rate of 0.3 mL min⁻¹ at 30 °C and toluene was used as an internal standard. The molecular weights of the polymers were calculated on the basis of linear polystyrene (PS) standards (Polymer Laboratories). Thermogravimetric analyses (TGA) were performed Perkin Elmer Diamond TG/DTS at 10 °C min⁻¹ heating rate under a flowing N₂ atmosphere. FT-IR spectra were recorded on an Agilent technologies Cary 630 FT-IR instrument over the range 4000-500 cm⁻¹.

4.1.3 General procedure for the preparation of azide end-functionalized PS (PS-N₃)

Synthesis procedure of azide end-functionalized PS consisted of two steps. In the first step, ω -bromide terminated PS (PS-Br) was prepared by ATRP of Styrene at 110 °C. St (10.00 mL, 87 mmol), PMDETA (0.091 mL, 0.43 mmol), CuBr (0.062 g, 0.43 mmol), and ethyl 2-bromoisobutyrate (EiBr) (0.064 mL, 0.43 mmol) were placed in a round bottom 25 mL Schlenk tube, respectively. Following this step, the reaction mixture was degassed by three FPT cycles and left in a vacuum. The tube was kept stirring (500 rpm) in a thermostated oil bath at 110 °C for 40 minutes. After that time, the dark-green polymerization mixture was diluted with THF, passed through a basic alumina column for removing the catalyst. Finally, the raw polymer intermediate was re-dissolved in THF and added dropwise into the methanol for purification. This precipitation step repeated twice and dried in a vacuum oven at 40 °C for 24h.

Yield= 0.4 g, $M_{n, GPC}$ = 1950; D = 1.13, relative to PS standards. ¹H NMR (CDCl₃, δ): 7.5-6.2 (br, ArH of PS), 4.4 (br, 1H, CH(Ph)-Br end group of PS), 3.7-3.4 (br, 2H, CH₃CH₂O), 2.2-0.8 (m, aliphatic protons of PS and CH₃).

Next, previously obtained PS-Br (0.40 g, 0.20 mmol, $M_{n, GPC}$ = 1950g/mol) and sodium azide (0.65 g, 10 mmol) were dissolved in DMF (20 mL). Then, the mixture stirred for overnight at ambient temperature. The product was precipitated in an excess amount of methanol. PS-N₃ was dried for 24 h in a vacuum oven at 40 °C.

Yield = 0.5 g, $M_{n, GPC}$ = 2720 g/mol; D = 1.07, relative to PS standards. ¹H NMR (CDCl₃, δ): 7.5-6.2 (br, ArH of PS), 3.9 (br, 1H, CH(Ph)-N₃), 3.7-3.4 (br, 2H, CH₃CH₂O), 2.2-0.8 (m, aliphatic protons of PS and CH₃).

4.1.4 General procedure for the preparation of amine end-functionalized PEG (PEG-NH₂)

Poly(ethylene glycol) methyl ether ($M_n = 2000$ g/mol, 3 gr, 1.50 mmol) and DMAP (0.09 g, 0.75 mmol) were dissolved in 100 mL of CH₂Cl₂ and Et₃N (0.42 mL, 3 mmol) was added. After cooling the reaction mixture to 0 °C, acryloyl chloride (0.18 mL, 2.25 mmol) was added dropwise within 30 min, stirred for 15 min at 0 °C, and then overnight at room temperature. The crude product was washed with 1 M HCl, saturated aqueous NaHCO₃ and distilled water (100 mL) respectively. The aqueous phase was further extracted with CH₂Cl₂, and the combined organic phases were dried over Na₂SO₄. The solution was concentrated, and the residue was quickly filtered through a short column (silica gel, ethyl acetate) to remove the ammonium salts. After concentration of the solution the polymers were then precipitated into cold diethyl ether.

Yield = 2.99 g, 97%, $M_{n, \text{theo}} = 2055$ g/mol, $M_{n, \text{GPC}} = 2300$ g/mol; $D = 1.08$, relative to PS standards. ¹H NMR (CDCl₃, δ): 6.39 (d, -CH=CH₂), 6.14 (d, -CH=CH₂), 5.83 (d, 1H, -CH=CH₂), 4.29 (m, 2H, -OCH₂CH₂OCO-), 3.67-3.59 (m, PEG backbone), 3.36 (s, 3H, -OCH₃).

Next, PEG-Acrylate (0.50 g, 0.24 mmol), 2-aminoethanethiol hydrochloride (0.27 g, 2.40 mmol), Et₃N (0.33 mL, 2.40 mmol) and CH₂Cl₂ (20 mL) were added in 25 mL Schlenk tube under nitrogen, respectively. Hereafter, the reaction mixture was stirred for 5 hours at room temperature. The solution was concentrated *in vacuo*. The product was precipitated in diethyl ether and the precipitation procedure was repeated twice. The obtained polymer was dried overnight under vacuum.

Yield = 0.50 g, 96%, $M_{n, \text{theo}} = 2130$ g/mol, $M_{n, \text{GPC}} = 2600$ g/mol; $D = 1.08$, relative to PS standards. ¹H NMR (CDCl₃, δ): 4.31 (m, 2H, -OCH₂CH₂OCO-), 3.67-3.59 (m, PEG backbone), 3.38 (s, 3H, -OCH₃), 2.96 (2H, -CH₂NH₂), 2.88 (2H, -CH₂S-), 2.71 (4 H, -OCOCH₂-, -SCH₂-).

4.1.5 Formation of carbonyl chloride groups on MWCNTs with oxalyl chloride (MWCNTs-COCl)

150 mg of MWCNTs-COOH were dispersed in 200 mL of DMF in an ultrasonic bath. After 20 minutes of dispersion, the mixture cooled at 0°C for 30 minutes and 6 mL oxalyl chloride was added dropwise to the mixture. Then, the mixture was heated to

60°C and stirred for 24 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 µm), to remove unreacted oxalyl chloride.

Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again. The recovered black powder was dried under vacuum.

4.1.6 Formation of carbonyl chloride groups on MWCNTs with thionyl chloride (MWCNTs-COCl)

150 mg of MWCNTs-COOH were stirred in a mixture of 120 mL thionyl chloride (SOCl₂) and 6 mL DMF at 70 °C for 36 hours. The excess SOCl₂ was then removed by filtration. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 µm), to remove unreacted SOCl₂. Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again. The recovered black powder was dried under vacuum.

4.1.7 Synthesis of MWCNTs-COOC₆F₅

50 mg of MWCNTs-COCl were dispersed in 25 mL of CH₂Cl₂ in an ultrasonic bath. After 20 minutes of dispersion, 0.5 g pentafluorophenol and 0.5 mL pyridine were added, and the mixture were stirred overnight at ambient temperature. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 µm), to remove pentafluorophenol. Residual solid on the filter was sonicated with using excessive amount of fresh CH₂Cl₂ and solid filtered again until the unreacted pentafluorophenol could not be detected in the solvent (monitored by FTIR). The recovered black powder was dried under vacuum.

4.1.8 Reaction of Active Pentafluorophenyl Ester Modified MWCNTs (MWCNTs-COOC₆F₅) with Amines

90 mg of MWCNTs-COOC₆F₅ were dispersed in 90 mL of THF in an ultrasonic bath. After 20 minutes of dispersion, 0.5 g PEG- NH₂ and 0.2 mL TEA were added, and the mixture were stirred overnight at ambient temperature. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 µm), to remove NH₂-PEG₂₀₀₀. Residual solid on the filter was sonicated with using excessive amount of fresh CH₂Cl₂ and solid filtered again until the unreacted NH₂-PEG₂₀₀₀ could not be detected in the solvent (monitored by FTIR). The recovered black powder was dried under vacuum.

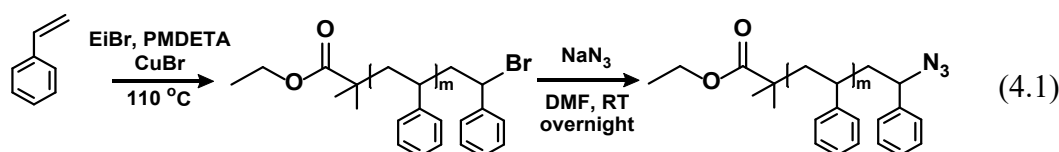
4.1.9 Second surface modification of MWCNTs-CONH-PEG via Nitrene addition

25 mg of MWCNTs-CONH-PEG were dispersed in 150 mL of 1,2-dichlorobenzene in an ultrasonic bath. After 10 minutes of dispersion, 250 g PS-N₃ was added, and the mixture were stirred at 130 °C for 72 hours. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 μm), to remove PS-N₃. Residual solid on the filter was sonicated with using excessive amount of fresh THF and solid filtered again until the unreacted PS-N₃ could not be detected in the solvent (monitored by FTIR). The recovered black powder was dried under vacuum.

4.2 Results and Discussion

As a wide-ranging view, this chapter describes the design and synthesis of carbon based-nanomaterials via a combination of active ester substitution reactions and nitrene addition. The present study concerns with the synthesis of amine terminated PEG and azido terminated St Polymers for the application of double “click” reactions (active ester substitution and nitrene addition) in sequential process.

First, azido terminated PS (PS-N₃) was carried out in two steps. After typical ATRP of styrene, the substitution of bromide into azide was performed in the presence of NaN₃ (4.1). A monomodal GPC traces presented in Figure 4.5 (a) displayed a clear shift to higher molecular weight region in proportion to its precursor (PS-Br) eventually an effective formation of PS-N₃ was proven.



¹H NMR spectra of PS-Br and PS-N₃ shown in Figure 4.2, and complete disappearance of the signal at 4.44 ppm corresponding to CH₂-Br protons of precursor PS-Br and appearance of new signal around 3.93 ppm owing to adjacent azido group to CH₂ protons is evidence of reactions successfully taking place (Figure 4.2). Observing azide-stretching band at 2095 cm⁻¹ from FT-IR spectrum supported the structure of PS-N₃ (Figure 4.4 (a)).

Next, PEG-NH₂ was obtained through two-step process. Firstly, the acrylate function was introduced by modification of hydroxyl-functionalized polymers (Me-PEG-OH, $M_n = 2000$ g/mol).

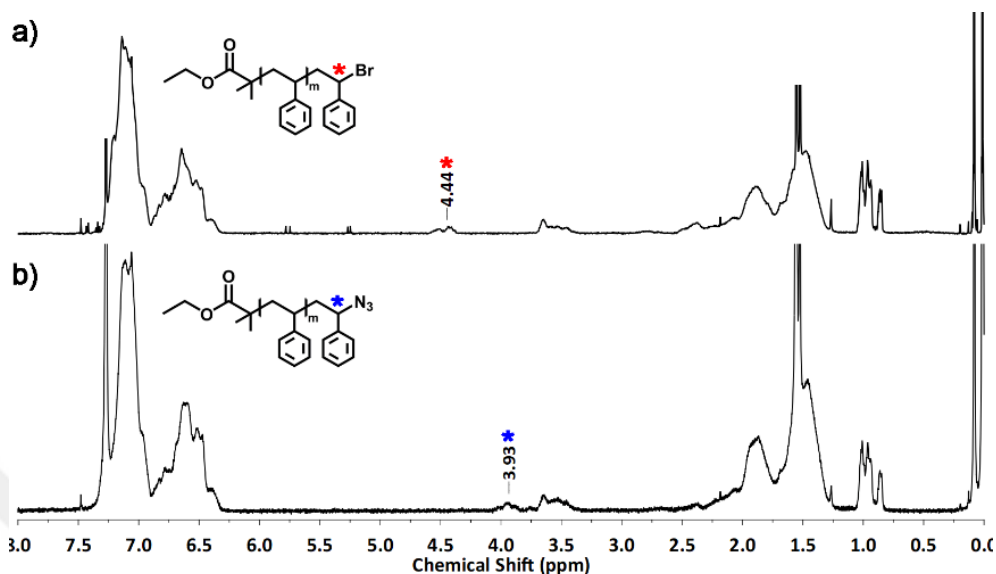
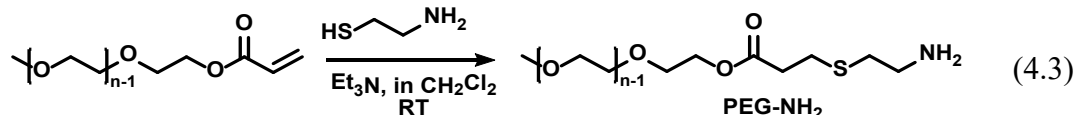
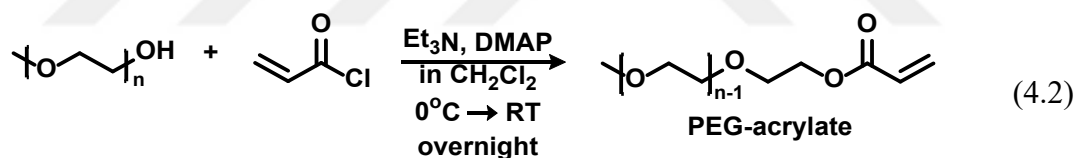


Figure 4.2 : ¹H NMR spectra of (a) PS-Br and (b) PS-N₃ in CDCl₃ (500 MHz).

