ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

Π-Π STACKING OF POLYESTERS CONTAINING PYRENE IN MAIN CHAIN TO THE MULTI-WALLED CARBON NANOTUBE SURFACE

M.Sc. THESIS

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ISTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

KARBON NANOTÜP YÜZEYİNE ANA ZİNCİRİNDE PİREN İÇEREN POLİESTERLERİN Π-Π İSTİFLENMESİ İLE TUTUNMASI

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HAZİRAN 2017

Burcu Alkan, a M.Sc. student of ITU Graduate School of Science Engineering and Technology student ID 515151006, successfully defended the thesis entitled "Π- Π STACKING OF POLYESTERS CONTAINING PYRENE IN MAIN CHAIN TO THE MULTI-WALLED CARBON NANOTUBE SURFACE", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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Date of Submission : 05 May 2017
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To my family,

FOREWORD

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ABBREVIATIONS

^{1}H NMR : Hydrogen Nuclear Magnetic Resonance Spectroscopy
^{13}C NMR : Carbon Nuclear Magnetic Resonance Spectroscopy
GPC : Gel Permeation Chromatography
EtOAc : Ethyl acetate
MWD : Molecular Weight Distribution
TGA : Thermal Gravimetric Analysis
FTIR : Fourier Transform Infrared Spectroscopy
UV : Ultra Violet
HR-TEM : High-Resolution Transmission Electron Microscopy
SWCNT : Single-Walled Carbon Nanotube
DWCNT : Double-Walled Carbon Nanotube
MWCNT : Multi-Walled Carbon Nanotube
CNT : Carbon Nanotube
DCC : N,N’-Dicyclohexylcarbodiimide
DMAP : 4-Dimethylaminopyridine
ADCA : Acetylenedicarboxylic Acid
THF : Tetrahydrofuran
PEG : Poly(ethylene glycol)
PTSA : p-Toluenesulfonic Acid
FPT : Freeze-Pump-Thaw

SYMBOLS

˚C : Celsius
***M*n** : The number average molecular wieght
***M*w** : The weight average molecular weight
***M*w/*M*n** : Polydispersity Index
ppm : Parts per million
nm : Nanometer

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Π-Π STACKING OF POLYESTERS CONTAINING PYRENE IN MAIN CHAIN TO THE MULTI-WALLED CARBON NANOTUBE SURFACE

SUMMARY

Nanotechnology has gained great interest among the researches due to its ability to encompasses both the production and application of interdisciplinary sciences such as physics, chemistry and biology. Developments and advancements in the field of nanotechnology and its applications to the various fields have an impressive impact on both the economy and society especially since 21st century. Nanotechnology can be basicy defined as a science and engineering involved in the design, synthesis, characterization and application of materials close to the atomic and molecular level. Nanotechnology will play a significant role in the future by either protecting the environment and providing energy for the growing world.

Nanomaterials are cornerstones of nanotechnology and they are defined as substances at least one dimension is less than 100 nanometers. While some nanomaterials are found in nature for centuries, most of them are produced commercially to be used in different engineering applications. Since nanomaterials have extremely small sizes and promising mechanical properties compared to conventional materials, they are considered as main constituents of especially the composites and other materials used in engineering applications. The main reason why nanomaterials can have desiring properties are directly related to their greater surface area to volume ratio than conventional materials and their structural properties.

While nanomaterials can be classified according to their dimensions and shapes, they are also divided into groups based on the variety of their structural units. Carbon nanomaterials are the most widely known and used group and all the members of this group have different desiring properties. Among these members such as graphene and fullerene, carbon nanotube has attracted tremendous interest. It has been almost twenty years since the carbon naotube was described as a carbon material with a tubular shape and a diameter on the nanometer scale. Thanks to the numerous studies related to the carbon nanotubes, their physical and chemical properties has been investigated. Carbon nanotubes can be considered as the sheet of graphite rolling into tubic shape. Single-walled nanotubes and multi-walled nanotubes are known as the two most important structures and both have various properties depending on the atomic arrangement, the sizes of the tubes and the morphology. While single-walled carbon nanotubes are obtained by the rolling of a single layer of graphite, multi-walled carbon nanotubes are the type of a collection of concentric single-walled nanotubes and both type of nanotubes have extraordinary mechanical and optical properties. Although nanotubes have desired properties, they also have some drawbacks that limit the use of nanotubes in engineering applications. Aside from their high production costs, efficient dispersion technologies are also not valid for carbon nanotubes and they tend to form aggregate due to the presence of strong interfacial forces. It is really important to enhance the dispersion of nanotubes in various solvents and even water to obtain better compatibility with the second component of a material. There are various modification techniques applied to the nanotubes to increase the compatibility and solubility. The first method involves the covalent attachment and it contains grafting of polymer chains to the nanotube surface by means of a chemical bond formation. In addition, different types of functional groups can be introduced to the surface of nanotube due to the presence of π orbitals having the ability to make covalent attachment. However, the main disadvantage of this method is the disruption of nanotube surface and therefore a decrease can be observed in the mechanical properties of nanotubes. Another approach applied for nanotube modification is noncovalent attachment. Polymer chains are mainly wrapped around the nanotube surface by using strong π-π stacking interactions to enhance both solubility and dispersion. This physical attachment maintains the basic properties of nanotubes, as well as it improves the solubility. However, since the weak forces are formed between the nanotube surface and polymer chains, this can be considered as a disadvantage when nanotubes are especially used in composite materials as reinforcing component. Countless studies has been carried out about the noncovalent attachment of aromatic groups to the nanotube surface by using various types of polymers involving aromatic moiety such as pyrene in their structure.

Since polymers play an essential role in modification of carbon nanotubes, it is important to discuss the topics including the types of polymers, polymerization methods and even further functionalization techniques. Among various polymerization methods, condensation polymerization is an efficient way to obtain engineering polymers. Polyesters are the most commonly used engineering polymers and they are basicly defined as the products of polycondensation reaction between diacids and diols. A wide variety of polyesters can be synthesized just by adjusting the diversity of structural units connected to ester functional group in the main chain of polyester. It is not always preferable to use polyesters as they are produced, therefore further functionalization reactions are carried out in some cases. 1,3-dipolar cycloaddition is one of the most commonly used reaction for the further functionalization of polymers. Since the first studies about 1,3-dipolar cycloaddition reactions were carried out by Rolf Huisgen, it is also known as Huisgen cycloaddition reaction.

In this study various types of polyesters having electron deficient alkyne units in the main chain were synthesized by using acetylene dicarboxylic acid and different diols. Then, 1,3-dipolar cycloaddition reactions were performed between these polyesters and an ester molecule having aromatic pyrene moiety to form triazole ring in the structure. These polyesters having pyrene functionality in the structure were interacted with carbon nanotubes in different types of solvent to obtain strong π-π interactions between nanotubes and polymer chains. All characterization processes are made by using GPC, ^{1}H NMR, TGA, FTIR, UV and TEM.

KARBON NANOTÜP YÜZEYİNE ANA ZİNCİRİNDE PİREN İÇEREN POLİESTERLERİN Π- Π İSTİFLENMESİ İLE TUTUNMASI

ÖZET

En basit anlamı ile, çok küçük boyutlardaki yapıların veya malzemelerin araştırılmasını ve incelenmesini kapsayan nanoteknoloji, özellikle 21. yüzyılın başlarından itibaren bilim insanları tarafından ilgi çeken bir konu olmuştur. Bir başka ifade ile nanoteknoloji malzemelerin tasarım, sentez, karakterizasyon ve hatta uygulamasına yönelik çalışmaları içeren gelecek vaadeden bir bilim dalı ve mühendisliktir. Fizik, kimya biyoloji ve diğer bilim dallarındaki nanoteknolojik çalışmaların, dünya ekonomisi ve toplum üzerindeki pozitif etkisinin yanısıra, büyüyen ve gelişen dünya için çevrenin korunması ve enerjinin sağlaması çalışmalarında da nanoteknolojinin önemli bir rolü vardır.

Nanoteknolojinin temelini oluşturan ve en az bir boyutları 100 nm'den az olan nanomalzemelerin bir çoğu mühendislik uygulamalarında kullanılmak üzere ticari olarak üretilmektedir. Geleneksel malzemelerle kıyaslandığında, oldukça küçük boyutlarda olan ve olağanüstü özellikleri bulunan nanomalzemeler, başta kompozitler olmak üzere mühendislik uygulamalarında kullanılan diğer malzemelerin de ana bileşenlerinden birini oluşturmaktadır.

Boyut ve şekillerinin yanısıra yapılarına göre de sınıflandırılabilen nanomalzemelerin arasında karbon nanomalzemeler en çok bilinen ve en yaygın olarak kullanılan gruptur. Karbon nanomalzemelerin ilk bilinen üyesini oluşturan grafen, tek bir düzlemde bal peteği görünümünde sıralanmış karbon atomlarından oluşmakta olup, atomlar arasındaki kuvvetli bağlar, aromatik yapısı ve yüzeyindeki reaktif grupların varlığı sebebiyle sahip olduğu fiziksel ve kimyasal özellikler, grafeni diğer karbon allotroplarına göre daha dikkat çekici bir malzeme yapmaktadır. 1980'li yılların ortasında, en iyi bilinen buckminsterfuleren molekülünün keşfedilmesiyle birlikte, farklı sayıda karbon içeren fuleren moleküllerinin varlığı kanıtlanmştır. Buckminsterfuleren, diğer bir deyişle C_{60}, en küçük ve en bol bulunan fuleren molekülüdür ve diğer fuleren molekülleri gibi karbon atomlarının yuvarlak bir şekil oluşturacak şekilde bir araya gelmesi ile oluşmuştur. Sahip olduğu yuvarlak şekli ve yüksek simetrisinin yanında, fuleren moleküllerinin elektriksel ve kimyasal özellikleri ilgi çekmektedir.

Grafen ve fuleren moleküllerinin dışında, karbon nanotüpler karbon yapılı nanomalzemeler içerisinde en çok bilinen ve en yaygın olarak kullanılan gruptur. Grafenin keşfinden neredeyse 200 yıl kadar sonra fuleren yapısının bildirilmesine rağmen, fuleren moleküllerine duyulan ilgi sebebi ile karbon nanotüplerin keşfi uzun sürmedi. İlk kez 1991 yılında, Japon bilim insanı Sumio Iijima tarafından sentezlenen karbon naotüpler; fizik, kimya ve özellikle malzeme biliminde kullanılmaktadır.

En basit ifade ile, karbon atomlarının düzlemsel ve altıgen sıralandığı grafit katmanlarının silindir şeklinde sarılması ile oluşan karbon nanotüpler, yapıdaki grafit katmanının sayısına göre tek katmanlı karbon nanotüpler ve çok katmanlı karbon

nanotüpler olmak üzere ikiye ayrılır. Birbirlerine göre avantaj ve dezavantajları bulunan tek ve çok katmanlı nanotüpler; yapılarındaki atomların dizilişi, tüplerin boyutları ve morfolojisine bağlı olmak üzere değişik fiziksel ve kimyasal özelliklere sahiptir. Karbon nanotüpleri farklı uygulamalar için ideal bir malzeme yapan üstün özelliklerinden en dikkat çekeni, çelikten 100 kat kadar daha sağlam olmasına rağmen bir o kadar da hafif olmasıdır. Sahip oldukları sıradışı mekanik özelliklerine rağmen, üretim maliyetlerinin fazla olması ve etkili dispersiyon teknolojisinin bulunmaması karbon nanotüplerin özellikle mühendislik uygulamalarındaki kullanımını sınırlandırmıştır. Çeşitli solventlerde ve hatta su içerisinde nanotüplerin dispersiyonunu arttırmak, özellikle kompozit malzemelerde kullanımında ikinci bileşen ile nanotüp uyumluluğunu arttırmak açısından oldukça önemlidir. Karbon nanotüpler, yapılarındaki Van der Walls kuvvetleri sebebi ile yığın oluşturma eğilimindedirler ve bu durum dispersiyon ve çözünürlüğün azalmasına sebep olabilir. Nanotüplerin uyumluluğunu ve çözünürlüğünü arttırmak için kullanılan birçok modifikasyon tekniği temelde kovalent bağlanma ve kovalent olmayan bağlanma olmak üzere iki çeşittir. Kovalent bağlanma, karbon nanotüp yüzeyine çeşitli fonksiyonel grupların ya da polimer zincirlerinin kimyasal bağ oluşumu ile bağlanmasıdır. Yapılarındaki π orbitallerinin varlığı sebebi ile farklı kimyasallar ile kovalent bağ yapabilme özelliğine sahip olan karbon nanotüplerin solvent içerisindeki çözünürlüğü ve dispersiyonu, yüzeye karboksilik asit veya hidroksil gruplarının modifiye edilmesi ile arttırılabilir. Ancak bu modifikasyon metodu nanotüp yüzeyinde kimyasal anlamda bir değişikliğe ve bozunmaya sebep olduğundan, nanotüplerin mekanik özelliklerinde de bir düşüşe sebep olabilir.