Modification was performed by reaction with acryloyl chloride and Me-PEG-OH, in the presence of triethylamine /DMAP catalyst system and CH₂Cl₂ as solvent (4.2).



In the next step, Michael addition was performed on acrylate end-functionalized PEG with 2-aminoethanethiol hydrochloride in the presence of trimethylamine as a catalyst. As a result of thiol-acrylate addition reaction, amine functionality was introduced to PEG (4.3).

From the ¹H NMR spectrum of PEG-acrylate the new peaks are seen, the presence of alkene protons can be assumed. These signals are multiplied and present between 6.39-5.83 ppm, which indicates a successful acryloylation reaction (Figure 4.3 (a)).

The nucleophilic (Michael) thiol-ene reaction was also confirmed by ¹H NMR spectroscopy on which the complete disappearance of characteristic CH=CH₂ protons for PEG-NH₂ are followed with the appearance of new signals of methylene protons

(C=OCH₂CH₂S- and -SCH₂-) at 2.88 and 2.71 respectively that can be seen in Figure 4.3 (b).

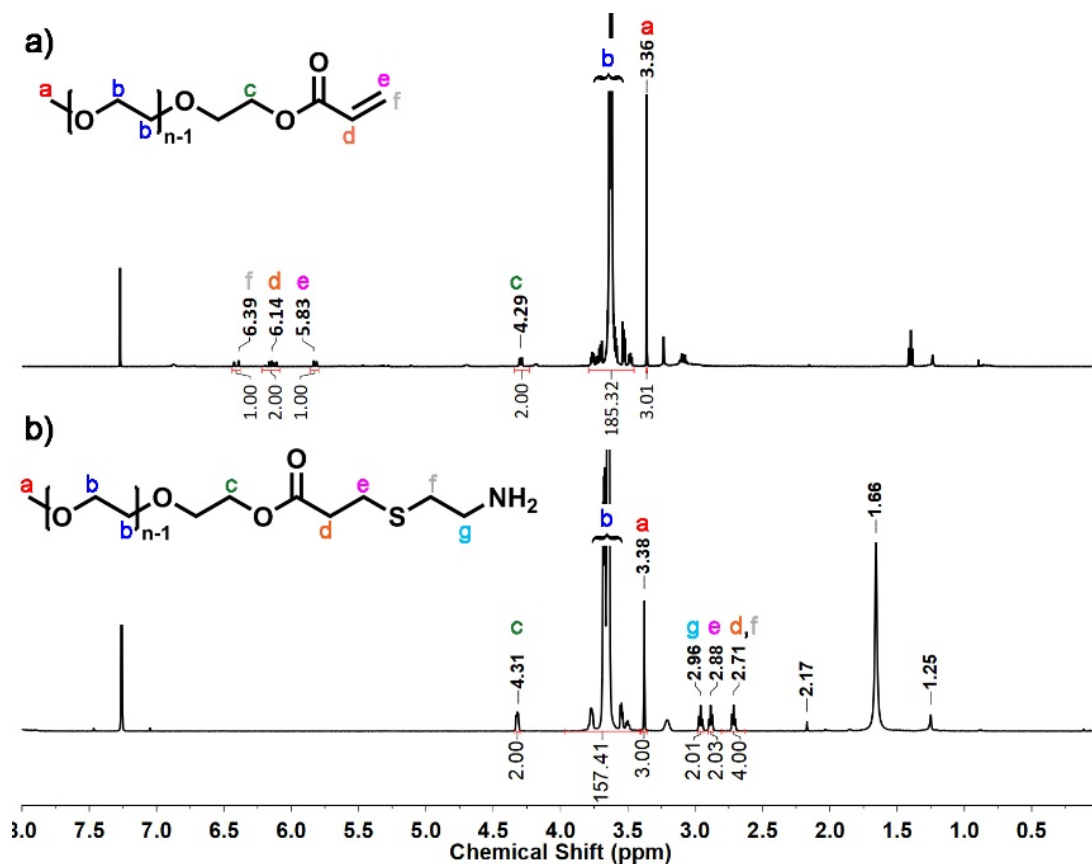


Figure 4.3 : ¹H NMR spectra of (a) PEG-acrylate and (b) PEG-NH₂ in CDCl₃ (500 MHz).

The characteristic peak of N-H absorption is clearly indicated at 3440 cm⁻¹ on FT-IR spectrum of PEG-NH₂ (Figure 4.4 (b)).

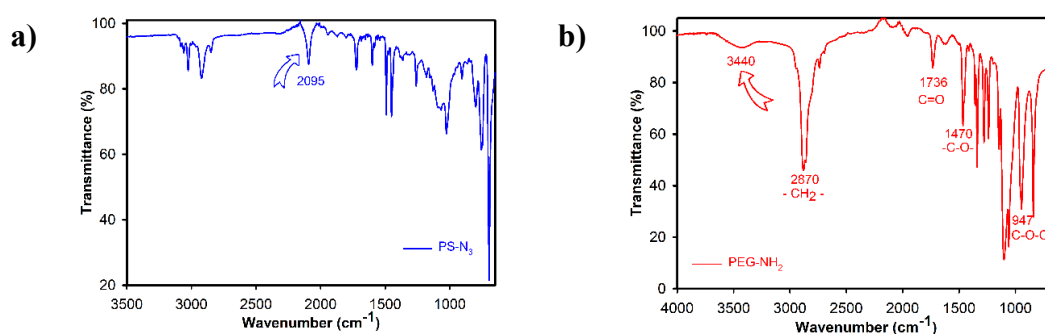


Figure 4.4 : Infrared spectra of (a) PS-N₃ and (b) PEG-NH₂.

For PEG-NH₂, a monomodal GPC traces presented in Figure 4.5 (b) displays no noteworthy shift to higher molecular weight region in proportion to its precursor (PEG-acrylate) since molecular weights of both polymers are similar to each other.

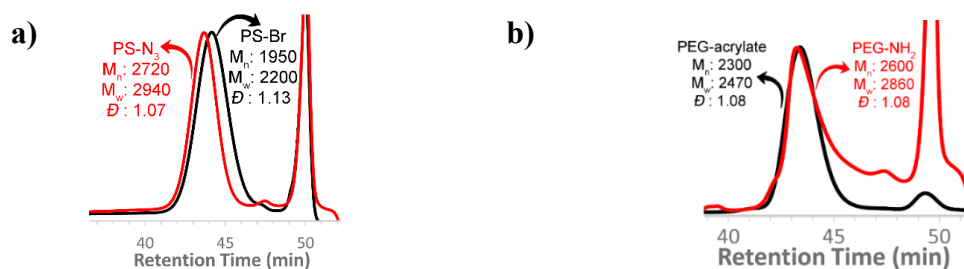


Figure 4.5 : Evolution of GPC traces of **(a)** PS-N₃ and **(b)** PEG-NH₂ and their precursors PS-Br and PEG-acrylate respectively in THF at 30 °C.

All polymerization conditions and results of the precursors used in the modification of MWCNTs are given in Table 4.1.

Table 4.1 : All polymerization conditions and results of the precursors used in the modification of MWCNTs.

Polymer	Time	M_n , GPC ^d	$\bar{D}$	M_n , NMR
PS-Br ^a	40 min	1950	1.13	-
PS-N ₃ ^b	overnight	2720	1.07	-
PEG-acrylate ^c	overnight	2300	1.08	2160
PEG-NH ₂	5 h	2600	1.08	2100

^a [M]₀/[I]₀ = 200, [I]₀: [CuBr]₀: [PMDETA]₀ = 1:1:1; polymerization was carried out at 110 °C.

^b Polymer and NaN₃ in DMF stirred at room temperature for overnight.

^c Obtained by an esterification reaction between acryloyl chloride and Me-PEG (2000).

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

As mentioned earlier, this study highlights the application of the active ester substitution reaction and nitrene addition reactions to perform double modification strategy to multiwalled (MWCNTs) carbon nanotubes for surface modification. For this purpose, after synthesizing polymers, commercially available carboxylic acid functionalized MWCNTs (MWCNTs-COOH) were converted to the acyl chlorides in the presence of oxalyl chloride or thionyl chloride in DMF. Reaction of the acyl chlorides with pentafluorophenol formed the active esters. Active ester modified MWCNTs (MWCNTs-COOC₆F₅) showed a high reactivity toward amines [26]. Following reaction occurred in the presence of MWCNTs-COOC₆F₅ and primary or secondary amines resulting in amide bonds. Finally, obtaining MWCNTs-CONHR double modified with PS-N₃ [10] (Figure 4.6).

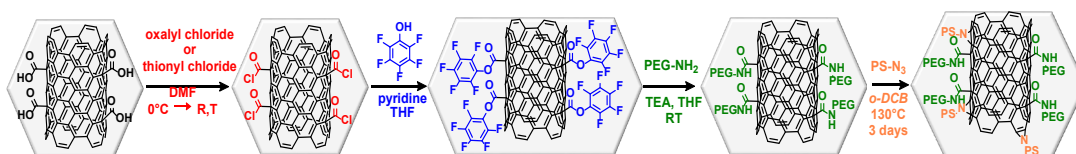


Figure 4.6 : Schematic illustration of modification steps of MWCNTs.

The thermal degradation of PEG and PS starts between 250-400 °C, in general [133] and they can be completely decomposed at a temperature of 650°C. Therefore, the evaluation of thermogravimetric profiles of carbon nanotubes were choose based on degradation temperature of polymers.

As a result of these analysis which have been performed between 30-650 °C, the weight loss of pristine carboxylic acid functionalized MWCNTs was 3 wt% between 250-650 °C. On the same analysis, MWCNTs-COCl and MWCNTs-COOC₆F₅ exhibited a uniform thermal degradation behavior with a 7.02% and 6.43 % weight loss respectively. The weight loss of the MWCNTs samples functionalized with polymers that have also measured between 250-650 °C, the amount of polymers that covalently attached to the MWCNTs surface was estimated

Table 4.2 : Thermogravimetric profiles of modified MWCNTs.

Entry	Name of the entry	Weight (%) ^a	Weight % of polymer attached ^b
<i>pristine-MWCNTs</i>	MWCNTs-COOH	2.3	-
1	MWCNTs-COCl	7.02	-
2	MWCNTs-COOC ₆ H ₅	6.43	-
3	MWCNTs-CONH-PEG	28.19	~ 21
4	MWCNTs-CONH-PEG - PS	17.31	~ 10

^aMeasured by TGA between 250-600 °C under nitrogen with a heat flow of 10 °C/min.

^bThe weight loss from the *f*-CNTs samples at 650 °C is used to estimate the amount of polymer that is covalently attached to the CNTs surface and measured by TGA. A weight loss, due to polymer decomposition, was observed to occur between temperatures of 250-650 °C for *f*-CNTs

Two-step degradations were detected for MWCNTs modified with polymers. MWCNTs-CONH-PEG started to decompose at much lower temperature when compared with MWCNTs-CONH-PEG – PS. as 28.19% and 17.31% (Table 4.2).

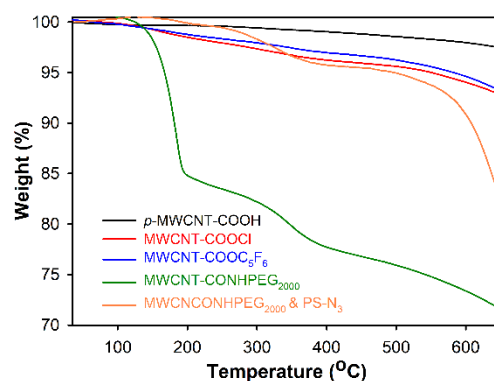


Figure 4.7 : Thermal gravimetric analysis curves of *p*-MWCNTs, CNTs (#1-4) at a heating rate of 10 °C/min under nitrogen atmosphere.

1 mg of *p*-MWCNT and CNTs (#1-4) in 1.5 mL of THF are added into vials and then sonicated for 20 minutes to prepare related dispersions (Figure 4.8). Prepared samples are photographed after standing for 1 week at room temperature.

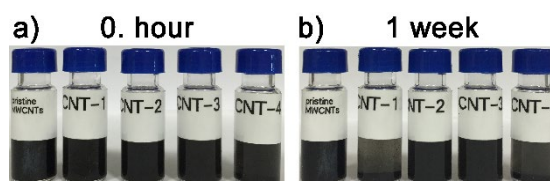


Figure 4.8 : All dispersions of MWCNTs were prepared through the sonication of 0.5 mg of MWCNTs/polymer in 1.5 mL solvent for 2 minutes.

Obtained functionalized MWCNTs which were expected to be more soluble in organic solvents will have a great potential for the future applications. Even after a week in THF, the resulting dispersion can be observed almost without any aggregation and with an admissible stability (Figure 4.8 (b)). CNT-1 (MWCNTs-OCCl) showed relatively poor solubility in THF when it is compared to other samples. This result corresponded by the literature since it was the precursor for MWCNTs-COOC₆F₅ [26]. In addition, CNT-4 showed relatively poor solubility in THF, this could be also explained by the decrease in the modification (amount of weight loss) showed on the TGA results (Figure 4.7).



5. INDIRECT FUNCTIONALIZATION OF MULTIWALLED CARBON NANOTUBES THROUGH NON-COVALENT INTERACTION OF FUNCTIONAL POLYESTERS¹

Carbon nanotubes (CNTs) have speedily turned into an interdisciplinary field because of showing their superior mechanical, electrical and chemical features. These features increase the usage of CNTs in many areas such as sensing systems, energy storage devices, and electronics [5, 134].

However, major limitation for application of CNTs is their poor solubility, dispersion, processability and tendency to agglomerate. Hence, key aspect to overcome these issues is the functionalization of CNTs [5]. Two main methodologies have been reported such as formation of covalent bonds and non-covalent interactions (van der Waals forces, π - π stacking interactions) [5-8]. During the last decade, many covalent functionalization approaches, which are oxidation, fluorination, free radical addition, addition of carbenes and nitrenes, 1,3-dipolar cycloaddition, nucleophilic addition, alkylation and Diels-Alder cycloaddition have been studied and explained in several publications [5, 6, 13, 90, 125, 131, 135-137]. However, after covalent functionalization, the intrinsic properties of CNTs such as conductivity and mechanical strength changes based upon destruction of the regular graphene-type structure on the carbon nanotubes walls. Therefore, to protect the intrinsic properties of CNTs, non-covalent approaches become more favorable [138-146]. Non-covalent functionalization of CNTs with polymers, which contain highly aromatic moiety such as pyrene, naphthalene, and porphyrin and fluorescein polyethylene glycol, is an effective way to disperse the CNTs in aqueous and non-aqueous solvents without damaging their unique structure and thus preserving their intrinsic properties [139-147]. The typical 1,3-dipolar cycloaddition reaction between azides and alkynes was the first discovered by Huisgen and coworkers. However, this reaction has some

¹ This chapter is based on the paper P.S. Omurtag, B. Alkan, H. Durmaz, G. Hizal, U. Tunca, Indirect functionalization of multiwalled carbon nano tubes through non-covalent interaction of functional polyesters, Polymer 141 (2018) 213-220, doi: 10.1016/j.polymer.2018.03.017.

disadvantages such as requirement of elevated temperature, low regioselectivity and slow reaction rate without using a proper catalyst [148-150].

On the other hand, the copper-catalyzed azide-alkyne cycloaddition reaction (CuAAC) displays high regioselectivity (only 1,4-disubstituted triazole), an accelerated reaction rate, high yields (up to 95%) at benign conditions and tolerance to various solvents [151, 152]. The CuAAC reaction rapidly takes an attention to polymer chemists both for the polymer-polymer conjugation and the post functionalization of polymers due to its faithful partner living polymerization systems that create well-defined individual polymer blocks [153-155]. In spite of the unique features of CuAAC, the disadvantage is the removal of the copper catalyst residues.

Particularly for biomedical applications, elimination of copper residues from the resulting product is required. All these problems pushed the scientists to carry this reaction one-step further with an idea: “metal-free cycloaddition reactions between azides and alkynes with high yields at mild temperatures”. Bertozzi group pioneered the use of strain promoted azide alkyne cycloaddition reactions by reacting the strained cyclooctyne derivatives with azide functionals under mild conditions [156]. Next, Ju and coworkers suggested a 1,3-dipolar cycloaddition of azides with electron-deficient alkynes in water at room temperature [157]. With this approach, either internal or terminal alkynes, which has at least one electron-withdrawing functional group adjacent to alkyne, can react with azide without using a catalyst. Recently, our group focused on the preparation of a series of polyesters containing electron deficient internal alkyne units derived from acetylene dicarboxylic acid and a variety of diols in the main backbone [158, 159]. Besides, two carbonyl units in the structure makes the triple bond very electron deficient and suitable for copper free cycloaddition reactions like 1,3-dipolar, Diels-Alder and further multicomponent reactions [158, 159].

In the current work, we report, for the first time, the synthesis of a series of polyesters possessing both pyrene and a variety of functional groups (-OH, -COOH, and -C≡CH) (Figure 5.1) and its non-covalent interactions on the surface of multiwalled carbon nanotubes (MWCNTs). Thus, we obtained a variety of functional CNTs via π - π interaction of the pre-functionalized polyesters and the pristine MWCNTs. Figure 5.1 presents the schematic illustration of the study.

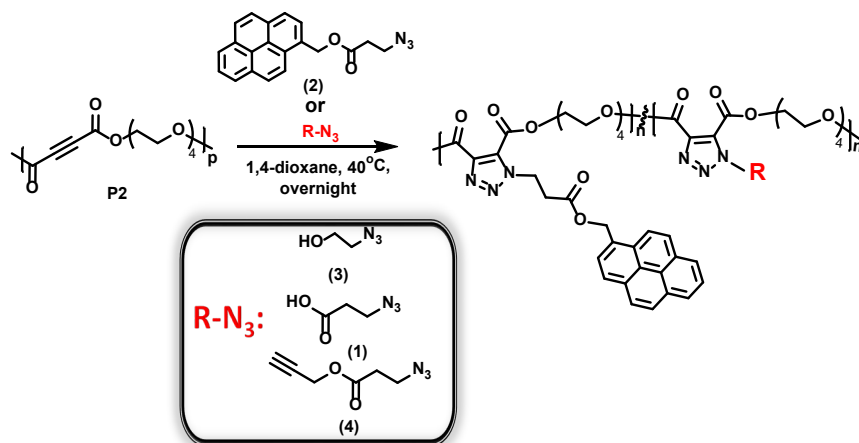


Figure 5.1 : Preparation of polyesters with pendant pyrene or various functional groups via Huisgen 1,3-dipolar cycloaddition reactions of polyester (*P2*) with organic azides in 1,4-dioxane at 40 °C.

5.1 Experimental Part

5.1.1 Materials

MWCNTs (3-15 walls, in average 14.5 nm wide and 1-10- μ m long) were kindly supplied by Bayer Material Science AG (Baytubes C 150 P) and used as received. 2-Bromoethanol, 3-bromopropionic acid, sodium azide, 1-pyrenemethanol, propargyl alcohol, N,N'-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), acetylenedicarboxylic acid (ADCA), tetraethylene glycol, 1,4-butanediol, 1,4-benzenedimethanol, p-toluenesulfonic acid monohydrate (PTSA), poly(ethylene glycol) (PEG, $M_n = 600$ g/mol), 1,4-cyclohexanedimethanol, benzene, acetone, methanol, diethyl ether and 1,4-dioxane were purchased from Sigma Aldrich and were all used without further purification. Tetrahydrofuran and dichloromethane were dried and distilled prior to use. Ethyl acetate (EtOAc) and hexane were in technical grade and distilled prior to use.

5.1.2 Instrumentation

^1H and ^{13}C NMR spectra were recorded on Agilent VNMRS 500 MHz in CDCl_3 . The conventional gel permeation chromatography (GPC) measurements were conducted with an Agilent instrument (Model 1100) with a pump, refractive index detector and four Waters Styragel columns (HR 5E, HR 4E, HR 3, HR 2), (4.6 mm internal diameter, 300 mm length, packed with 5 μ m particles). The effective molecular weight ranges of columns were 2000–4000000, 50–100000, 500–30000, and 500–20000 $\text{g}\cdot\text{mol}^{-1}$, respectively. All samples were passed through a 0.22 μ m PTFE filter prior to

analysis. THF was used as an eluent at a flow rate of 0.3 mL min^{-1} at 30°C and toluene was used as an internal standard. The molecular mass and dispersity of the polymers were calculated on the basis of linear polystyrene (PS) standards (Polymer Laboratories). Thermogravimetric analyses (TGA) were performed Perkin Elmer Diamond TG/DTS at $10^\circ\text{C min}^{-1}$ heating rate under a flowing nitrogen atmosphere. Between 3–5 mg of sample weights were arranged and then loaded into ceramic pans. The samples were heated from 30°C to 650°C at a heating rate of 10°C/min . UV measurements were recorded with an Agilent Cary 100 spectrophotometer. High-resolution transmission electron microscopy (HR-TEM) micrographs were collected using a JEOL 2100 instrument operating at 200 kV. The HR-TEM samples were prepared by drop coating a dilute solution of the sample in THF on a holey carbon-coated copper grid.

Synthesis of 3-azidopropionic acid (**1**) [160] and 2-azidoethanol (**3**) [161] were carried out according to literature procedures.

5.1.3 Synthesis of pyrene-1-ylmethyl 3-azidopropanoate (**2**)

3-Azidopropionic acid (**1**) (1.27 g, 11.0 mmol), 1-pyrenemethanol (3.0 g, 13 mmol) and DMAP (1.35 g, 11.0 mmol) were dissolved in 60 mL of CH_2Cl_2 . After stirring 5 minutes, a solution of DCC (2.73 g, 13 mmol) in 40 mL of CH_2Cl_2 was added into reaction mixture and stirred overnight at ambient temperature. Hereafter, filtering off the urea byproduct, the solution was concentrated *in vacuo* and purified by column chromatography over silica gel eluting with ethyl acetate/hexane (1:6) to afford pale yellow powder (Yield=2.53 g, 70 %).