Kovalent olmayan bağlanma türünde en yaygın kullanılan teknik, polimer zincirlerinin nanotüp yüzeyini π-π istiflenmesi ile sarmasıdır. Karbon nanotüplerin hem çözünürlüğünü hem de dispersiyonunu arttıran kovalent olmayan bağlanma fiziksel bir bağlanma türü olduğundan, nanotüp yüzeyinde deformasyona sebep olmamakta dolayısıyla da nanotüplerin temel özellikleri korunmaktadır. Ancak, nanotüp yüzeyi ile polimer zincirleri arasında oluşan kovalent bağlanmaya kıyasla kısmen zayıf fiziksel etkileşim, nanotüplerin özellikle kompozit malzemelerde güçlendirici bileşen olarak kullanımında bir dezavantaj olarak görülmektedir. Polimer zincirlerinin yapısında bulunan piren gibi aromatik grupların varlığı, nanotüp yüzeyi ile polimer zinciri arasında daha kuvvetli bir etkileşime sebep olmakta ve dolayısıyla nanotüplerin çözünürlüğünü ve dispersiyonunu büyük ölçüde arttırmaktadır.

Nanotüp yüzeyinin modifiye edilmesinde kullanılan polimer türleri farklı polimerizasyon teknikleri ile sentezlenebilmesine rağmen, kondenzasyon polimerizasyonu özellikle poliesterler ve poliamidler gibi mühendislik polimerlerinin sentezinde kullanılan etkili bir polimerizasyon tekniğidir. Kondenzasyon reaksiyonu, iki molekülün fonksiyonel grupları arasında yapıdan su gibi küçük moleküllerin ayrılması ile daha büyük bir molekül oluşturmak üzere gerçekleşen organik bir reaksiyondur. Art arda gerçekleşen kondenzasyon reaksiyonlarının bir ürünü olan poliesterler, polimer zincirlerinde ester grubu bulunduran ticari öneme sahip polimerlerdir. Diasitlerin dioller ile esterleşmesi reaksiyonu sonucu elde edilen poliesterin ester gruplarına bağlı bulunan yapı birimlerinin çeşitliliği, farklı özelliklere ve kullanım alanlarına sahip olan poliester çeşitliliğini arttırmakla birlikte, nihai polimerin fonksiyonlandırılması da çeşitlilik için itici bir etkendir. Bu amaçla kullanılan reaksiyonlarından biri olan ve Rolf Huisgen tarafından 1960 yılında ortaya konan 1,3-dipolar siklokatılma reaksiyonu, yapısında doymamış bağ içeren moleküller ile 1,3-dipolar bileşikleri arasında beşli halka vermek üzere gerçekleşir. Azidler ve

alkinler siklokatılma reaksiyonlarında kullanılan en etkili reaktanlar olup, bunların siklokatılma reaksiyonları triazol halkasının oluşmasıyla sonlanır. Organik reaksiyonlarda sıklıkla kullanılan 1,3-dipolar siklokatılma reaksiyonlarının yavaş olması ve kabul edilebilir verimlerde sonlanması için yüksek sıcaklık gerektirmesi dezavantajlarındandır.

Bu çalışmada, asetilen dikarboksilik asit ve çeşitli dioller kullanılarak ana zincirlerinde elektronca yoksun alkin birimine sahip polyesterler sentezlenmiştir. Elde edilen polyesterler, yapısında aromatik piren grubu bulunduran ester molekülü ile 1,3-dipolar siklokatılma reaksiyonları kullanılarak yapıda triazol halkası oluşturmak üzere modifiye edildi. Yapısında piren fonksiyonalitesi bulunduran bu poliesterler, farklı çeşitte çözücüler içerisinde, karbon nanotüp ve polimer zincirleri arasında kuvvetli π-π etkileşimini oluşturmak üzere reaksiyona sokuldu. Bütün karakterizasyonlar GPC, ^{1}H NMR, TGA, FTIR, UV ve TEM kullanılarak gerçekleştirildi.

1. INTRODUCTION

Nanotechnology is described any technology on a nanoscale that has chance to affect both our society and economy by developing already existing products or creating new ones [1]. The materials used in nanotechnological studies are known as nanomaterials which present on the scale of nanometer. It is clear that the size of nanomaterials is quite small compared to bulky materials, therefore they are used for modifiying the conventional materials to enhance the properties such as high mechanical, optical or magnetic properties [2]. Among different types of nanomaterials, carbon nanotubes has gained great concern in the field of nanotechnology since it was discovered in 1991. The unique and extraordinary properties of carbon nanotubes give chance to researchers for the development of new material systems [3]. However, nanotubes are prone to form aggregates due to the presence of intermolecular forces in the structure which make them insoluble in organic solvents and even in water. This situation decreases the solubility and the compatibility and therefore restricts the usage areas of the nanotubes. To overcome this problem, various modification and functionalization techniques are applied to the nanotube surface by introducing the functional groups or polymer chains. This surface functionalization can be achieved by either covalent or noncovalent manner. Basicly, polymer chains are chemically attached to the nanotube surface by grafting methods in covalent attachment which can cause deterioration of the nanotube surface, and thereby can decrease the mechanical property of the tubes. In noncovalent attachment, polymer chains are just wrapped around the surface of nanotube. This wrapping occurs via physical bonding and desired properties of nanotubes are not affected adversely.Since noncovalent functionalization does not affect the structural properties of nanotubes, it has attracted major interest among the researchers. Especially, π-π stacking interactions of polymer chains to the nanotube surface has become a popular subject. Although various types of polymers has been used for the wrapping around the carbon nanotube surface, condensation polymers including polyesters are one of the most commonly preferable type of commercial polymer. This “condensation polymers” statement was first introduced by W.H.

Carothers to separate this types of polymers especially from vinyl polymers produced by chain-growth reactions. General representation for polycondensation reaction reaction is shown in Figure 1.1. The most completely understood condensation reaction takes place between difunctional monomers such as diols and dicarboxylic acids to produce polyesters which are the first family of condensation polymers. A wide range of polyesters with high molecular weights are obtained by reacting dicarboxylic acids with excess amount of diols. Due to the presence of promising and desired properties of polyesters, they are used in various commercial applications.

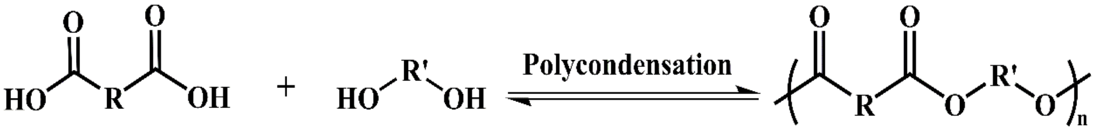


Figure 1.1 : General representation for polycondensation reaction.

Chemically, polyesters includes all the polymers containing ester groups in their main chain and they can be easily diversified by either adjusting the functionalities in the structure or introducing functional groups via further functionalization methods [4]. General representation for 1,3-dipolar cycloaddition reaction in Figure 1.2. The 1,3-Dipolar cycloaddition reaction, also known as Huisgen cycloaddition reaction, is one of these functionalization methods. Azides and alkyne compounds are the most commonly and efficiently used reactants in Huisgen cycloaddition since they can be combined with a wide range of substituents. The polymers having alkyne unit in their backbone can be esily functionalized with a suitable 1,3-dipolar compound to form five-membered ring in the structure.

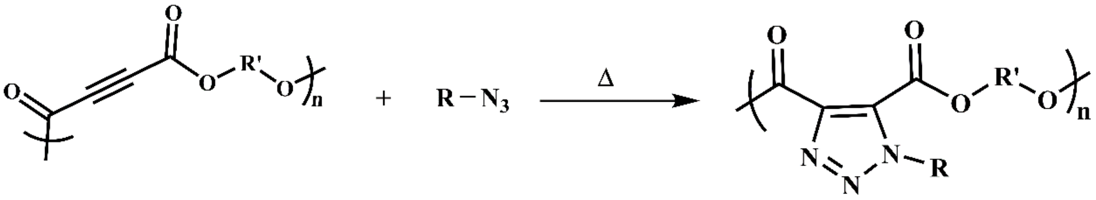


Figure 1.2 : General representation for 1,3-dipolar cycloaddition reaction.

Although carbon nanotubes have improved properties, they also have some disadvantages that limit their usages in commercial applications. The main drawback of carbon nanotube is about their solubility and dispersion problem. This situation decreases the compatibility as well as the mechanical properties of the nanotube. Therefore, polymer chains are wrapped around the nanotube surface by means of π-π stacking interactions as represented in Figure 1.3. to increase both the interaction and compatibility of the nanotubes. Since this wrapping occurs via physical interactions, the surface structure of nanotube does not affected adversely. The presence of aromatic moieties in the polymer structure such as pyrene increases the interaction between nanotube surface and polymer chain [5].

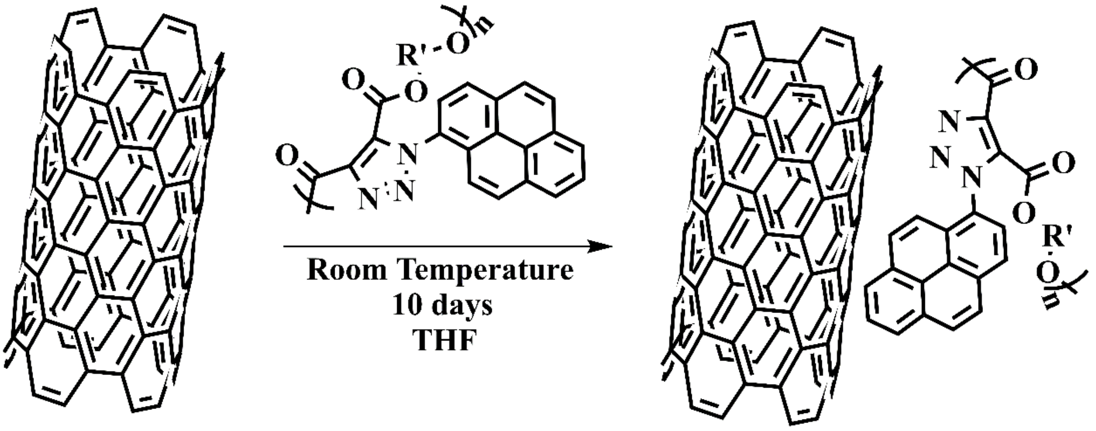


Figure 1.3 : General representation for formation of π-π stacking interaction between carbon nanotube surface and polymer chain.

2. THEORETICAL PART

2.1 Nanotechnology

Nanotechnology can be either simply defined as a study of small structures or as a promising science and engineering that include the design, synthesis, characterization and even application of materials, having size of 0.1 to 100 nm. According to another definition, nanotechnology basicly deals with the substances which having at least one dimension 100 nm or less. The main aim in nanotechnological studies is to process of individual atoms or molecules into larger structures to obtain materials having special and unique properties [6,7]. Since nanotechnology is a science that deals with matters and substances in nanometer scale, it opens a way for nanomaterials to use them in wide range of application areas such as health, medicine, electronics, transportation, energy, environment and even space exploration just by integrating the resulting nanostructures into the larger systems [8]. In fact, nanotechnology has a recent history. The term “nanotechnology” was used in 1974 for the first time and it gained a major interest with the discoveries and developments all around the world. Today, it can be said that the era of molecular nanotechnology has started [7].

2.2 Nanomaterials

Nanomaterials can be considered as headstones in the fields of nanoscience and nanotechnology due to their unique properties and characteristics. Since nanomaterials exhibit different physical and chemical behaviours from normal chemicals and bulky structures, they are easily incorparated into other materials on atomic scale to improve mechanical and physical properties of the substance. Recently, nanomaterials draw great attention due to their developed individual optical, electrical, mechanical and magnetic properties at atomic scale. All these properties have enhancing effect on the structure of nanomaterials which most of them are produced artificially to be used in engineering applications ranging from electronics to biological studies [7,9].

2.3 Classification of Nanomaterials

As it mentioned before, nanomaterials are extremely small sized materials and they can be classified based on their various properties. The common classification of nanomaterials can be made either according to their sizes or atomic structures as in shown in Figure 2.1. Nanomaterials can have zero dimensional, one dimensional, two dimensional and three dimensional structures. They are found in single, fused, aggregated forms with spherical, tubular and irregular shapes [9].

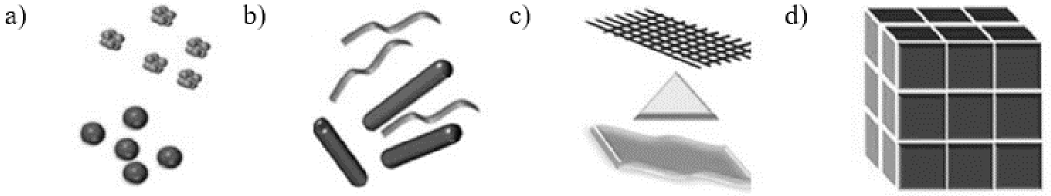


Figure 2.1 : Classification of nanomaterials based on their shapes and dimensions.

Since nanomaterials display different types of features, it can be easily said that there are many various nanoscale materials. However, the most attractive and popular type of nanomaterial is the ones having carbon atoms in their structure. It is called as carbon nanomaterial, and this group basicly includes graphenes, fullerenes and carbon nanotubes. This diversity between carbon-based nanomaterials basicly come from the structural conformation, that is, hybridization state of the carbon atoms in the molecule [10].

2.3.1 Graphene

Basicly, graphene is a two dimensional sheet of sp^2 hybridized carbon atoms arrange in honeycomb lattice on a single plane. Although graphene is the thinnest material in the world, it is also the strongest and stiffest material which has ever known [11]. Graphene also can be viewed as main constituent of other carbon allotrops. Figure 2.2. represents the illustration of graphene as main constituent in carbon allotrops. It can be easily converted to 3D graphite, 1D nanotubes and 0D fullerenes just by stacking, rolling or wrapping [12].

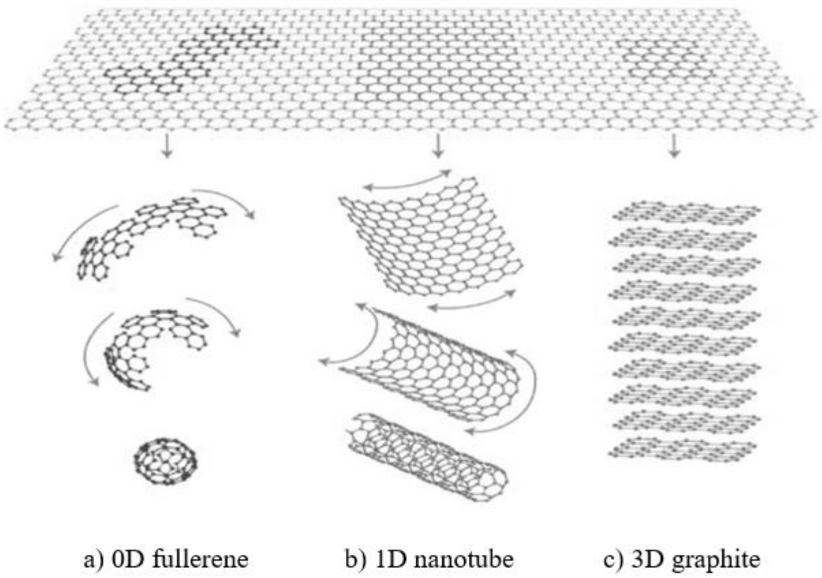


Figure 2.2 : The illustration of graphene as main constituent in carbon allotrops.

To enlighten the structure of graphene in more detail, first it should be clearly understood that graphene is actually one single layer of graphite. While there is a strong bond between carbon atoms in graphite structure, the weak Van der Waals interactions exist between interlayers which make graphite a soft material. Thanks to other structural properties such as aromaticity, presence of π electrons in the structure and even the reactive sites on the surface, graphene has become a promising material since it has both proper physical and chemical properties [13]. As stated before, graphene is a so strong material that it is even 200 times stronger than steel. Also, graphene has a high thermal conductivity and unique electrical properties which make the structure attractive compared to other allotrops of carbon. However, tendency to aggregate and unstability are the main drawbacks of graphene. To overcome this problem, a third component is generally introduced into the graphene surface either physically or chemically [14].

2.3.2 Fullerene

In the middle of 1980s, fullerenes have been started to take into account as carbon allotropes by the discovery of buckminsterfullerene, that is, C_{60} which is the best known fullerene molecule [13,15]. Three different illustration of C_{60} is represented in Figure 2.3. It is also the smallest and the most abundant fullerene molecule having sixty sp^2-hybridized carbon atoms that occur twelve pentagonal and twenty hexagonal rings. This new carbon allotrop, the C_{60}, is a closed- cage carbon molecule with carbon atoms getting together spherically to form almost a shape of a soccer ball [15,16].

Figure 2.3 : Three different illustration of buckminsterfullerene, C_{60}.

It is fair to say that fullerene molecules have various attractive features. While their round shape and high symmetry are the most general properties, both electrical and chemical properties of fullerene molecules can be really considered as eye-catching features [13]. Normally, fullerene molecules have semiconducting structure; but their conductivity can be improved just by doping with alkali metals such as Rb, K or Cs [17]. Another property that make fullerene molecules attractive is their chemical reactivity. The alternation of bonds which already exists in fullerene molecules has an significant effect in chemical reactions. In C_{60}, for example, the half of the bonds between carbon atoms are double bonds, and that makes C_{60} available to interact with other atoms or molecules [13]. Different functional groups like phenols are added to the structure through these double bonds, and this ability has become a leading progress in the field of cycloaddition reactions of C_{60} [18].

2.3.3 Carbon nanotubes

Since carbon atom is one of the most abundant and versatile element that found in nature, it has been used for various applications. These application areas are directly related to the arrangement of carbon atoms in the structure. Therefore, the study of atomic structure of carbon allotrops has been an interesting research field among the scientists. Fullerene structure was reported by the researchers after almost two centuries of the graphite discovery. Due to the great interest for fullerenes-especially for buchminsterfullerene(C_{60})- the exploration of carbon nanotubes did not take a long time. Just a few years later, carbon nanotubes were synthesized by Sumio Iijima, a Japanese scientist, in 1991 and they have gained great interest in the field of physics, chemistry and material sciences since then [19]. The sheets of graphite with planar-hexagonal arrangement of carbon atoms distributed in a honeycomb lattice are rolled into cylinders to form carbon nanotubes which are considered one-dimensional structures because of their very high aspect ratio [16]. While this feature directly affect to the nanotube properties, there are also other factors that have effects on the nanotube properties such as atomic arrangement, the rolling way of the graphite sheets and the sizes of the tubes. In addition, the morphology and nanostructure should be taken into account for a desired nanotube property [20].

Carbon nanotubes (CNTs) can be classified into three main types with respect to the rolling frequency of the graphene sheets. These are single-walled carbon nanotubes (SWCNTs), double-walled carbon nanotubes (DWCNTs) and multi-walled carbon nanotubes (MWCNTs). While single-walled and multi-walled nanotubes are being used more often, double-walled nanotubes have limited usages. Single-walled carbon nanotube (SWCNTs) are cylinders formed by the rolling of a single sheet of graphene as represented in Figure 2.4. Both the inner and the outer side of the SWCNTs have different characteristics. It displays extraordinary mechanical, electrical and chemical properties mainly because of the excellent sequence of carbon atomic lattice through the nanotube surface. SWCNTs also have high modulus, strength and stiffness which make them suitable reinforcing materials in composite materials. Aside from improved mechanical properties, they are also very light in weight.

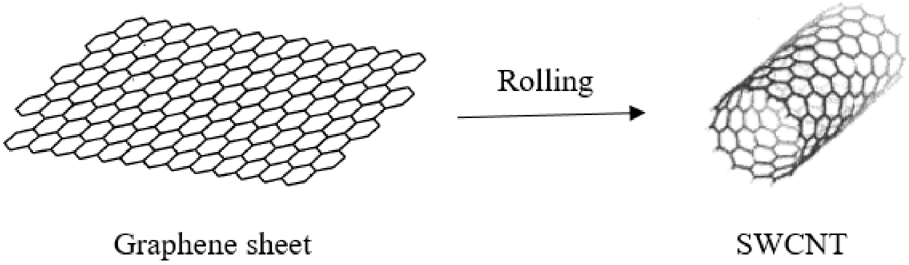


Figure 2.4 : Illustration of a graphene sheet rolled up to form SWCNT.

Multi-walled carbon nanotubes (MWCNTs) can be view as a collection of concentric SWCNTs having different diameters. Several layers of graphite are rolled to form a tube shape of MWCNT. In Figure 2.5., both CNT types are represented molecularly. Since MWCNTs have various size of lengths and diameters, they have different properties compared to SWCNTs [21]. In Table 2.1.,the comparison of SWCNTs and MWCNTs were made.

Table 2.1 : Comparison of SWCNTs and MWCNTs

SWCNT	MWCNT
Composed of a single layer of graphene	Composed of multiple layer of graphene
Diameter: 0.4-3 nm	Diameter: 5-100 nm
Not fully dispersed	Homogeneously dispersed
Ideal structure, low defects	High defects
Easy characterization and evaluation	Characterization is harder
Easily twisted	Hardly twisted
Only high-price application areas	Wide range of applications

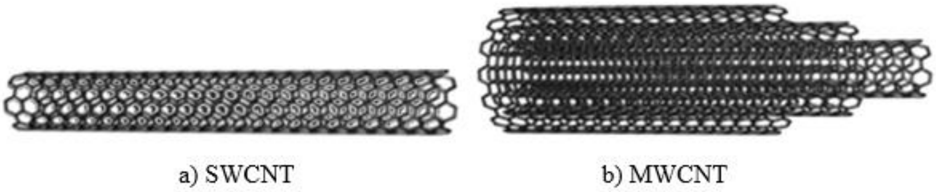

a) SWCNT b) MWCNT

Figure 2.5 : Molecular representation of a) SWCNT and b) MWCNT.

Although CNTs have excellent mechanical, electrical and thermal properties which make them a suitable candidate for different applications, they also exhibit some drawbacks that limit the usage areas. For instance, CNTs have so high strength and high stiffness that they are regarded as a material that 100 times stronger than steel but conversely, their density is quite low. Therefore, CNTs are one of the most commoly used reinforcing material especially in polymeric nanocomposites. It is no wonder that the dispersion and the interfacial adhesion between CNTs and polymeric matrix should be good enough to obtain highly qualified polymer based nanocomposites. However, the insolubility of CNTs in organic solvents and water and the tendency of CNTs to form agglomerate due to the Van der Walls forces in the structure cause a weak dispersion and low compatibility between the nanotubes and polymer matrix. To obtain a better dispersion and strong interfacial interactions, carbon nanotube surface should be modified by various functionalization methods [22,23]. The modification methods of carbon nanotubes are basicly divided into two main groups as noncovalent attachment and covalent attachment. While noncovalent attachment is carried out by using surfactants or wrapping of the nanotube surface with polymer chains, covalent attachment is based on grafting approaches of the polymer chains to the nanotube surface. As a matter of fact, both methods have advantages and disadvantages. In covalent attachment, while some functional groups are introduced to the carbon nanotube surface to increase the compatibility, it also should be considered that the nearly perfect structure of the carbon nanotube might be damaged and that damage can cause a decrease in the strength of nanotube as filler. Since the surface structure of the carbon nanotube does not change in noncovalent attachment, its promising mechanical properties remains same, but the weak forces occuring between the wrapping molecule and nanotube can be considered as a disadvantages. Carbon nanotubes have the ability to make covalent attachment with different chemicals due to the presence of π-orbitals of the sp^2-hybridized carbon atoms in the structure. Both solubility and dispersion of carbon nanotubes in solvents may be increased by modification of functional groups such as carboxylic acid or hydroxyl groups on the nanotube surface [24]. Introducing of functional groups on nanotube surface is represented in Figure 2.6.