^1H NMR (CDCl_3 , δ): 8.30-8.03 (m, 9H, ArH), 5.90 (s, 2H, pyrene- CH_2), 3.60 (t, 2H, - CH_2N_3), 2.65 (t, 2H, - $\text{CH}_2\text{CH}_2\text{N}_3$). ^{13}C NMR (CDCl_3 , δ): 170.82, 131.89-122.76, 65.26, 46.78, 34.06.

5.1.4 Synthesis of prop-2-yn-1-yl 3-azidopropanoate (**4**)

3-Azidopropionic acid (**1**) (2.46 g, 20.0 mmol), propargyl alcohol (1.07 mL, 17.0 mmol) and DMAP (2.10 g, 17 mmol) were dissolved in 60 mL of CH_2Cl_2 . After stirring 5 minutes, a solution of DCC (4.26 g, 20 mmol) in 40 mL of CH_2Cl_2 was added into the reaction mixture and stirred overnight at ambient temperature. Hereafter, filtering off the urea byproduct, the solution was concentrated *in vacuo* and purified

by column chromatography over silica gel eluting with ethyl acetate/hexane (1:4) to afford pale yellow powder (Yield=1.50 g, 58 %).

^1H NMR (CDCl_3 , δ): 4.73 (d, $-\text{CH}_2\text{C}\equiv\text{CH}$), 3.60 (t, $-\text{CH}_2\text{N}_3$), 2.63 (t, $-\text{CH}_2\text{CH}_2\text{N}_3$), 2.50 (t, $-\text{C}\equiv\text{CH}$), ^{13}C NMR (CDCl_3 , δ): 170.06, 75.23, 52.37, 46.55, 33.73.

5.1.5 Synthesis of polyester (P1)

A solution of acetylene dicarboxylic acid (ADCA) (1.0 g, 8.8 mmol), 1,4-butanediol (0.77 mL, 8.8 mmol) and p-toluene sulfonic acid monohydrate (PTSA) (0.15 g, 0.87 mmol) in 20 mL of benzene was stirred in a flask equipped with a Dean-Stark apparatus in an oil bath set to 100 °C overnight. The product was then precipitated in methanol and the dissolution-precipitation procedure was repeated twice. The obtained polymer was dried overnight under vacuum. (Yield: 1.10 g; $M_{n,\text{GPC}} = 6560$ g/mol, $\bar{D} = 1.63$, relative to the PS standards).

^1H NMR (CDCl_3 , δ) 4.30 (s, 4H, $\text{C}=\text{OOCCH}_2$), 1.82 (s, 4H, $\text{C}=\text{OOCCH}_2\text{CH}_2$); ^{13}C NMR (CDCl_3 , δ): 151.67, 74.72, 66.11, 30.92, 24.81.

5.1.6 Synthesis of polyester (P2)

A solution of ADCA (1.00 g, 8.76 mmol), tetraethylene glycol (1.51 mL, 8.76 mmol) and PTSA (0.15 g, 0.87 mmol) in 20 mL of benzene was stirred in a flask equipped with a Dean-Stark apparatus in an oil bath set to 100 °C overnight. The product was then precipitated in methanol and the dissolution-precipitation procedure was repeated twice. The obtained polymer was dried overnight under vacuum (Yield: 2.18 g, $M_{n,\text{GPC}} = 5810$ g/mol, $\bar{D} = 1.46$, relative to the PS standards).

^1H NMR (CDCl_3 , δ) 4.39 (m, 4H, $\text{C}=\text{OOCCH}_2\text{CH}_2\text{O}$), 3.75 (m, 4H, $\text{C}=\text{OOCCH}_2\text{CH}_2\text{O}$), 3.68 (s, 8H, $\text{OCH}_2\text{CH}_2\text{O}$); ^{13}C NMR (CDCl_3 , δ): 151.66, 74.89, 70.69, 68.41, 65.83.

5.1.7 Synthesis of polyester (P3)

A solution of ADCA (1.00 g, 8.76 mmol), PEG ($M_n = 600$ g/mol) (5.26 g, 8.76 mmol) and PTSA (0.15 g, 0.87 mmol) in 20 mL of benzene was stirred in a flask equipped with a Dean-Stark apparatus in an oil bath set to 100 °C overnight. The product was precipitated in methanol and the dissolution-precipitation procedure was repeated twice. The obtained polymer was dried overnight under vacuum. (Yield: 3.99 g; $M_{n,\text{GPC}} = 2350$ g/mol, $\bar{D} = 1.32$, relative to the PS standards)

^1H NMR (CDCl_3 , δ) 4.40 (m, 4H, $\text{C}=\text{OOCH}_2\text{CH}_2\text{O}$), 3.75 (m, 4H, $\text{C}=\text{OOCH}_2\text{CH}_2\text{O}$), 3.66 (m, H, OCH_2CH_2 of PEG); ^{13}C NMR (CDCl_3 , δ): 151.68, 74.89, 72.62, 70.52, 68.40, 65.85, 61.55.

5.1.8 Synthesis of polyester (P4)

A solution of ADCA (1.00 g, 8.76 mmol), 1,4-cyclohexanedimethanol (1.26 g, 8.76 mmol) and PTSA (0.15 g, 0.87 mmol) in 20 mL of benzene was stirred in a flask equipped with a Dean-Stark apparatus in an oil bath set to 100 °C overnight. The product was precipitated in methanol and the dissolution-precipitation procedure was repeated twice. The obtained polymer was dried overnight under vacuum (Yield: 2.32 g; $M_{n,\text{GPC}} = 7800$ g/mol, $D = 1.69$, relative to the PS standards).

^1H NMR (CDCl_3 , δ): 4.16-4.08 (m, 4H, $\text{C}=\text{OOCH}_2$), 2.0-1.0 (m, aliphatic protons of cyclohexane); ^{13}C NMR (CDCl_3 , δ): 151.88, 74.76, 71.47, 69.40, 36.62, 34.10, 28.44, 24.98.

5.1.9 Synthesis of polyester (P5)

A solution of ADCA (1.00 g, 8.76 mmol), 1,4-benzenedimethanol (1.21 g, 8.76 mmol) and PTSA (0.15 g, 0.87 mmol) in 20 mL of benzene was stirred in a flask equipped with a Dean-Stark apparatus in an oil bath set to 100 °C overnight. The product was precipitated in methanol and the dissolution-precipitation procedure was repeated twice. The obtained polymer was dried overnight under vacuum (Yield: 2.37 g; $M_{n,\text{GPC}} = 2200$ g/mol, $D = 1.17$, relative to the PS standards).

^1H NMR (CDCl_3 , δ): 7.38-7.20 (bs, 4H, ArH), 5.25 (bs, 4H, $\text{C}=\text{OOCH}_2\text{Ph}$), 4.57 (s, 4H, $\text{C}=\text{OOCH}_2\text{Ph}$); ^{13}C NMR (CDCl_3 , δ): 151.44, 134.77, 129.20, 128.93, 128.0, 126.2, 74.86, 71.64, 67.97.

5.1.10 Preparation of P1-pyrene polyester via 1,3-dipolar cycloaddition reaction between P1 and 2

P1 (0.34 g, 2.0 mmol) and the 2 compound (1.3 g, 4.0 mmol) were dissolved in 10 mL of 1,4-dioxane in a 25 mL of Schlenk tube. Next, the reaction mixture was degassed by two FPT cycles and the tube was placed in a thermostated oil bath at 40 °C overnight. After that time, the solution was concentrated under reduced pressure, then purified by precipitation twice in methanol and finally dried in a vacuum oven at 40 °C for 24 h yielding P1-pyrene polyester ($M_{n,\text{GPC}} = 8000$ g/mol, $D = 2.53$, relative to PS standards). ^1H NMR (CDCl_3 , δ): 8.30-7.60 (b, 9H, ArH), 5.68 (s, 2H, pyrene- CH_2),

4.75 (s, 2H, triazole-CH₂), 4.30 (bs, 4H, C=OOCH₂ of polyester), 3.00 (s, 2H, triazole-CH₂CH₂), 1.80 (bs, 4H, C=OOCH₂CH₂ of polyester).

5.1.11 Preparation of pyrene-functional polyester via 1,3-dipolar cycloaddition reaction of polyester (P2) with 2

P2 (0.27 g, 1.0 mmol) and 2 (0.65 g, 2.0 mmol) were dissolved in 10 mL of 1,4-dioxane in a 25 mL of Schlenk tube. The tube was placed in a thermostated oil bath at 40 °C overnight after the reaction mixture was degassed by two freeze-pump-thaw (FPT) cycles. Then, the solution was evaporated under reduced pressure and the polymerization mixture was purified by precipitation twice in 10-fold excess methanol and dried in a vacuum oven at 40 °C for 24 h yielding P2-pyrene (Yield=0.53 g; $M_{n, \text{GPC}}$ = 6300 g/mol, D = 1.14, relative to PS standards).

¹H NMR (CDCl₃, δ): 8.25-7.75 (br, 9H, ArH), 5.75 (s, 2H, pyrene-CH₂), 4.82 (s, 2H, triazole-CH₂), 4.43 (m, 4H, C=OOCH₂ of polyester), 3.81-3.30 (m, 4H, C=OOCH₂CH₂O of polyester and 8H, CH₂O of polyester), 3.05 (s, 2H, triazole-CH₂CH₂).

5.1.12 Preparation of P3-pyrene polyester via 1,3-dipolar cycloaddition reaction between P3 and 2

P3 (0.35 g, 0.50 mmol) and the 2 compound (0.33 g, 1.0 mmol) were dissolved in 10 mL of 1,4-dioxane in a 25 mL of Schlenk tube. Next, the reaction mixture was degassed by two FPT cycles and the tube was placed in a thermostated oil bath at 40 °C overnight. After that time, the solution was concentrated under reduced pressure, then purified by precipitation twice in methanol and finally dried in a vacuum oven at 40 °C for 24h yielding P3-pyrene polyester (Yield: 0.46 g; $M_{n, \text{GPC}}$ = 2950 g/mol, D = 1.14, relative to PS standards).

¹H NMR (CDCl₃, δ): 8.25-7.80 (b, 9H, ArH), 5.85 (s, 2H, pyrene-CH₂), 4.92 (s, 2H, triazole-CH₂), 4.50 (bs, 4H, C=OOCH₂ of polyester), 3.64-3.62 (m, 4H, -OCH₂CH₂, repeating unit of PEG), 3.12 (s, 2H, triazole-CH₂CH₂).

5.1.13 Preparation of P4-pyrene polyester via 1,3-dipolar cycloaddition reaction between P4 and 2

P4 (0.22 g, 1.0 mmol) and the 2 compound (0.65 g, 2.0 mmol) were dissolved in 10 mL of 1,4-dioxane in a 25 mL of Schlenk tube. Next, the reaction mixture was degassed by two FPT cycles and the tube was placed in a thermostated oil bath at 40

°C overnight. After that time, the solution was concentrated under reduced pressure, then purified by precipitation twice in methanol and finally dried in a vacuum oven at 40 °C for 24 h yielding P4-pyrene polyester (Yield: 0.22 g; $M_{n, \text{GPC}} = 10,100$ g/mol, $\bar{D} = 1.86$, relative to PS standards).

^1H NMR (CDCl_3 , δ): 8.25-7.75 (b, 9H, ArH), 5.79 (s, 2H, pyrene- CH_2), 4.84 (s, 2H, triazole- CH_2), 4.30-3.80 (m, 4H, $\text{C}=\text{OOCH}_2$), 3.06 (s, 2H, triazole- CH_2), 1.90-1.00 (m, aliphatic protons of cyclohexane).