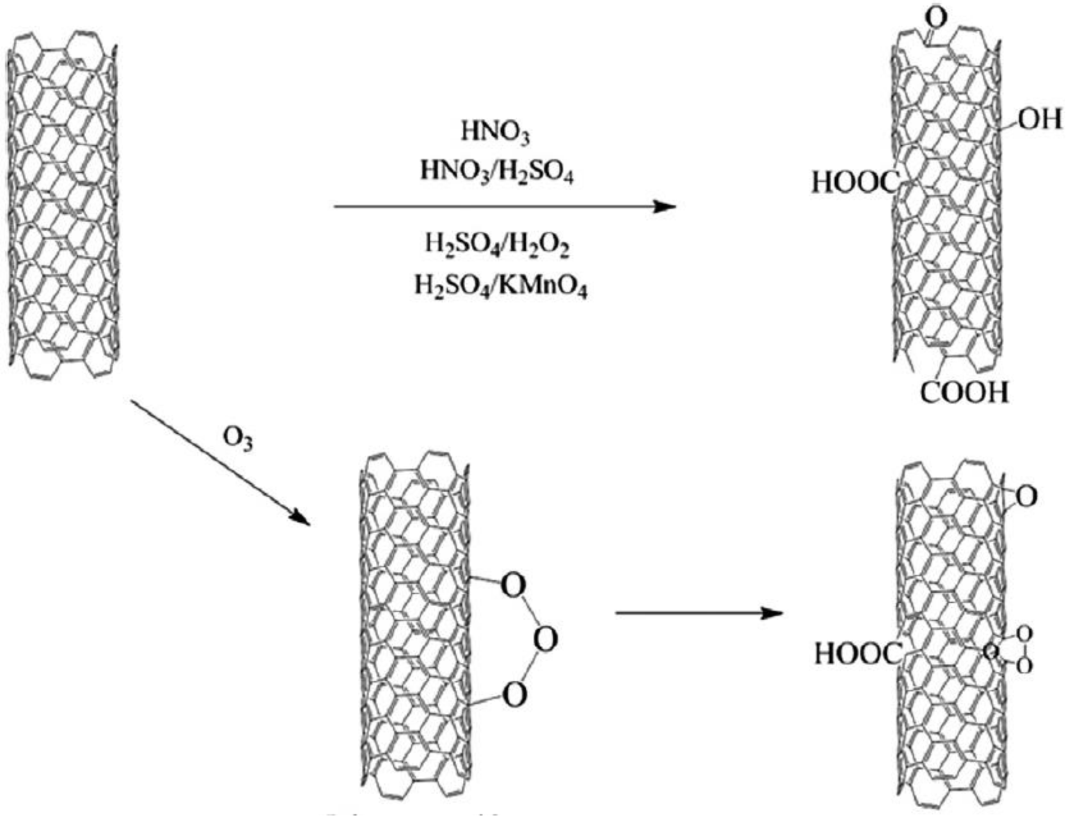


Figure 2.6 : Prepresentation of introducing functional groups on nanotube surface.

These functional groups are introduced to the surface through oxidation by oxygen, air, various acids or hydrogen peroxide. It is more proper way to carry out various chemical reactions such as fluorination, radical addition or thiolation through these carboxylic acids or hydroxyl groups as in represented in Figure 2.7.. According to a study accomplished by Kim et al., thiol groups are introduced to the nanotube surface by the reduction of carboxyl groups to methylol groups, the chlorination of methylol groups to methyl chloride and the thiolation of the methylol groups, respectively [25].

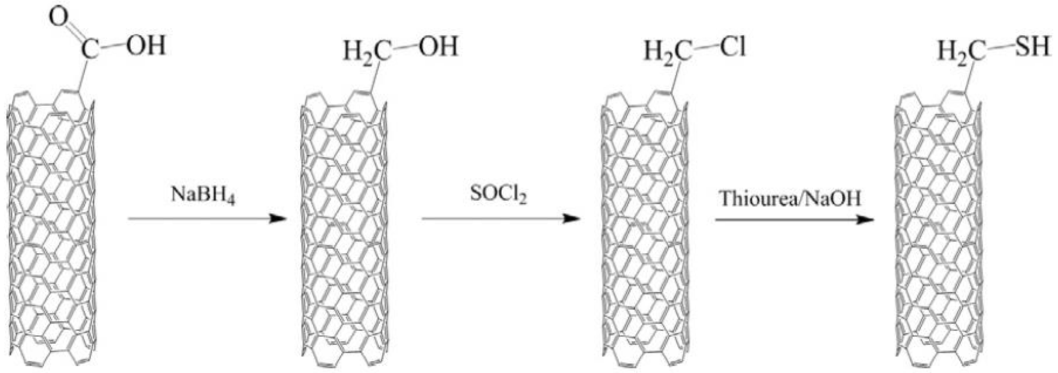


Figure 2.7 : Schematic representation of the thiolation reaction of CNTs.

Another important approach for covalent attachment is the modification of CNTs with polymer chains by either grafting to or grafting from methods. In grafting to method, polymer chains that contains reactive end groups in their structure are attached to the functional groups on the nanotube surface by various chemical reactions. This attachment is taken place between the carboxylic acid groups found in the nanotube surface and the polymer chains terminated with amino or hydroxyl groups. In grafting from method, the chemical reaction that provides the covalent attachment occurs between monomers and reactive groups on the nanotube surface. After introducing the reactive groups to the nanotube surface, the polymers are grafted from these reactive groups. Since the structure and the properties of CNTs might be affected adversely in the case of covalent attachment, another way of modification called as noncovalent attachment has drawn attention among the researchers. The solubility and dispersion of CNTs may be enhanced by using noncovalent attachment methods without altering the properties of nanotubes. This attachment can be established by using surfactants or more commonly by wrapping polymer chains around the nanotube surface. However, it might be considered as a disadvantage of noncovalent bonding that the weak forces between the wrapping molecule and the nanotube surface can cause a decrease in the mechanical properties of the nanotube. In the case of surfactant use, stabilizing agents having hydrophobic part surround the nanotube surface and an interaction occurs between the surfactant molecule and nanotube surface by this way. If the surfactant molecule has aromatic groups in its structure, the interaction gets stronger due to the presence of aromaticity in the nanotube surface. Another way to form noncovalent attachment is the wrapping of polymer chains around the carbon nanotube. This wrapping basicly takes place by means of π-π stacking interactions between nanotubes and polymer chains. The solubility of nanotubes can be greatly increased by wrapping with polymers containing aromatic moiety such as pyrene. It is a general fact that the use of amphiphilic molecules to functionalize CNTs surface is considered as one of the most convenient way. The dispersion and the solubility of the CNTs can be improved in aqueous media due to the movement of hydrophilic part of the molecule towards aqueous phase and the movement of hydrophobic part to the surface of nanotube [26,27].

2.4 Polymerization

Conventional polymerization methods are mainly divided into two main groups as step-growth polymerization and chain-growth polymerization. It may not be totally true to indicate the step-growth polymerization as condensation polymerization, or the chain-growth polymerization as addition polymerization. Because, while the condensation-addition classification is actually based on the structure of polymers, the step-chain classification is directly related to the polymerization mechanism [28].

The monomers having carbon-carbon double bond in their structure are polymerized by using various reactive species in chain polymerization. These reactive species including free radicals, cations or anions initiate the polymerization by adding the monomer molecule to form a new radical. After adding these new radicals to the monomer molecules and terminating the polymer chains by combination or disproportionation, different types of polymers are obtained. These polymers are commonly called as addition polymerization due to the chain-growth mechanism. However, the step-growth polymerization which leads to the formation of condensation polymers is another way of polymerization and it will be discussed in detail in following title [29].

2.4.1 Condensation polymerization

Since the polymerization mechanism of most condensation polymers proceeds in a step-growth polymerization manner, it is not totally wrong to use condensation polymerization instead of step-growth polymerization term. Condensation polymerization is known as an effective method to obtain various engineering plastics such as polyamides or polyesters having functional groups in both their backbones and side chains. Due to the presence of strong intermolecular interactions between the polymer backbones, high thermal and high mechanical properties as well as chemical resistancy is observed in condensation polymers. Nevertheless, it is not easy to synthesize controlled molecular weigth polymers with a narrow molecular weight distribution by using step-growth polymerization [30]. Chemically, condensation polymerization can be considered as same as a condensation reaction that occurs between small organic molecules. In condensation reactions, larger molecules are obtained by the reaction taken place between two functional groups of different molecules with the elimination of a small molecule such as water. Several condensation reaction occurs alternately by combining monomers in condensation polymerization and long polymer chains called as condensation polymers are obtained as a result. Polyesters, polyamides, polyethers are the most common examples of condensation polymers [28].

2.4.2 Polyesters

The condensation reaction of difunctional reactants provide the formation of polyesters having ester functions along the polymer chain [31]. In other definition, polyesters are large range of commercial polymers produced by either direct esterification of a diacid with a diol or self-condensation of a hydroxy carboxylic acid. Polyesterification reaction is an equilibrium reaction, therefore the water by-product should be removed from the system to reach high conversion and high molecular weight. It is important to adjust the proper reaction temperature to prevent the side reactions. Due to the variety of structural units connecting to the ester groups, a wide range of polymers having different properties and application areas are obtained. Different types of diols and dicarboxylic acids used in esterification [28].

2.5 1,3-Dipolar Cycloaddition Reaction

The molecules having unsaturated bond in their structure such as alkenes or alkynes can undergo 1,3-dipolar cycloaddition reactions with any suitable 1,3-dipolar compound to form a five-membered ring. Here, the 1,3-dipolar compund is an *a-b-c* structure having at least one mesomeric structure. While the *a* atom is an incomplete valence shell combined with a positive formal charge, the *c* atom is a negatively charged center with an unshared electron pair. The central *b* atom can be nitrogen, oxygen or sulfur [32]. Basic resonance structure of 1,3-dipoles are represented in Figure 2.8.

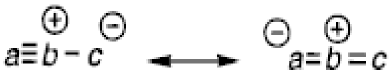


Figure 2.8 : Basic resonance structure of 1,3-dipoles.

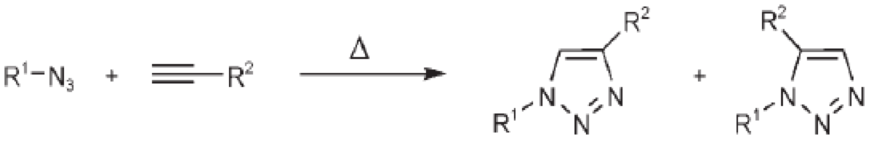


Figure 2.9 : Thermal azide-alkyne cycloaddition reaction.

Among various 1,3-dipolar compounds and alkynes, azides and terminal alkynes are the most efficiently used reactants and their cycloaddition reactions lead to the formation of triazole ring as shown in Figure 2.9. These reactions are relatively slow and require high temperature to obtain acceptable yield. Although various publications has been reported previously, the studies has been made by Rolf Huisgen in 1960 are considered as the first general approaches related to 1,3-dipolar cycloaddition reactions. Therefore 1,3-dipolar cycloaddition reaction is also known as Huisgen cycloaddition reaction and it has become a popular subject among organic chemists [33].

3. EXPERIMENTAL PART

3.1 Material

3-bromopropionic acid (97%, Aldrich), sodium azide (99.5%, Aldrich), Acetone (99.8% for HPLC, Sigma-Aldrich), 1-pyrenemethanol (98%, Aldrich), N,N'-dicyclohexylcarbodiimide (DCC, 99%, Aldrich), 4-dimethylaminopyridine (DMAP, 99%, Aldrich), acetylenedicarboxylic acid (ADCA, 95%, Aldrich), tetraethylene glycol (99%, Aldrich), 1,4-butanediol (99%, Aldrich), 1,4-benzenedimethanol (99%, Aldrich), p-Toluenesulfonic acid monohydrate (PTSA 99%, Aldrich), Poly(ethylene glycol) (Mn=600 g/mol, Aldrich), 1,4-cyclohexanedimethanol (99% Aldrich) were used as received. Benzene (99%, Aldrich), methanol (99.8%, Aldrich), diethyl ether (99.7%, Aldrich), 1,4-dioxane (99.8%, Aldrich), were used without further purification. MWCNTs (3-15 walls, in average 14.5-nm wide and 1-10-µm long) were kindly supplied by Bayer Material Science AG (Baytubes C 150 P) and used as received. Tetrahydrofuran (THF; 99.8%, J.T. Baker) was dried and distilled over benzophenone-Na. Dichloromethane (CH2Cl2, 99%, J. T. Baker) was dried and distilled over and P_2O_5. Ethyl acetate (EtOAc) and hexane were in technical grade and distilled prior to use.

3.2 Instruments

^{1}H (500 MHz) spectra were recorded on an Agilent VNMRS 500 instrument in CDCl3. The conventional gel permeation chromatography (GPC) measurements were carried out with an Agilent instrument (Model 1100) consisting of a pump, refractive index (RI) detector and four Waters Styragel columns (guard, HR 5E, HR 4E, HR 3, and HR 2), (4.6 mm internal diameter, 300 mm length, packed with 5 µm particles). The effective molecular weight ranges are 2000-4,000,000, 50-100,000, 500-30,000, and 500-20,000 g/mol, respectively. THF and toluene were used as eluent at a flow rate of

0.3 mL/min at 30 °C and as an internal standard, respectively. The apparent molecular weights (Mn,GPC and Mw,GPC) and polydispersities (Mw/Mn) were determined with a calibration based on linear PS standards using PL Caliber Software from Polymer Laboratories. FT-IR spectra was recorded on a Perkin Elmer FT¬IR Spectrum One B spectrometer. UV measurements were recorded using VWR UV-1600 PC spectrophotometer in THF. Thermal gravimetric analyses (TGAs) were performed on Perkin–Elmer Diamond TA/TGA in the temperature range of 30–600 ˚C, with a heating rate of 10 ˚C/min under nitrogen. High-resolution transmission electron microscopy (HR-TEM) micrographs were collected using a JEOL 2100 instrument operating at 200 kV. HR-TEM samples were prepared by drop coating a dilute solution of the sample (in THF) on a holey carbon-coated copper grid.

3.3 Synthesis Methods

3.3.1 Synthesis of 3-azidopropionic acid (1)

To a 250 mL of round bottom flask was added 3-bromopropionic acid (6 g, 0.039 mole, 1 equiv.) in 125 mL of water/acetone (1/4, v/v) mixture. NaN_3 (3.82 g, 0.058 mole, 1.5 equiv.) was added in one portion to the reaction and the mixture was stirred at 60 ˚C for overnight. After acetone was removed under reduced pressure, remaining liquid was dissolved in CH_2Cl_2 and extracted with water. The aqueous layer was extracted with CH_2Cl_2 (150 mL) and combined organic layers were dried over Na_2SO_4. Solvent was removed under vacuum to give yellow oil. Obtained was 2.72 g. (Yield=60%) ^1H NMR ($CDCl_3$, δ) 3.60 (t, 2H, $N_3CH_2CH_2C{=}O$), 2.65 (t, 2H, $N_3CH_2CH_2C{=}O$).

3.3.2 Synthesis of pyrene-1-ylmethyl 3-azidopropanoate (2)

1-Pyrenemethanol (3 g, 0.013 mole, 1.2 equiv.) was dissolved in 60 mL of CH_2Cl_2 and previously obtained product (1) (1.27 g, 0.0107 mole, 1 equiv.) and DMAP (1.31 g, 0.0107 mole, 1 equiv.) were added to the reaction mixture in that order. After stirring at 5 min at room temperature, DCC (2.68 g, 0.013 mole, 1.2 equiv.) dissolved in 40 mL CH_2Cl_2 was added. Reaction mixture was stirred overnight at room temperature and urea byproduct was filtered. The solution was concentrated, and the crude product purified by column chromatography over silica gel eluting with ethyl acetate/hexane

(1:6) to give as a viscous oil, which solidified by time. Obtained was 2.53 g. (Yield=72%) ^{1}H NMR ($CDCl_3$, δ) 8.30-8.03 (m, 9H, Ar*H*), 5.90 (s, 2H, pyrene-$CH_2OC=OCH_2CH_2N_3$), 3.60 (t, 2H, pyrene-$CH_2OC=OCH_2CH_2N_3$), 2.65 (t, 2H, pyrene-$CH_2OC=OCH_2CH_2N_3$)

3.3.3 Synthesis of polyester (P1)

Acetylenedicarboxylic acid (ADCA) (2 g, 0.017 mole, 1 equiv.) was dissolved in 40 mL of benzene and stirred under nitrogen and 1,4-butanediol (1.55 mL, 0.017 mole, 1 equiv.) and PTSA (0.32 g, 0.0017 mole, 0.1 equiv.) were added to the solution in that order. The mixture was gradually heated in a round bottomed flask, with a Dean-Stark apparatus attached, in an oil bath set to 100 ˚C and stirred overnight. After that time, solvent was removed under reduced pressure, THF was added to the residue and finally precipitated in methanol. The dissolution–precipitation (THF-methanol) procedure was repeated two times. The obtained polymer was dried overnight in a vacuum oven at 40 ˚C. ^{1}H NMR ($CDCl_3$, δ) 4.30 (bs, 4H, $C=OOCH_2CH_2CH_2CH_2OC=O$), 1.82 (bs, 4H, $C=OOCH_2CH_2CH_2CH_2OC=O$) ($M_{n,GPC}$=6050 g/mol, M_w/M_n=1.95, relative to the PS standart.)

3.3.4 Synthesis of polyester (P2)

Acetylenedicarboxylic acid (ADCA) (3 g, 0.026 mole, 1 equiv.) was dissolved in 60 mL of benzene and stirred under nitrogen and tetraethylene glycol (4.48 mL, 0.026 mole, 1 equiv.) and PTSA (0.49 g, 0.0026 mole, 0.1 equiv.) were added to the solution in that order. The mixture was gradually heated in a round bottomed flask, with a Dean-Stark apparatus attached, in an oil bath set to 100 ˚C and stirred overnight. After that time, solvent was removed under reduced pressure, THF was added to the residue and finally precipitated in methanol. The dissolution–precipitation (THF-methanol) procedure was repeated two times. The obtained polymer was dried overnight in a vacuum oven at 40 ˚C. ^{1}H NMR (CDCl3, δ) 4.39 (m, 4H, C=OOCH2CH2O), 3.75 (m, 4H, C=OOCH2CH2O), 3.66 (s, 8H, OCH2CH2O) (Mn,GPC=5250 g/mol, Mw/Mn=1.46, relative to the PS standart.)

3.3.5 Synthesis of polyester (P3)

Acetylenedicarboxylic acid (ADCA) (2 g, 0.017 mole, 1 equiv.) was dissolved in 60 mL of benzene and stirred under nitrogen and polyethylene glycol (10.5 ml, 0.017 mole, 1 equiv.) and PTSA (0.3 g, 0.0017 mole, 0.1 equiv.) were added to the solution in that order. The mixture was gradually heated in a round bottomed flask, with a Dean-Stark apparatus attached, in an oil bath set to 100 ˚C and stirred overnight. After that time, solvent was removed under reduced pressure, THF was added to the residue and finally precipitated in methanol. The dissolution–precipitation (THF-methanol) procedure was repeated two times. The obtained polymer was dried overnight in a vacuum oven at 40 ˚C. ^{1}H NMR (CDCl3, δ) 4.39 (m, 4H, C=OOCH2CH2O), 3.75 (m, 4H, C=OOCH2CH2O), 3.66 (s, 8H, OCH2CH2O) (Mn,GPC=5250 g/mol, Mw/Mn=1.46, relative to the PS standart.)

3.3.6 Synthesis of polyester (P4)

Acetylenedicarboxylic acid (ADCA) (2 g, 0.017 mole, 1 equiv.) was dissolved in 40 mL of benzene and stirred under nitrogen and 1,4-cyclohexanedimethanol (2.52 g, 0.017 mole, 1 equiv.) and PTSA (0.3 g, 0.0017 mole, 0.0017 equiv.) were added to the solution in that order. The mixture was gradually heated in a roundbottomed flask, with a Dean-Stark apparatus attached, in an oil bath set to 100 ˚C and stirred overnight. After that time, solvent was removed under reduced pressure, THF was added to the residue and finally precipi tated in methanol. The dissolution–precipitation (THF methanol) procedure was repeated two times. The obtained polymer was dried overnight in a vacuum oven at 40 ˚C. ^{1}H NMR ($CDCl_3$, δ) 4.16 (m, 4H, CH_2CH), 4.08 (m, 4H, CH_2CH), 2.1-1.0 (m, aliphatic protons of cyclohexane) ($M_{n,GPC}$=3950 g/mol, M_w/M_n=3.18, relative to the PS standart.)

3.3.7 Synthesis of polyester (P5)

Acetylenedicarboxylic acid (ADCA) (1 g, 0.008 mole, 1 equiv) was dissolved in 20 mL of benzene and stirred under nitrogen. 1,4-benzenedimethanol (1.21 g, 0.008 mole, 1 equiv) and PTSA (0.15 g, 0.0008 mole, 0.1 equiv) were added to the solution in that order. The mixture was gradually heated in a round bottomed flask, with a Dean-Stark apparatus attached, in an oil bath set to 100°C and stirred overnight. After that time, solvent was removed under reduced pressure, THF was added to the residue and finally precipitated in methanol. The dissolution–precipitation (THF-methanol) procedure was repeated two times. The obtained polymer was dried overnight in a vacuum oven at 40 ˚C. ^{1}H NMR (CDCl$_3$, δ) 7.38 (bs, 4H, ArH), 5.25 (bs, 4H, $\mathrm{C{=}OOC}H_2\mathrm{Ph}$), 4.57 (s, 4H, $\mathrm{C{=}OOC}H_2\mathrm{Ph}$)

3.3.8 1,3-Dipolar cycloaddition reaction between (P1) and (2) (P1-py)

(P1) (0.37 g, 0.002 mole, 1 equiv.) was dissolved in 10 mL of 1,4-dioxane and transferred to 25 mL Schlenk tube. Next, the (2) compound (1.52 g, 0.004 mole, 2 equiv.) was added to the solution and the reaction mixture was degassed by two FPT cycles, left under vacuum.The tube was then placed in a thermostated oil bath and stirred at 40˚C for overnight. After that time, the solution was precipitated in methanol and the residual solvent was removed by decantation. The dissolution-precipitaion (THF-Methanol) procedure was repeated two times and the recovered polymer was dried in a vacuum oven at 40 ˚C for 24h. ^{1}H NMR (CDCl$_3$, δ) 8.07-7.90 (m, 9H, ArH), 5.66 (s, 2H, $\mathrm{ArHC}H_2\mathrm{OC{=}OCH_2CH_2}$), 4.77 (s, 2H, $\mathrm{ArHCH_2OC{=}OCH_2C}H_2$), 2.99 (s, 2H, $\mathrm{ArHCH_2OC{=}OC}H_2\mathrm{CH_2}$) 4.30 (bs, 4H, $\mathrm{C{=}OOC}H_2\mathrm{CH_2CH_2C}H_2\mathrm{OC{=}O}$), 1.77 (bs, 4H, $\mathrm{C{=}OOCH_2C}H_2\mathrm{C}H_2\mathrm{CH_2OC{=}O}$) $M_{\mathrm{n,GPC}}$ = 6700 g/mol, $M_{\mathrm{w}}/M_{\mathrm{n}}$ = 5.48, relative to PS standards)

3.3.9 1,3-Dipolar cycloaddition reaction between (P2) and (2) (P2-py)

(P2) (0.29 g, 0.001 mole, 1 equiv.) was dissolved in 10 mL of 1,4-dioxane and transferred to 25 mL Schlenk tube. Next, the (2) compound (0.75 g, 0.002 mole, 2 equiv.) was added to the solution and the reaction mixture was degassed by two FPT cycles, left under vacuum.The tube was then placed in a thermostated oil bath and stirred at 40˚C for overnight. After that time, the solution was precipitated in methanol and the residual solvent was removed by decantation. The dissolution-precipitaion (THF-Methanol) procedure was repeated two times and the recovered polymer was dried in a vacuum oven at 40 ˚C for 24h. ^{1}H NMR (CDCl$_3$, δ) 8.31-8.04 (m, 9H, ArH), 5.74 (s, 2H, $\mathrm{ArHC}H_2\mathrm{OC{=}OCH_2CH_2}$), 4.84 (s, 2H, $\mathrm{ArHCH_2OC{=}OCH_2C}H_2$), 3.02 (s, 2H, $\mathrm{ArHCH_2OC{=}OC}H_2\mathrm{CH_2}$) 4.44 (m, 4H, $\mathrm{C{=}OOC}H_2\mathrm{CH_2O}$), 3.76 (m, 4H,