5.1.14 Preparation of P5-pyrene polyester via 1,3-dipolar cycloaddition reaction between P5 and 2

P5 (0.22 g, 1.0 mmol) and the 2 compound (0.65 g, 2.0 mmol) were dissolved in 10 mL of 1,4-dioxane in a 25 mL of Schlenk tube. Next, the reaction mixture was degassed by two FPT cycles and the tube was placed in a thermostated oil bath at 40 °C overnight. After that time, the solution was concentrated under reduced pressure, then purified by precipitation twice in methanol and finally dried in a vacuum oven at 40 °C for 24h yielding P5-pyrene polyester ($M_{n, \text{GPC}} = 2700$ g/mol, $\bar{D} = 1.11$, relative to PS standards).

^1H NMR (CDCl_3 , δ): 8.25-7.75 (b, 9H, ArH), 7.30-7.10 (bs, 4H, ArH), 5.74 (s, 2H, pyrene- CH_2), 5.21 (bs, 4H, $\text{C}=\text{OOCH}_2$), 4.79 (s, 2H, triazole- CH_2), 2.98 (s, 2H, triazole- CH_2CH_2).

5.1.15 Preparation of pyrene/OH-functional polyester (P2-pyrene/OH) via 1,3-dipolar cycloaddition reaction of polyester (P2) with 2 and 3

P2 (0.26 g, 0.94 mmol), 2 (0.16 g, 0.47 mmol) and 3 (0.04 g, 0.47 mmol) were dissolved in 10 mL of 1,4-dioxane in 25 mL Schlenk tube. Hereafter, the reaction mixture was degassed by two FPT cycles. The tube was placed in a thermostated oil bath at 40 °C overnight. After that time, the solution was concentrated under reduced pressure. Finally, the polymerization mixture was purified by precipitation in twice in methanol and dried in a vacuum for yielding P2-pyrene/OH (Yield= 0.32 g).

^1H NMR (CDCl_3 , δ): 8.30-7.87 (br, 9H, ArH), 5.80 (s, 2H, pyrene- CH_2), 4.87 (bs, 2H, triazole- CH_2), 4.71 (s, 2H, triazole- CH_2), 4.46 (m, 4H, $\text{C}=\text{OOCH}_2\text{CH}_2\text{O}$), 3.81-3.30 (m, 4H, $\text{C}=\text{OOCH}_2\text{CH}_2\text{O}$, 8H, CH_2O , and 2H, CH_2OH) 3.08 (s, 2H, triazole- $\text{CH}_2\text{CH}_2\text{C}=\text{O}$).

5.1.16 Preparation of pyrene/COOH-functional polyester (P2-pyrene/COOH) via 1,3-dipolar cycloaddition reaction of polyester (P2) with 1 and 2

P2 (0.26 g, 0.94 mmol), 1 (0.060 g, 0.47 mmol) and 2 (0.16 g, 0.47 mmol) compound were dissolved in 10 mL of 1,4-dioxane in 25 mL Schlenk tube. Hereafter, the reaction mixture was degassed by two FPT cycles and placed in a thermostated oil bath at 40 °C overnight. Following removal of the solvent under vacuum, the polymer was collected by precipitation twice in excess methanol and dried in a vacuum oven at 40 °C for 24 h yielding P2-pyrene/COOH (Yield = 0.30 g).

^1H NMR (CDCl_3 , δ): 8.30-7.87 (br, 9H, ArH), 5.80 (s, 2H, pyrene- CH_2), 4.83 (bs, 4H, triazole- CH_2), 4.46 (m, 4H, $\text{C}=\text{OOCH}_2$ of polyester), 3.81-3.30 (m, 4H, $\text{C}=\text{OOCH}_2\text{CH}_2$ of polyester and 8H, CH_2O of polyester), 3.08 and 2.94 (br, 4H, triazole- CH_2CH_2).

5.1.17 Preparation of pyrene/alkyne-functional polyester (P2-pyrene/ $\text{C}\equiv\text{CH}$) via 1,3-dipolar cycloaddition reaction of polyester (P2) with 2 and 4

P2 (0.26 g, 0.94 mmol), 2 (0.16 g, 0.47 mmol) and 4 (0.07 g, 0.47 mmol) were dissolved in 10 mL of 1,4-dioxane in 25 mL Schlenk tube. Hereafter, the reaction mixture was degassed by two FPT cycles. The tube was placed in a thermostated oil bath at 40 °C for overnight. The polymer was collected after the precipitation of the polymerization mixture twice in 10-fold excess methanol followed by drying in a vacuum oven at 40 °C for 24 h yielding P2-pyrene/ $\text{C}\equiv\text{CH}$ (Yield= 0.36 g).

^1H NMR (CDCl_3 , δ): 8.30-7.87 (br, 9H, ArH), 5.82 (s, 2H, pyrene- CH_2), 4.88 (bs, 2H, triazole- CH_2 and 2H, $\text{CH}_2\text{C}\equiv\text{CH}$), 4.67 (s, 2H, triazole- CH_2), 4.48 (m, 4H, $\text{C}=\text{OOCH}_2\text{CH}_2\text{O}$), 3.81-3.30 (m, 4H, $\text{C}=\text{OOCH}_2\text{CH}_2\text{O}$, and 8H, CH_2O), 3.08 (s, 4H, triazole- CH_2CH_2), 2.52 (s, 1H, $\text{C}\equiv\text{CH}$).

5.1.18 Typical protocol for modification of *p*-MWCNTs with pyrene-functional polyesters: CNT-1 to CNT-5

50 mg of *p*-MWCNTs was dispersed in 150 mL of dry THF in an ultrasonic bath. After 20 minutes of dispersion, 250 mg of pyrene-functional polyester was added, and the mixture was stirred at ambient temperature for ten days. Then, the dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 μm) to remove nonattached polyester. Residual solid on the filter was sonicated with using excessive amount of fresh THF and filtered again until the nonattached pyrene-functional polyester could

not be detected in the solvent (monitored by UV-spectrophotometer). The recovered black powder was dried under vacuum.

5.1.19 Typical protocol for modification of *p*-MWCNTs with pyrene-functional polyesters: CNT-6 and CNT-7

25 mg of *p*-MWCNTs was dispersed in 75 mL of distilled water in an ultrasonic bath. After 20 minutes of dispersion, 125 mg of pyrene-functional polyester was added, and the mixture was stirred at ambient temperature for ten days. Following that period, nonattached polyester successfully removed from the dispersion via filtration through a filter (Sartorius, PTFE; pore size, 0.2 μm). Excessive amount of fresh THF was added to residual solid on the filter and sonicated. Then the nonattached pyrene-functional polyester was removed by washing THF (monitored by UV-spectrophotometer). The recovered black powder was dried in a vacuum oven at 40 °C.

5.1.20 Typical protocol for modification of *p*-MWCNTs with P2-pyrene/-COOH, P2-pyrene/-OH, or P2-pyrene/-C $\equiv$ CH functional polyesters: CNT-8 to CNT-10

20 mg of *p*-MWCNTs were dispersed in 50 mL of dry THF in an ultrasonic bath. After 20 min, 150 mg of functional polyester was added, and the mixture were stirred at ambient temperature for ten days. The dispersion was filtered through a filter (Sartorius, PTFE; pore size, 0.2 μm), to remove nonattached polyester. Residual solid on the filter was sonicated with using excessive amount of fresh THF and filtered again until the nonattached polyester could not be detected in the solvent monitoring by UV-spectrophotometer. The recovered black powder was dried under vacuum.

5.2 Results and Discussion

In this chapter, we aimed an indirect modification of MWCNTs using functional polyesters through the π - π stacking of the pyrene functional polymer scaffold to the aromatic structures of carbon nanotubes. Recently, we demonstrated that polyesters having electron deficient alkyne groups between two carbonyls are very effective in the cycloaddition reactions, for example, Huisgen and Diels-Alder reactions [158]. Therefore, here we successfully prepared a variety of polyesters having electron deficient alkyne moieties in the main chain that subsequently allow us to quantitatively introduce various pendant functions, such as pyrene, or pyrene/hydroxyl,

pyrene/COOH, and pyrene/alkyne through Huisgen 1,3-dipolar cycloaddition reaction.

Pyrene-1-ylmethyl 3-azidopropanoate (**2**) was obtained via an esterification reaction between (**1**) and slightly excess amount of 1-pyrenemethanol in the presence of DCC as a coupling agent and DMAP as a catalyst. After the reaction, the purified compound was characterized by ^1H NMR. From the spectrum, a signal related to methylene protons of Py-CH₂OH at 5.24 ppm completely disappeared and a new methylene protons regarding Py-CH₂OC=O was observed at 5.90 ppm (Figure 5.2). Moreover, the structure of (**2**) was further supported by the disappearance of broad acid stretching around 3600-2800 cm⁻¹ as well as the appearance of aromatic -CH stretching around 1500-1200 cm⁻¹ (Figure 5.3).

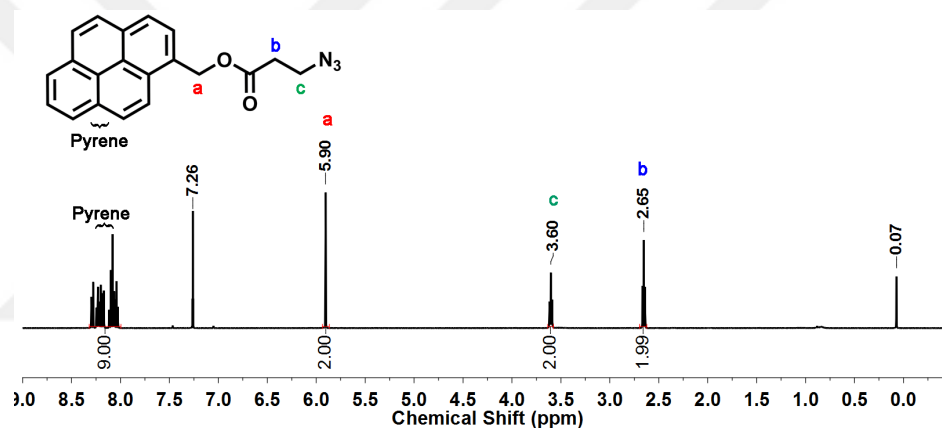


Figure 5.2 : ^1H NMR spectrum of pyrene-1-ylmethyl 3-azidopropanoate (**2**) in CDCl_3 (500 MHz).

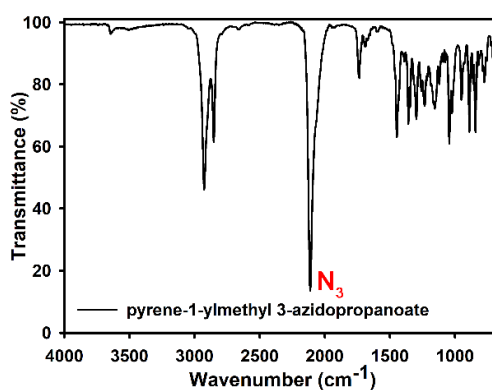


Figure 5.3 : FT-IR spectrum of pyrene-1-ylmethyl 3-azidopropanoate (**2**).

Prop-2yn-1-yl 3-azidopropanoate (**4**) was obtained via an esterification reaction between propargyl alcohol and slightly excess amount of (**1**) in the presence of DCC as a coupling agent and DMAP as a catalyst. After the reaction, the purified compound

was characterized by ^1H NMR. From the spectrum, a signal related to methylene protons of propargyl alcohol at 4.28 ppm completely disappeared and a new methylene protons regarding $-\text{CH}_2\text{C}\equiv\text{CH}$ was observed at 4.73 ppm (Figure 5.4).

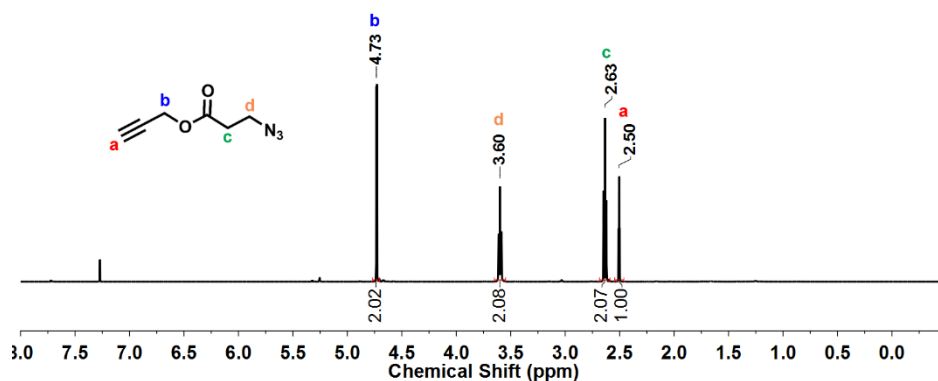


Figure 5.4 : ^1H NMR spectrum of prop-2yn-1-yl 3-azidopropanoate (4) in CDCl_3 (500 MHz).

The acetylene dicarboxylic acid (ADCA) and various available diols (butanediol, tetraethylene glycol, PEG ($M_n = 600$ g/mol), 1,4-cyclohexanedimethanol, or 1,4-benzenedimethanol) were reacted overnight in benzene at 100°C using a Dean Stark apparatus in the presence of a catalytic amount of *p*-toluenesulfonic acid monohydrate (PTSA) to yield related polyesters. From ^{13}C NMR spectra, two distinguished signals detected at 151.70 and 74.80 ppm are assignable to the $\text{C}=\text{O}$ and $\text{C}\equiv\text{C}$ groups, respectively displaying the structure of polyester main backbone (Figure 5.5).

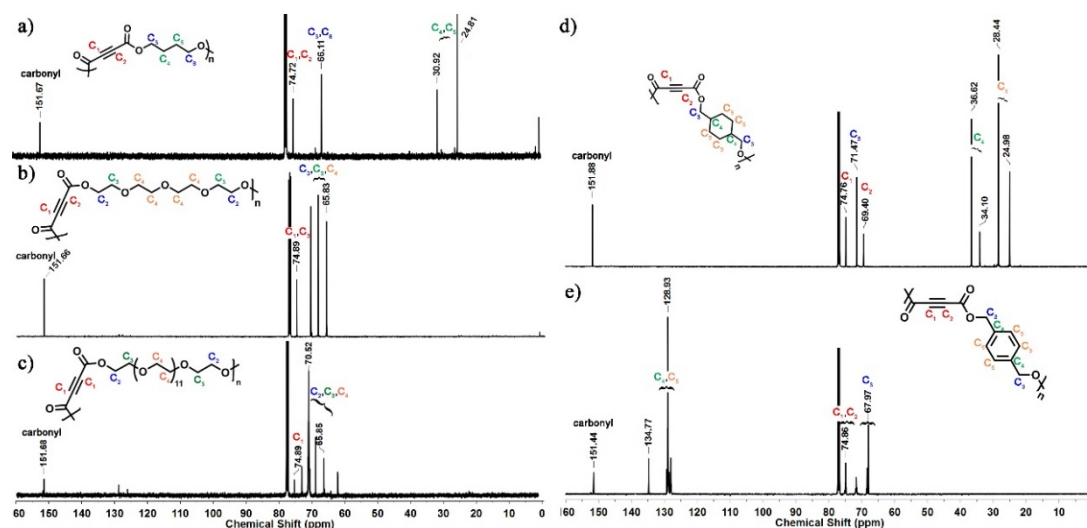


Figure 5.5 : ^{13}C NMR spectra of polyester (a) P1, (b) P2, (c) P3, (d) P4, (e) P5 in CDCl_3 (125 MHz).

Furthermore, the GPC traces of whole polyesters exhibited monomodal distributions and low molar mass (M_n of 7800 to 2200 g/mol) with dispersity index (D) in the range of 1.69-1.17. Figure 5.6 (a) show the related figure of GPC traces for polyesters.

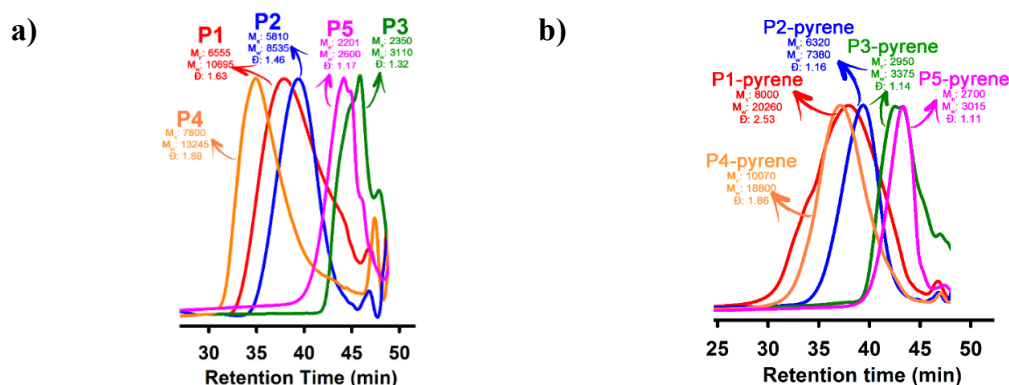


Figure 5.6 : GPC traces of polyesters in THF at 30 °C.

Next, pendant pyrene-functional polyesters were achieved via reacting polyesters (1 equiv) with pyrene-1-ylmethyl 3-azidopropanoate (2) (2 equiv) in 1,4-dioxane at 40 °C overnight. The remaining unreacted pyrene compound was simply removed through precipitation twice from methanol. The structure of pyrene-functional polyesters was confirmed using ^1H NMR spectroscopy. The new signals at 8.25-7.75, 5.75, 4.82, and 3.05 ppm can be assigned to the aromatic protons of pyrene and the CH_2 linkage protons between triazole and pyrene, respectively along with the main backbone signals.

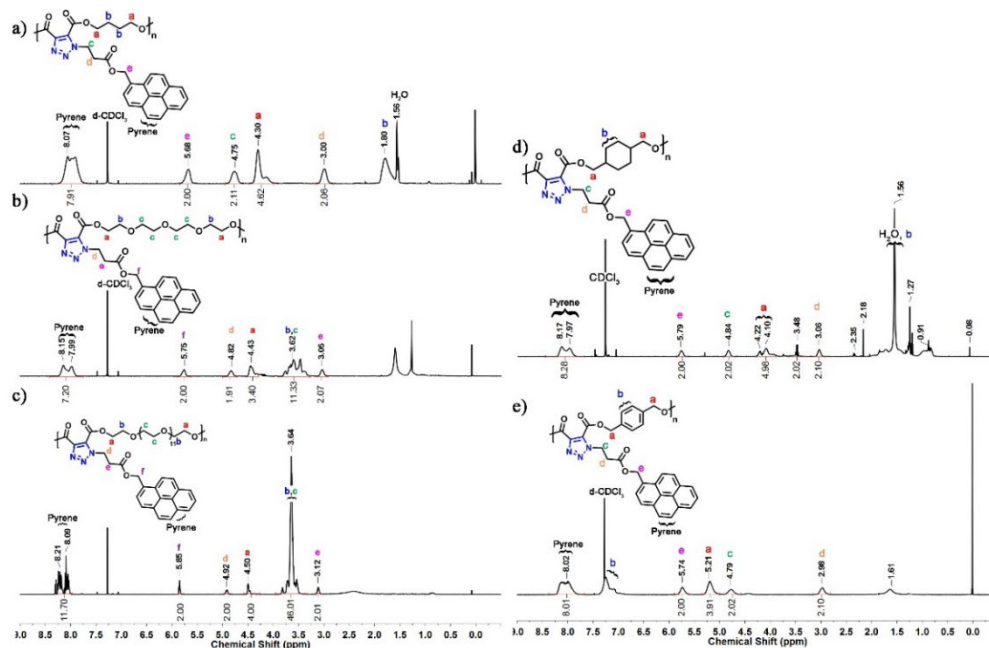


Figure 5.7 : ^1H NMR spectra of pyrene-functional polyester (a) P1-pyrene, (b) P2-pyrene, (c) P3-pyrene, (d) P4-pyrene, (e) P5-pyrene in CDCl_3 .

The 1,3-dipolar cycloaddition reaction efficiency for whole polyester patterns was found to be quantitative using ^1H NMR spectroscopy, while comparing the integrated area ratios of distinct protons of pendant functional (the ArHs of pyrene, the triazole- CH_2CH_2 , and the ester CH_2 linked to pyrene) to the OCH_2 protons of the polyester backbone. Figure 5.7 gives detailed information for ^1H NMR spectra of pyrene-functional polyesters. Thus, these results indicate that the pyrene unit could be attached very effectively onto a polyester possessing electron deficient alkyne moieties regardless of the backbone structures whether it contains aliphatic or aromatic groups. Besides, it is also clear with this study that when a functionalized-polyester is desired for a specific purpose through the MWCNT, the electron deficient alkyne structure in the polyester backbone might eliminate some additional synthetic steps, such as special monomer design before the polymerizations.

Moreover, the GPC traces of all pyrene-functional polyesters exhibited monomodal distributions and low molar mass (M_n of 10070 to 2700 g/mol) with dispersity index (D) in the range of 2.53-1.17. Figure 5.6 (b) shows the related figure of GPC traces for polyesters.

Before demonstrating the main purpose of this study involving one-step preparation of polyester with both pyrene and a specific functional group, first, the pyrene pendant polyesters were reacted with the MWCNT to demonstrate the reactivity of polyesters with different backbone toward the non-covalent interaction with the MWCNT. To this end, preformed polyesters (*P1-pyrene* to *P5-pyrene*) were reacted with MWCNT in THF for 10 days at ambient temperature, keeping the weight ratio of the polyesters to MWCNT as 5:1 to ensure a strong π - π stacking interactions between MWCNT and the polyesters [8]. Then, the resulting CNT-hybrids (CNT-1 to CNT-5) were rinsed with fresh THF to remove the excess polyesters. Furthermore, due to the water-soluble feature of *P2-pyrene* and *P3-pyrene*, two new additional CNT-hybrids (CNT-6 and CNT-7) were prepared according to previous procedure in distilled water.

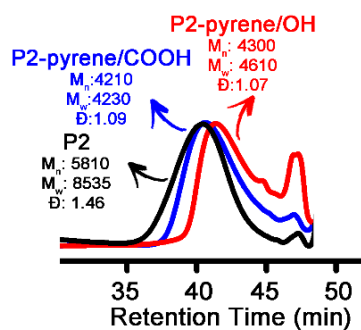


Figure 5.8 : GPC traces of P2-pyrene/COOH and P2-pyrene/OH in THF at 30 °C.

In the following study, a combination of pyrene and a variety of functional moieties, such as hydroxyl, carboxylic acid, or alkyne was employed to yield heterofunctional polyesters using Huisgen cycloaddition reaction. To this end, *P2* derived from tetraethylene glycol, was selected purposely because of its hydrophilic character that can able to show compatibility with the acid and the alcohol groups used in the study. On the other hand, *P3* (derived from PEG-600) was not utilized since this polymer exhibited an affinity toward column stationary phase, which prevented the reliable GPC measurement (Figure 5.8).