$\mathrm{C{=}OOCH_2C}H_2\mathrm{O}$), 3.60 (s, 8H, $\mathrm{OC}H_2\mathrm{C}H_2\mathrm{O}$) ($M_{\mathrm{n,GPC}}$ = 6300 g/mol, $M_\mathrm{w}/M_\mathrm{n}$ = 1.23, relative to PS standards)

3.3.10 1,3-Dipolar cycloaddition reaction between (P3) and (2) (P3-py)

(P3) (0.49 g, 0.0007 mole, 1 equiv.) was dissolved in 10 mL of 1,4-dioxane and transferred to 25 mL Schlenk tube. Next, the (2) compound (0.5 g, 0.0014mole, 2 equiv.) was added to the solution and the reaction mixture was degassed by two FPT cycles, left under vacuum. The tube was then placed in a thermostated oil bath and stirred at 40˚C for overnight. After that time, the solution was precipitated in diethyl ether and the residual solvent was removed by decantation. The dissolution-precipitaion (THF-Diethyl ether) procedure was repeated two times and the recovered polymer was dried in a vacuum oven at 40 ˚C for 24h. ^{1}H NMR ($\mathrm{CDCl_3}$, δ) 8.31-7.97 (m, 9H, ArH), 5.90 (s, 2H, $\mathrm{ArHC}H_2\mathrm{OC{=}OCH_2CH_2N_3}$), 4.91 (t, 2H, $\mathrm{CH_2OC{=}OCH_2C}H_2\mathrm{N_3}$), 3.10 (s, 2H, $\mathrm{ArHCH_2OC{=}OC}H_2\mathrm{CH_2}$) 4.50 (bs, 4H, $\mathrm{C{=}OOC}H_2\mathrm{CH_2CH_2C}H_2\mathrm{OC{=}O}$), 3.71 (m, 4H, $\mathrm{C{=}OOC}H_2\mathrm{CH_2O}$), 3.62 (m, 4H, $\mathrm{C{=}OOCH_2C}H_2\mathrm{O}$) ($M_{\mathrm{n,GPC}}$ = 2600 g/mol, $M_\mathrm{w}/M_\mathrm{n}$ = 1.26, relative to PS standards.)

3.3.11 1,3-Dipolar cycloaddition reaction between (P4) and (2) (P4-py)

(P4) (0.16 g, 0.0007 mole, 1 equiv.) was dissolved in 10 mL of 1,4-dioxane and transferred to 25 mL Schlenk tube. Next, the (2) compound (0.5 g, 0.0014 mole, 2 equiv.) was added to the solution and the reaction mixture was degassed by two FPT cycles, left under vacuum.The tube was then placed in a thermostated oil bath and stirred at 40˚C for overnight. After that time, the solution was precipitated in methanol and the residual solvent was removed by decantation. The dissolution-precipitaion (THF-Methanol) procedure was repeated two times and the recovered polymer was dried in a vacuum oven at 40 ˚C for 24h. ^{1}H NMR ($\mathrm{CDCl_3}$, δ) 8.25-7.82 (b, 9H, ArH), 5.78 (s, 2H, $\mathrm{ArHC}H_2\mathrm{OC{=}OCH_2CH_2}$), 4.84 (s, 2H, $\mathrm{ArHCH_2OC{=}OCH_2C}H_2$), 3.06 (s, 2H, $\mathrm{ArHCH_2OC{=}OC}H_2\mathrm{CH_2}$) 2.1-1.0 (m, aliphatic protons of cyclohexane), 4.10 (m, 4H, $\mathrm{C}H_2\mathrm{CH}$) ($M_{\mathrm{n,GPC}}$ = 9100 g/mol, $M_\mathrm{w}/M_\mathrm{n}$ = 2.32, relativ to PS standards)

3.3.12 1,3-Dipolar cycloaddition reaction between (P5) and (2) (P5-py)

(P5) (0.16 g, 0.0007 mole, 1 equiv.) was dissolved in 10 mL of 1,4-dioxane and transferred to 25 mL Schlenk tube. Next, the (2) compound (0.5 g, 0.0014 mole, 2 equiv.) was added to the solution and the reaction mixture was degassed by two FPT cycles, left under vacuum.The tube was then placed in a thermostated oil bath and stirred at 40˚C for overnight. After that time, the solution was precipitated in methanol and the residual solvent was removed by decantation. The dissolution-precipitaion (THF-Methanol) procedure was repeated two times and the recovered polymer was dried in a vacuum oven at 40 ˚C for 24h. ^{1}H NMR ($CDCl_3$, δ) 8.23-7.72 (m, 9H, ArH), 7.42 (bs, 4H, ArH), 4.71 (t, 2H, $\mathrm{CH_2OC{=}OCH_2C}H_2\mathrm{N_3}$), 3.03 (t, 2H, $\mathrm{CH_2OC{=}OC}H_2\mathrm{CH_2N_3}$), 5.90 (s, 2H, $\mathrm{ArHC}H_2\mathrm{OC{=}OCH_2CH_2N_3}$), ($M_{\mathrm{n,GPC}}$ = 1800 g/mol, $M_\mathrm{w}/M_\mathrm{n}$ = 2.32, relative to PS standards)

3.3.13 Modification of MWCNTs with pyrene functional polyester, (Py-P1)

To a 250 mL round-bottomed flask were added MWCNTs (50 mg) and (Py-P1) (0.25 g) (polymer to nanotubes ratio: 5, w/w). Next, 150 mL of dry THF was added. The resulting heterogenous mixture was sonicated for 30 min in a low power sonic bath under nitrogen and stirred for additional 10 days at room temperature. After that time, to removed nonattached Py-P1, the mixture was filtered through a filter (Sartorious, PTFE; pore size, 0.2 µm), then residual solid on the filter was sonicated well with using excessive amount of fresh THF and filtered again. The recovered black powder was then dried under vacuum oven at 40 ˚C for 24 h.

3.3.14 Modification of MWCNTs with pyrene functional polyester, (Py-P2)

To a 250 mL round-bottomed flask were added MWCNTs (50 mg) and (Py-P2) (0.25 g) (polymer to nanotubes ratio: 5, w/w). Next, 150 mL of water was added. The resulting heterogenous mixture was sonicated for 30 min in a low power sonic bath under nitrogen and stirred for additional 10 days at room temperature. After that time, to removed nonattached Py-P2, the mixture was filtered through a filter (Sartorious, PTFE; pore size, 0.2 µm), then residual solid on the filter was sonicated well with using excessive amount of fresh THF and filtered again. The recovered black powder was then dried under vacuum at 40 ˚C for 24 h.

3.3.15 Modification of MWCNTs with pyrene functional polyester, (Py-P3)

To a 250 mL round-bottomed flask were added MWCNTs (50 mg) and (Py-P3) (0.25 g) (polymer to nanotubes ratio: 5, w/w). Next, 150 mL of water was added. The resulting heterogenous mixture was sonicated for 30 min in a low power sonic bath under nitrogen and stirred for additional 10 days at room temperature. After that time, to removed nonattached Py-P3, the mixture was filtered through a filter (Sartorious, PTFE; pore size, 0.2 μm), then residual solid on the filter was sonicated well with using excessive amount of fresh THF and filtered again. The recovered black powder was then dried under vacuum at 40 ˚C for 24 h.

3.3.16 Modification of MWCNTs with pyrene functional polyester, (Py-P4)

To a 250 mL round-bottomed flask were added MWCNTs (25 mg) and (Py-P4) (0.12 g) (polymer to nanotubes ratio: 5, w/w). Next, 80 mL of dry THF was added. The resulting heterogenous mixture was sonicated for 30 min in a low power sonic bath under nitrogen and stirred for additional 10 days at room temperature. After that time, to removed nonattached Py-P4, the mixture was filtered through a filter (Sartorious, PTFE; pore size, 0.2 μm), then residual solid on the filter was sonicated well with using excessive amount of fresh THF and filtered again. The recovered black powder was then dried under vacuum at 40 ˚C for 24 h.

3.3.17 Modification of MWCNTs with Pyrene Functional Polyester, (Py-P5)

To a 250 mL round-bottomed flask were added MWCNTs (50 mg) and (Py-P5) (0.25 g) (polymer to nanotubes ratio: 5, w/w). Next, 150 mL of dry THF was added. The resulting heterogenous mixture was sonicated for 30 min in a low power sonic bath under nitrogen and stirred for additional 10 days at room temperature. After that time, to removed nonattached Py- P5. The mixture was filtered through a filter (Sartorious, PTFE; pore size, 0.2 μm), then residual solid on the filter was sonicated well with using excessive amount of fresh THF and filtered again. The recovered black powder was then dried under vacuum at 40 ˚C for 24 h.

4. RESULTS AND DISCUSSION

4.1 Preparation of 3-Azidopropionic acid

3-bromopropionic acid was converted to 3-azidopropionic acid in water/acetone (1:4) mixture by using NaN_3. Reaction mixture was stirred for 24h at 60 ˚C and product (1) was obtained as yellow oil as shown in Figure 4.1.

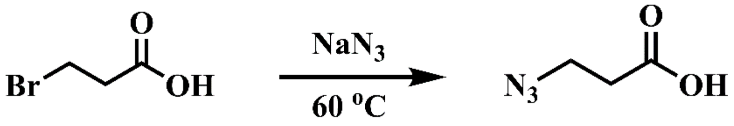


Figure 4.1 : Synthesis of 3-azidopropionic acid.

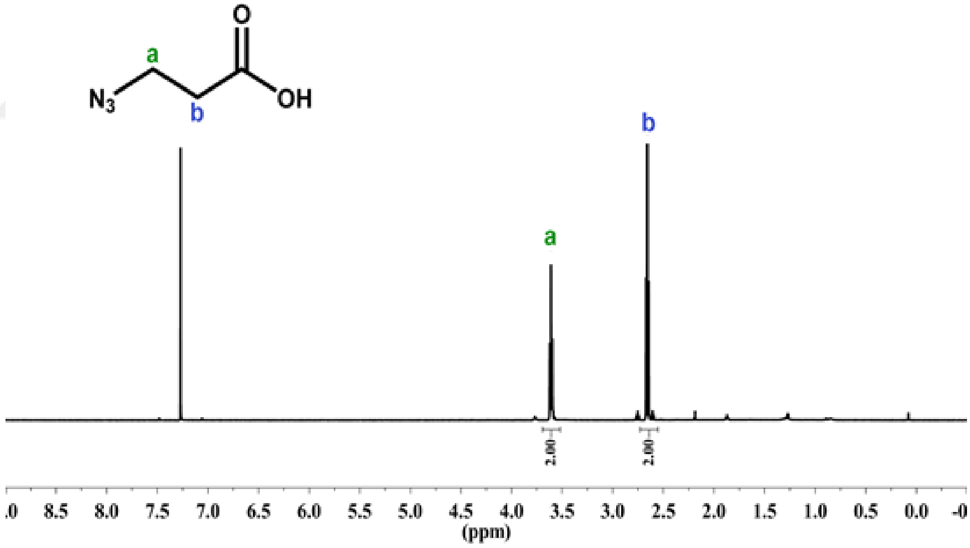


Figure 4.2 : ^1H NMR spectrum of 3-azidopropionic acid in $CDCl_3$. (500 MHz)

Figure 4.2. represents the ^1H NMR spectrum of 3-azidopropionic acid. It was clearly seen that methylene protons next to azide ($N_3CH_2CH_2C{=}O$, first H_2 italic: $N_3C\mathit{H_2}CH_2C{=}O$) are found at 3.60 ppm and the methylene protons next to carboxylic acid ($N_3CH_2C\mathit{H_2}C{=}O$) are found at 2.65 ppm. The integrated values of these signals are confirmed the number of protons on the molecule.