Polyester, *P2* (1 equiv) was modified using pyrene-1-ylmethyl 3-azidopropionate (**2**) (0.5 equiv), together with 2-azidoethanol (**3**), 3-azidopropionic acid (**1**) (0.5 equiv), or (0.5 equiv), or prop-2-yn-1-yl 3-azidopropionate (**4**) (0.5 equiv) to give rise to final polyesters, *P2-pyrene/OH*, *P2-pyrene/COOH*, *P2-pyrene/C≡CH*, respectively. From ^1H NMR spectra, it was deduced that signals at 5.80, and 4.83 ppm were assignable to the pyrene- CH_2 , triazole- CH_2 , respectively (Figure 5.9, Figure 5.10, Figure 5.11). The signal integration ratio of them separately against the ester CH_2 of the polyester backbone at around 4.46 ppm showed that the 1,3-dipolar azide alkyne cycloaddition reaction occurred with high efficiency.

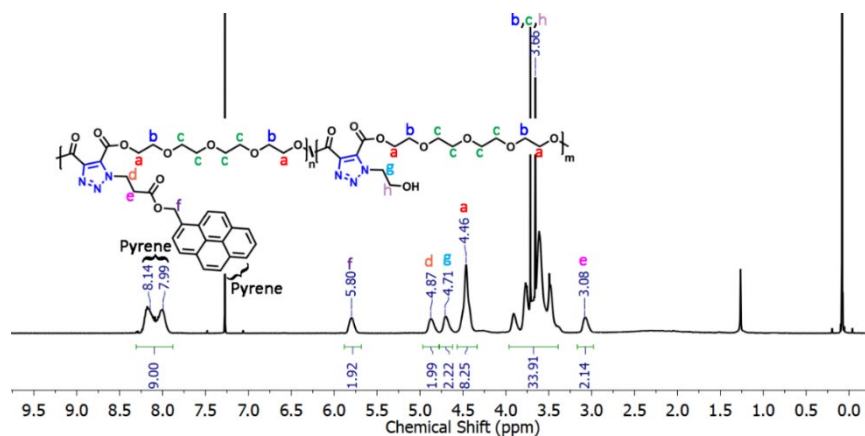


Figure 5.9 : ^1H spectrum of *P2-pyrene/OH* functional polyester in CDCl_3 .

Moreover, ^1H NMR spectra confirmed that a molar ratio of the pyrene to the $-\text{OH}$, $-\text{COOH}$, or $-\text{C}\equiv\text{CH}$ in final structure of polyesters was found to be 1/1 as similar as a feeding ratio of reactants.

Next, the *P2-pyrene/OH*, *P2-pyrene/COOH*, and *P2-pyrene/ C $\equiv$ CH* functional polyesters were attached to MWCNTs via $\pi - \pi$ stacking methodology in THF at ambient temperature for 10 days. In this case, the weight ratio of *P2-pyrene/OH*, *P2-pyrene/COOH*, and *P2-pyrene/ C $\equiv$ CH* to the MWCNT was arranged as 7.5 due to decrease in the pyrene unit in the polyester backbone. The unbound functional polyester was removed from the modified MWCNT by repetitive sonicating the dispersion using excessive amount of fresh THF and subsequently filtration until the solution does not contain a trace amount of functional-polyester by monitoring UV-spectrophotometer.

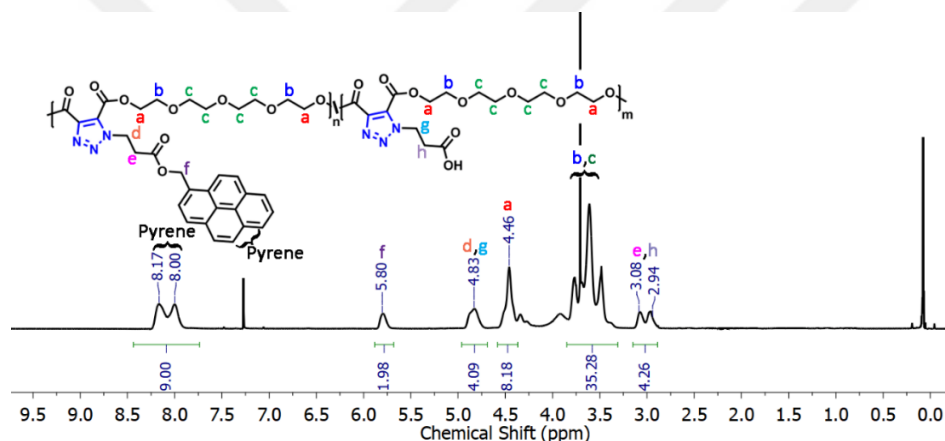


Figure 5.10 : ^1H NMR spectrum of *P2-pyrene/COOH* functional polyester in CDCl_3 .

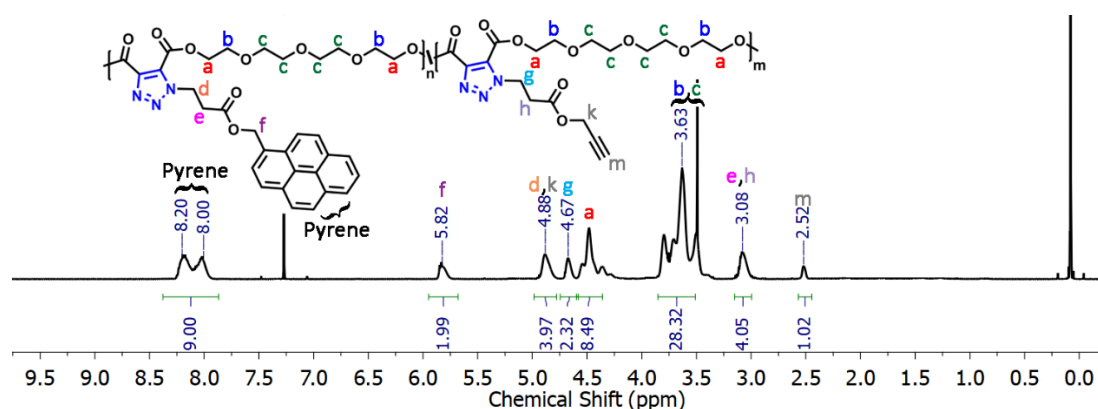


Figure 5.11 : ^1H NMR spectrum of *P2-pyrene/ C $\equiv$ CH* functional polyester in CDCl_3 .

The analysis of modified MWCNTs were carried out using thermogravimetric analysis (TGA), ultraviolet (UV) and high-resolution transmission electron microscopy (HR-

TEM) measurements. TGA was performed in the temperature range of 30-600 °C with a heating rate of 10 °C/min under nitrogen and weight loss was recorded in the temperature range of 250 °C - 600 °C. In addition to the pristine MWCNT (*p*-MWCNT) displayed 2% of weight loss till 600 °C due to the release of adsorbed water [122], the CNT-hybrids exhibited weight loss ranging from 10% to 62%. Moreover, there is no clear difference in associated with characteristic temperatures starting weight losses regarding pendant functional groups in CNT-hybrids. On the other hand, CNT-9 displays the lowest and exceptionally CNT-10 displays the highest weight loss among the samples because of the hydrogen bonding or crosslinking of pendant C≡CH units (Figure 5.12 (b)). Overall, the TGA profiles of the modified CNTs prove that functional-polyesters were non-covalently attached to the surface of MWCNTs (Table 5.1).

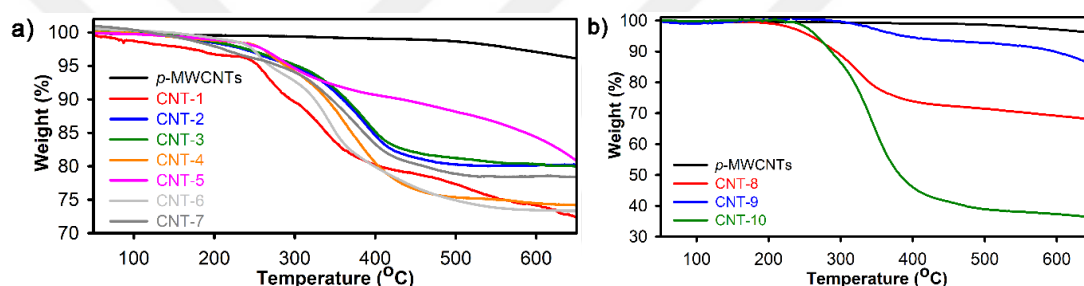


Figure 5.12 : Thermal gravimetric analysis curves of *p*-MWCNTs, CNTs (#1-10) at a heating rate of 10 °C/min under nitrogen atmosphere (For abbreviations see Table 5.1).

Table 5.1 : Thermogravimetric profiles of the different pyrene bearing polyesters on MWCNTs.

Entry	Polyester used for modification ^a	Weight (%) ^d
<i>p</i> -MWCNT	-	~2
CNT-1	P1-pyrene	25
CNT-2	P2-pyrene	20
CNT-3	P3-pyrene	20
CNT-4	P4-pyrene	26
CNT-5	P5-pyrene	15
CNT-6	P2-pyrene ^b	24
CNT-7	P3-pyrene ^b	19
CNT-8	P2-pyrene/OH ^c	28
CNT-9	P2-pyrene/COOH ^c	10
CNT-10	P2-pyrene/alkyne ^c	62

^a Reaction conditions for #1-5: 50 mg of *p*-MWCNTs with 250 mg of functional polyester in 150 mL of THF at ambient temperature for 10 days

^b Reaction conditions for #6-7: 25 mg of *p*-MWCNTs with 125 mg of functional polyester in 75 mL of distilled water at ambient temperature for 10 days.

^c Reaction conditions for #8-10: 20 mg of *p*-MWCNTs with 150 mg of functional-polyester in 150 mL of THF at ambient temperature for 10 days.

^dMeasured by TGA in the temperature range between 250-600 °C under nitrogen with a heat flow of 10 °C/min.

The weight loss data are compatible with those in literature, where non-covalent functionalization of carbon nanotubes and graphenes were carried out using polymers having pendant electron rich functional groups, pyrene and fluorene derivatives [141-146, 162, 163].

The samples for UV measurements were prepared by dissolving 1 mg of CNTs in 4 mL of THF in a vial (Figure 5.13). The mixtures were dispersed using ultrasonic treatment for 15 min and a 3 mL of aliquot was placed in a UV cell, still in small quantities of precipitation observed because of the unreacted MWCNTs. Therefore, UV measurements were carried out after precipitation of particles within 1-2 min. It can be easily detected that *p*-MWCNT displayed no signals between 200-400 nm. However, the modified CNTs (CNT-1 to CNT-5) displayed characteristic features of pyrene moieties rising from functional polyesters, thus confirming the interaction of polyester to the MWCNTs.

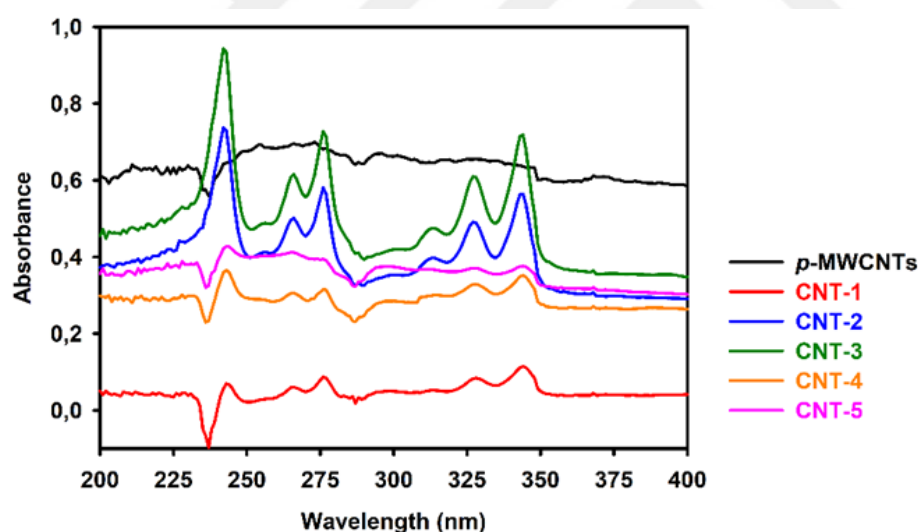


Figure 5.13 : UV absorption spectra of *p*-MWCNTs and CNTs (#1-5) in THF.

The microscopic proof of the non-covalent interaction on the surface of MWCNTs with pyrene- functional polyesters came from HRTEM images, which are given in Figure 5.14. It is found from Figure 5.14 that MWCNT was covered with a thin layer of polymer molecules. While the TEM image of *p*-MWNT indicates a tubular structure with a neat and clean surface, after noncovalent attachment, the pyrene-functional polyester layer of about 18, 13, 10, 8.5, and 10 nm uniformly wraps the surface of the CNT-1, CNT-3, CNT-4, CNT-8 and CNT-9, respectively (Table 5.2). Moreover, it is

observed that a maximum layer in about 10 nm wrapped MWCNTs for CNT-6 and CNT-7 that were prepared in water.

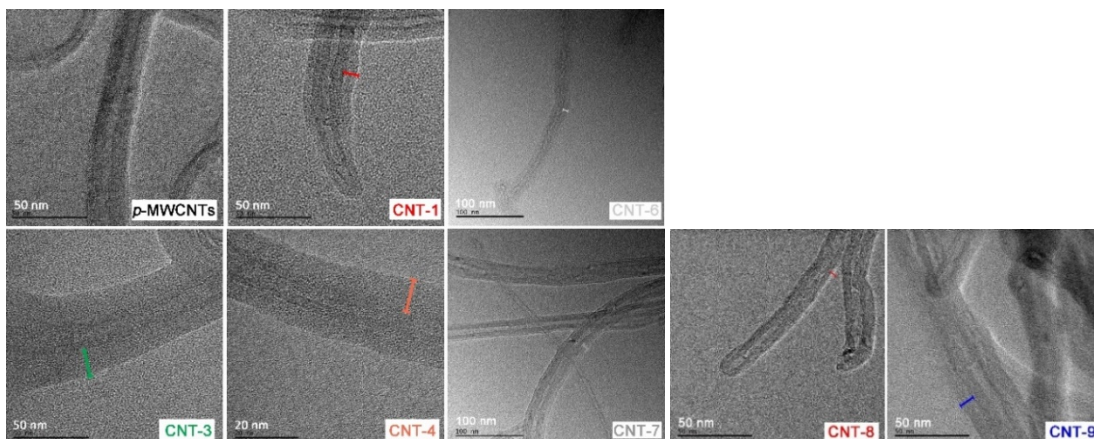


Figure 5.14 : TEM images of *p*-MWCNTs, CNT-1, CNT-3, CNT-4, CNT-6, CNT-7, CNT-8, and CNT-9 with a scale bar 20 nm, 50 nm and 100 nm.

Table 5.2 : TEM results showing thickness of polyester modified-MWCNTs.

Entry ^a	Polyester used for Modification ^b	Minimum thickness of polyester on CNT (nm)	Maximum thickness of polyester on CNT (nm)
CNT-1	P1-pyrene	3	18
CNT-3	P3-pyrene	3	13
CNT-4	P4-pyrene	4	10
CNT-6	P2-pyrene	2	11
CNT-7	P3-pyrene	2	10
CNT-8	P2-pyrene/OH	5	8.5
CNT-9	P2-pyrene/COOH	4.2	10

^aSee for reaction conditions in Table 5.1; ^bSamples were prepared by drop coating a dilute solution of the sample in THF on a holey carbon-coated copper grid;

Moreover, the simplest way to prove the functionalization of MWCNTs is to disperse them in various solvents with different polarities and observe their stability with time. Thus, 1 mg of *p*-MWCNT and CNTs (#1-5, 8-9) in 1.5 mL of solvent are added into vials and then sonicated for 20 minutes to prepare related dispersions (Figure 5.15 and Figure 5.16). It is concluded that DMF is suitable solvent for a good dispersion during 1 weeks (Figure 5.15 (b)).

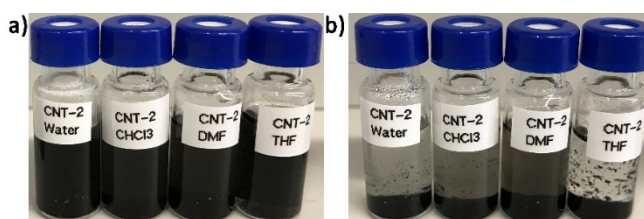


Figure 5.15 : Durability images of CNT-2 different solvents: distilled water, CHCl₃, DMF, THF **a)** *t* = 0 and **b)** after a week.

For example, as can be seen from Figure 5.16, CNT-1 to CNT-5, CNT-8 and CNT-9 that are non-covalently modified with *P1-pyrene* to *P5-pyrene*, *P2-pyrene/OH* and *P2-pyrene/COOH* functional polyesters, respectively show good dispersions in DMF within that period. Unfortunately, CNT-1 demonstrates a poor dispersion in DMF after 3 weeks. CNT-9 showed relatively low noncovalent attachment based upon weight loss in its TGA measurement, so this causes poor dispersion (in spite of having pendant units of $-\text{COOH}$), after it had been left for 3 weeks in distilled water. As is shown in Figure 5.16 (b), CNT-8 modified with *P2-pyrene/OH* shows good dispersion in water even after 3 weeks. This could be associated with a combination of hydrophilic nature of tetraethylene glycol units and pendant hydroxyl groups in the backbone of the polyester.

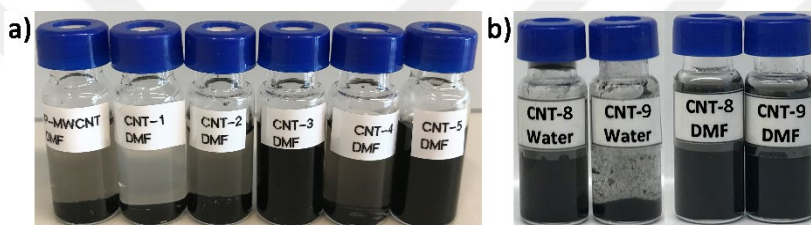


Figure 5.16 : a) Durability images of *p*-MWCNTs and CNTs #1-5 after 3 weeks in DMF b) CNTs #8-9 in DMF and in distilled water after 3 weeks.

6. CONCLUSIONS AND RECOMMENDATIONS

Carbon nanotubes have speedily turned into an interdisciplinary field because of showing their superior structural, mechanical, electrical, and electromechanical features. These features increase the usage of carbon nanotubes (CNTs) in many areas such as sensing, nerve cell stimuli, drug delivery, and cancer therapy. However, major limitation for application of CNTs is their poor solubility, dispersion, processibility and self-aggregation. Hence, functionalization of CNTs is necessary. Therefore, some methods have been reported such as non-covalent functionalization (π - π stacking interactions) and covalent functionalization (Diels-Alder reaction, nitrene addition or thiol-ene click reaction).

The first part of the thesis is about the application of various double combinations of Diels-Alder, nitrene addition and thiol-ene click reactions to perform double modification strategy to carbon nanotubes. This part is performed in three steps: model reactions, mono modifications and double modifications. The results of the model reactions motivated us to level up this study to next step which is mono modification of CNTs with polymers. A series of polymers which had maleimide, anthracene, furan, azide and thiol, were prepared by utilizing either controlled/living radical polymerization techniques (ATRP, RAFT) or esterification reactions. Then, polymers are covalently interacted with the surface of MWCNTs and SWCNTs by the selected modification technique according to the functional group contained in the polymer. TGA measurements revealed that modified CNTs contain within the range of 4-25 weight % of polymer for Diels-Alder reaction, 4.5-13 weight % of polymer for nitrene addition and 4-27 weight % of polymer for thiol-ene reaction. The findings of the study were satisfying, so some of the mono modified CNTs were chosen to perform double modification. 7 double modification reactions and 3 one-pot double modification by sequential approach were performed. TGA measurements revealed that double modified CNTs contain within the range of 4-78 weight % of second polymer for 4 of 7 double modified reactions. There is only one experiment showed a decrease in grafting yield by 7% compared to its precursor step. This result is related to unexpected *retro* Diels-Alder reaction which could happen during the second step of modification

due to the relatively high temperature (80 °C). However, in the remaining two, there was no change in the thermal analysis results. TGA measurements revealed that one-pot double modified CNTs by sequential approach contain within the range of 13-19 weight % of polymers.

However, double modification of carbon nanotubes via covalent functionalization approach has a limitation to obtain reliable results. To overcome this, reactions might be done under nitrogen or argon atmosphere and carbon nanotubes can be purified before being used the reaction to remove unwanted oxidation on sidewall of CNTs.

In the second part of the thesis, active ester substitution and nitrene addition reactions have been chosen, and their combination was suggested as a new route for double modification of sidewalls of MWCNTs. The study concerns with the synthesis of amine terminated PEG and azido terminated Styrene polymers for the application of double modification strategy (active ester substitution and nitrene addition) in sequential process. Synthesized amine terminated PEG and azido terminated PS polymers were characterized by using ¹H-NMR, GPC and FT-IR. Firstly, pentafluorophenol anchor was introduced to sidewalls of MWCNTs to perform active ester substitution reaction with PEG-amine. Commercially available acid bearing MWCNTs used as a starting material for the synthesis of MWCNT-COOC₅F₆ in two steps. Then, as a first “click” modification, amine-terminated PEG coupled with MWCNT-COOC₅F₆. Secondly, PS-N₃ was coupled to MWCNT-CONHPEG at high temperature (130 °C) by nitrene addition reaction. Thermal analysis was performed on the products in order to understand nanotube functionalization and receive educatory information. TGA measurement of MWCNT-CONHPEG showed that *f*-CNTs contain around 21 % weight loss of PEG. However, after the second modification of MWCNT-CONHPEG with PS-N₃, TGA measurement of PS-*g*-MWCNT-CONHPEG showed around 10 total weight loss % of both polymers. Similar results are obtained once the experiments are repeated consecutively. So, this decrease of 10 % weight loss thought to be correlated with high temperature (130 °C) medium that is necessary for nitrene addition reaction in the second step of modification.

In the last part of the thesis, a series of polyesters possessing electron deficient alkyne moieties in the main chain were prepared. This type of polyesters allows us to efficiently introduce a variety of pendant functional groups, such as pyrene, hydroxyl, carboxylic, and alkyne through Huisgen 1,3-cycloaddition reactions. Next, functional

polyesters are non-covalently interacted with the surface of MWCNTs via π - π stacking of pyrene anchor groups. TGA measurements revealed that modified CNTs contain within the range of 10-62 weight % of polyester. Moreover, TEM analyses showed that polyester with thickness of approximately over 10 nm wrapped the surface of MWCNTs without disturbing their tubular shape. The non-covalent π - π interaction methodology for the functionalization of MWCNTs provide many advantages over covalent modification featuring lower reaction temperatures and free from the disruption of some sp^2 carbons into the sp^3 . The covalent modification methodologies of CNTs, Diels-Alder, thiol-ene and nitrene addition generally need higher temperatures ranging from 80 to 130 °C, however shorter reaction times. Moreover, the polymer content of the modified CNTs using noncovalent interaction route is almost similar to those obtained in the covalent modification.



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PUBLICATIONS ON THE THESIS:

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- **OMURTAG, P.S.**, DURMAZ, H., HIZAL, G., TUNCA, U., “*Surface Modification of Various Carbon Nanotubes via Double Click Strategy*”, 6th EuCheMS Chemistry Congress, Seville, Spain, (11-15 September 2016) (Oral Presentation in English)
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