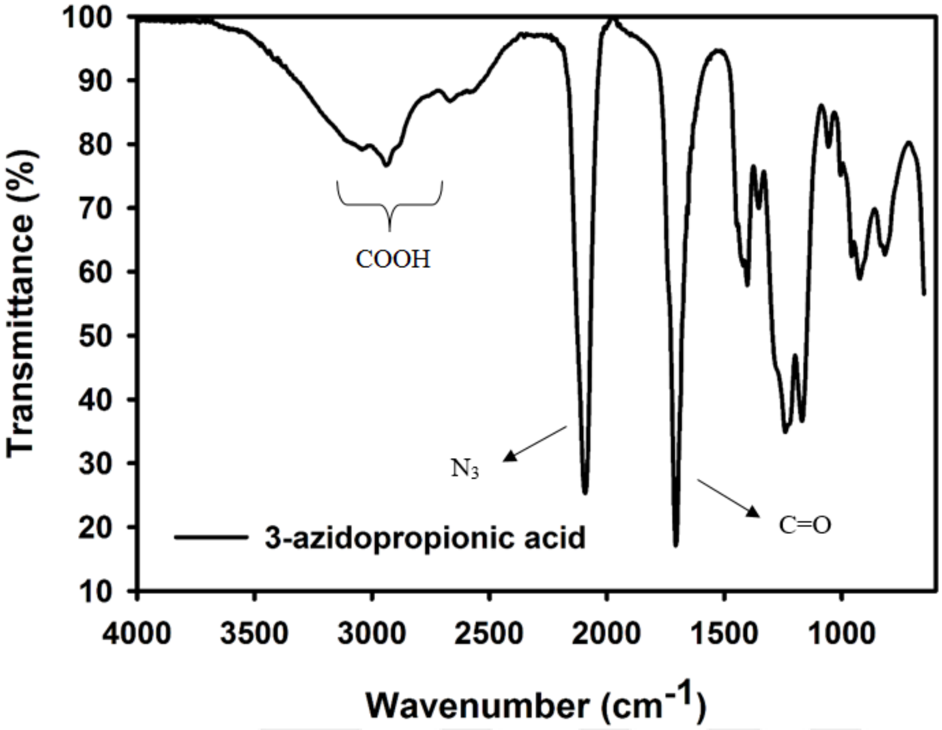


Figure 4.3 : FTIR result of 3-azidopropionic acid.

Figure 4.3. represents the FTIR spectrum of 3-azidopropionic acid. It was clearly seen that while the azide peak is indicated at 2100 cm^{-1} wavenumber, carbonyl peak is indicated at 1740 cm^{-1} wavenumber approximately. The broad peak displays the aromatic COOH group in the structure.

4.2 Preparation of pPyren-1-ylmethyl 3-azidopropanoate (2)

1-Pyrenemethanol and previously obtained product (1) was esterified in the presence of DMAP and DCC. Reaction mixture was stirred for 24h at room temperature. After the purification made by using column chromatography, the product (2) was obtained as viscous oil as shown in Figure 4.4.

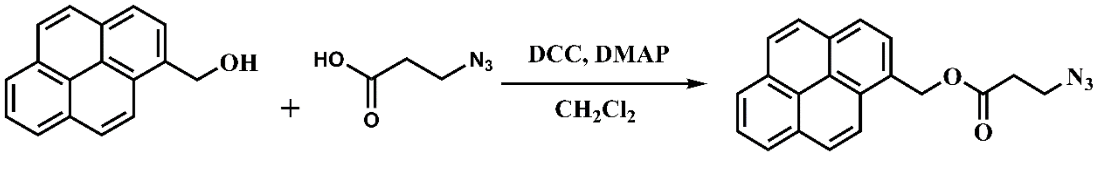


Figure 4.4 : Synthesis of pyren-1-ylmethyl 3-azidopropanoate.

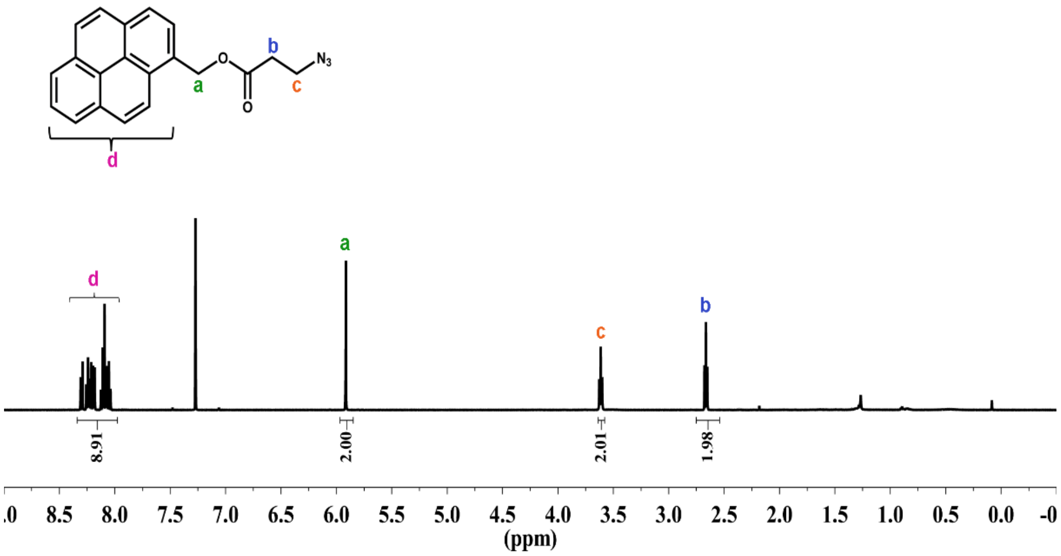


Figure 4.5 : ^{1}H NMR Spectrum of pyren-1-ylmethyl 3-azidopropanoate in CDCl$_3$ (500 MHz)

Figure 4.5. represents the ^{1}H NMR spectra of pyren-1-ylmethyl 3-azidopropanoate (2). It was clearly seen that aromatic protons of pyrene moiety (Ar*H*) is detected between 8.30-8.03 ppm, methylene protons next to pyrene moiety (ArHC*H*$_2$OC=OCH2CH2N3) are found at 5.90 ppm, methylene protons next to ester carbonyl (ArHCH$_2$OC=OC*H*$_2$CH$_2$N$_3$) are found at 2.65 ppm and the methylene protons next to azide (ArHCH$_2$OC=OCH$_2$C*H*$_2$N$_3$) are found at 3.60 ppm. The integrated values of these signals are validated the number of protons on the molecule.

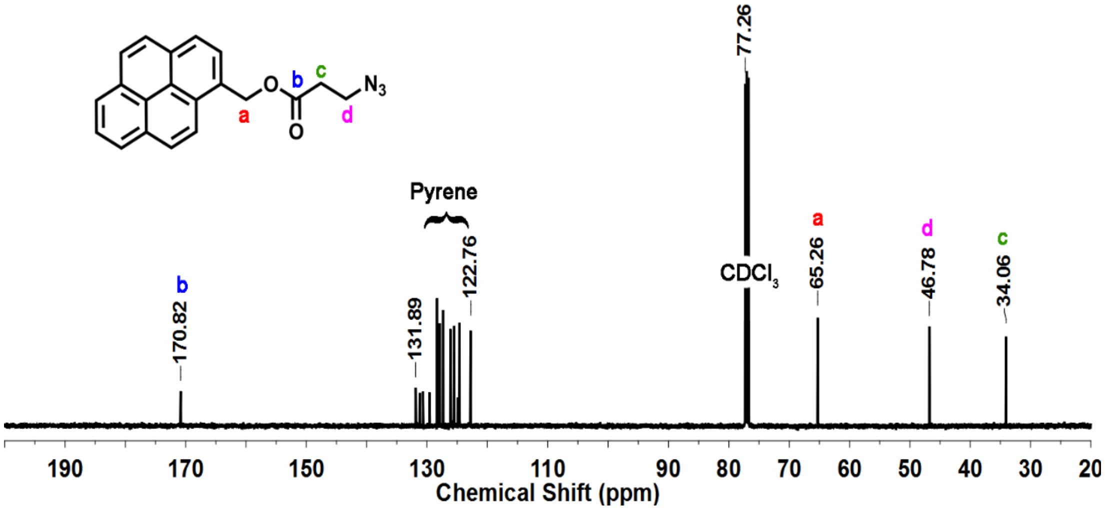


Figure 4.6 : ^{13}C NMR Spectrum of pyren-1-ylmethyl 3-azidopropanoate in CDCl$_3$ (500 MHz)

In ^{13}C NMR as shown in Figure 4.6., the peak of 170 ppm indicates the C=O group, the peak of 65 ppm indicates the C-C next to aromatic pyrene structure, the peak of

46.7 ppm indicates the C-C next to azide and the peak of 34 ppm indicates the C-C next to ester carbonyl. The aromatic carbons of pyrene moiety is displayed between 131.8 and 122.7 ppm.

4.3 Preparation of Polyesters

Various polyesters were prepared through polyesterification reactions by using ADCA and various diols in the presence of PTSA catalyst in benzene for 24h. For the preparation of polyesters; ADCA, the diol compound and PTSA was first suspended in benzene, then gradually heated in a round bottom flask, with a Dean-Stark apparatus attached, in an oil bath set to 100 ˚C as shown in Figure 4.7.. After the dissolution-precipitation process, the recovered polymers was dried in a vacuum oven at 40 ˚C for 24h.

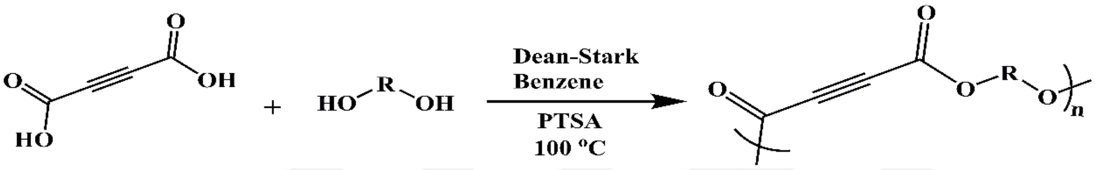


Figure 4.7 : General preparation procedure of polyesters

For the preparation of P1; the reaction mechanism which is represented in Figure 4.8. is completely the same as general polyester synthesis procedure. Here, 1,4-butanediol was used as diol.

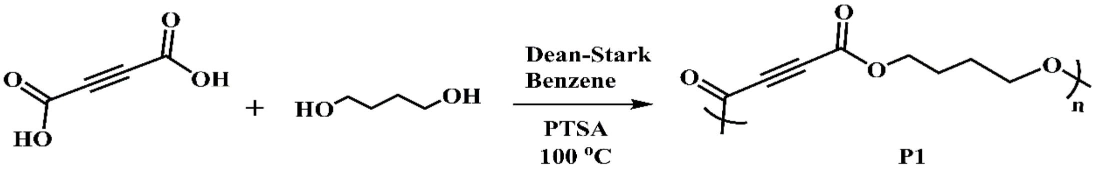


Figure 4.8 : Synthesis of P1 by using ADCA and 1,4-butandiol

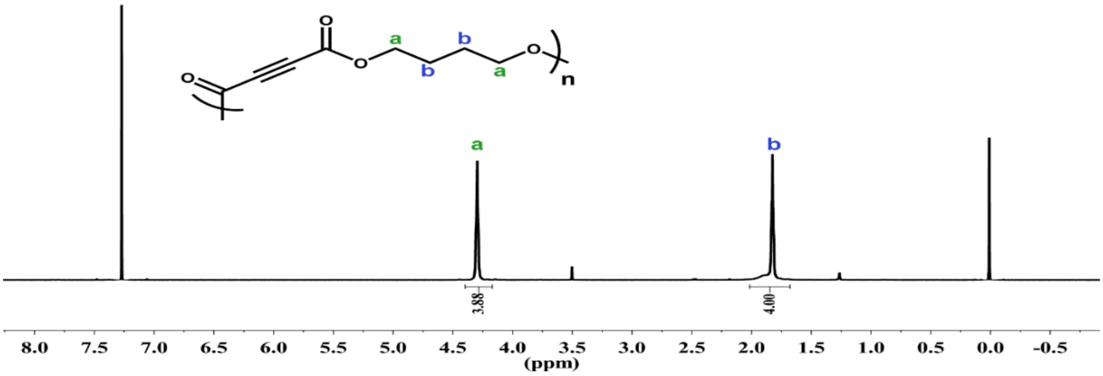


Figure 4.9 : ^{1}H NMR spectrum of P1 in $CDCl_3$ (500 MHz)

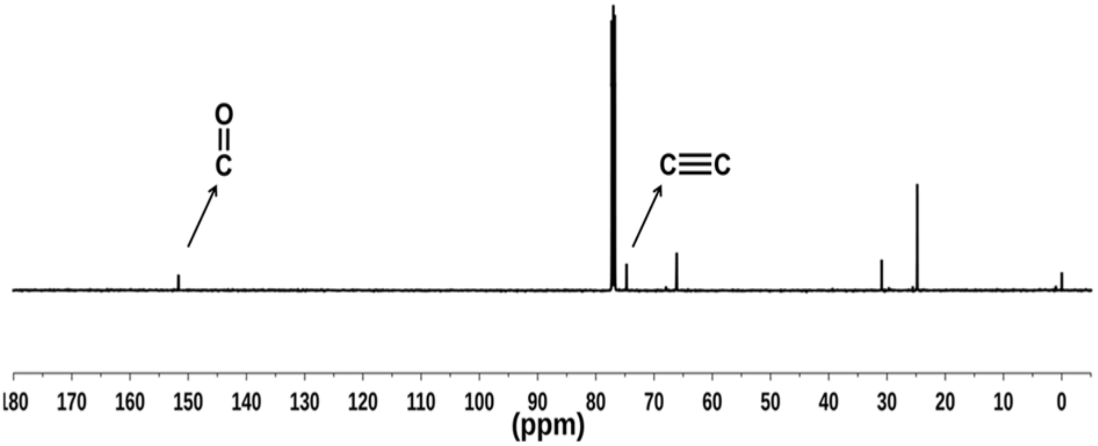


Figure 4.10 : ^{13}C NMR spectrum of P1 in $CDCl_3$ (500 MHz)

Figure 4.9. represents the ^{1}H NMR spectrum of P1. It was clearly seen that the OCH_2 protons of polyester backbone are found at 4.30 ppm and 1.82 ppm after polymerization. In ^{13}C NMR spectrum which is given in Figure 4.10., while the peak of 151 ppm indicates the C=O group, the peak of 74 ppm indicates the C≡C group.

For the preparation of P2; the reaction mechanism which is represented in Figure 4.11. is completely the same as general polyester synthesis procedure. Here, tetraethylene glycol was used as diol.

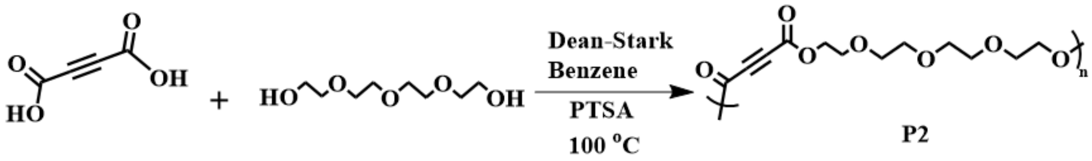


Figure 4.11 : Synthesis of P2 by ssing ADCA and Tetraethylene Glycol

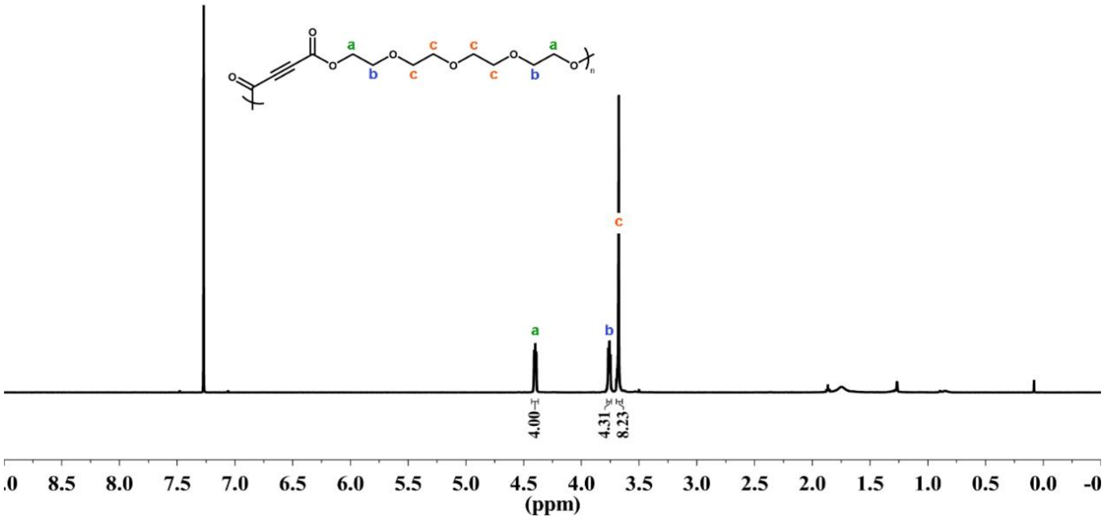


Figure 4.12 : ^{1}H NMR spectrum of P2 in $CDCl_3$ (500 MHz)

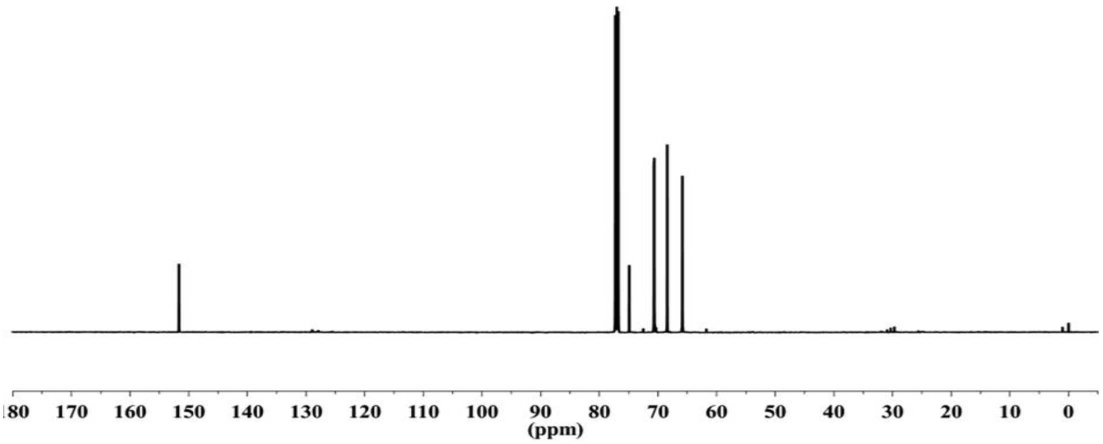


Figure 4.13 : ^{13}C NMR spectrum of P2 in $CDCl_3$ (500 MHz)

Figure 4.12. represents the ^{1}H NMR spectrum of P2. It was clearly seen that the protons next to ester units ($C{=}OOC\mathit{H}_2CH_2O$) are found at 4.39 ppm, the methylene groups ($C{=}OOCH_2C\mathit{H}_2O$) are found at 3.75 ppm and the protons of the tetraethylene's interior ethylene groups are found at 3.66 ppm. In ^{13}C NMR spectrum which is given in Figure 4.13., the peaks of 151.5 and 74.5 ppm are indicates the C=O and C≡C groups. The carbons of ethylene groups are appeared between 70.4 ppm and 65.6 ppm.

For the preparation of P3; the reaction mechanism which is represented in Figure 4.14. is completely the same as general polyester synthesis procedure. Here, PEG_{600} was used as diol.

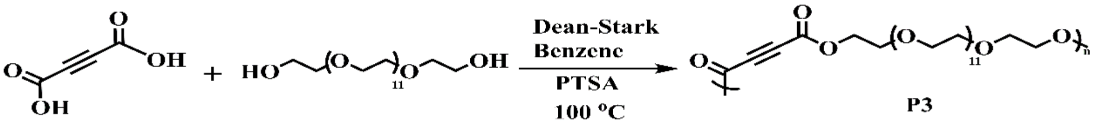


Figure 4.14 : Synthesis of P3 by using ADCA and PEG_{600}

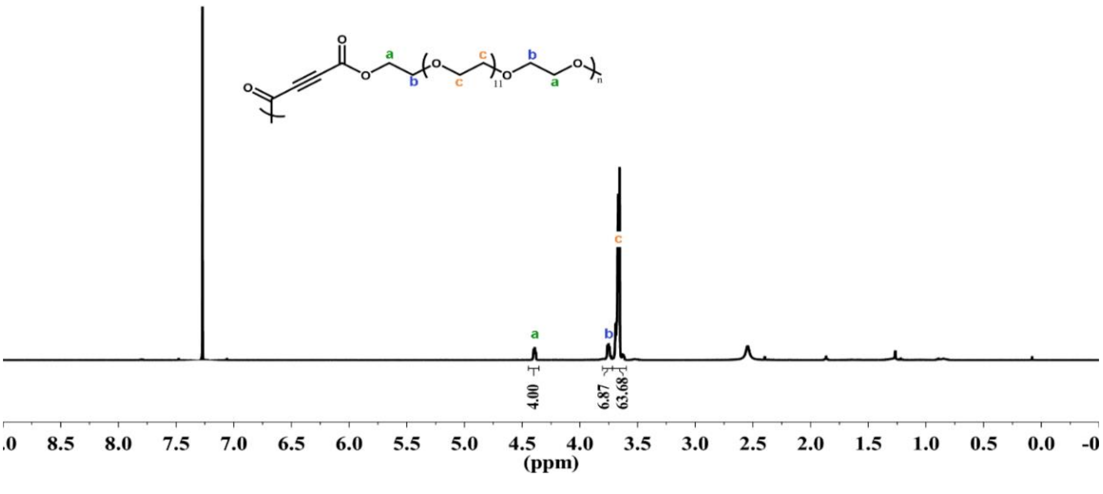


Figure 4.15 : ^{1}H NMR spectrum of P3 in $CDCl_3$ (500 MHz)

Figure 4.15. represents the ^1H NMR spectrum of P3. It was clearly seen that the protons next to ester units ($C{=}OOC\mathit{H}_2CH_2O$) are found at 4.39 ppm, the methylene groups ($C{=}OOCH_2C\mathit{H}_2O$) are found at 3.76 and the protons of the tetraethylene's interior ethylene groups are found at 3.66 ppm.

For the preparation of P4; the reaction mechanism which is represented in Figure 4.16. is completely the same as general polyester synthesis procedure. Here, 1,4-cyclohexanedimethanol was used as diol.

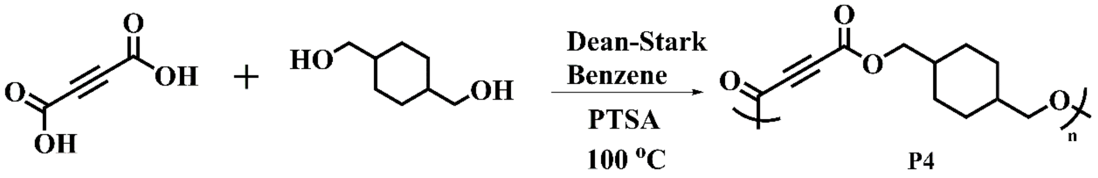


Figure 4.16 : Synthesis of P4 by using ADCA and 1,4-cyclohexanedimethanol

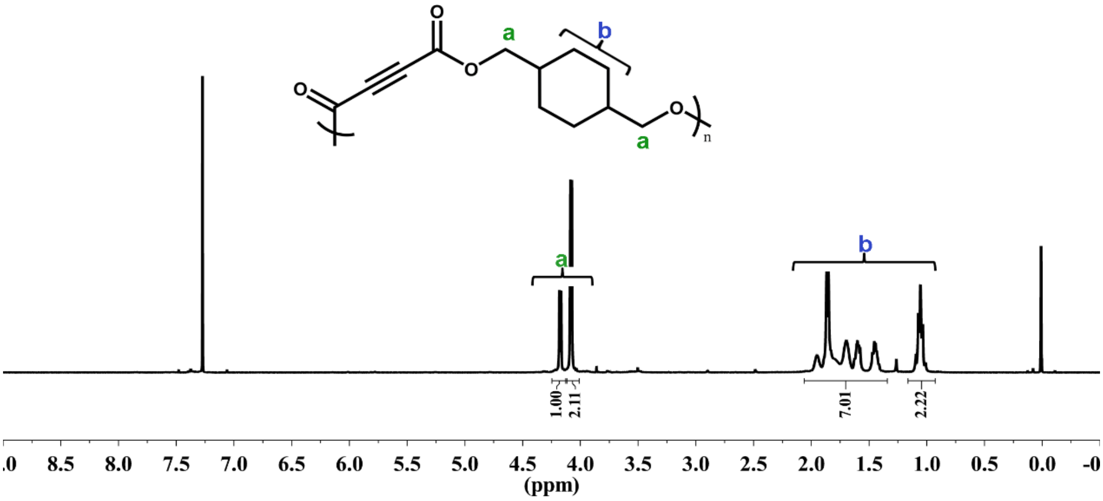


Figure 4.17 : ^1H NMR spectrum of P4 in $CDCl_3$ (500 MHz)

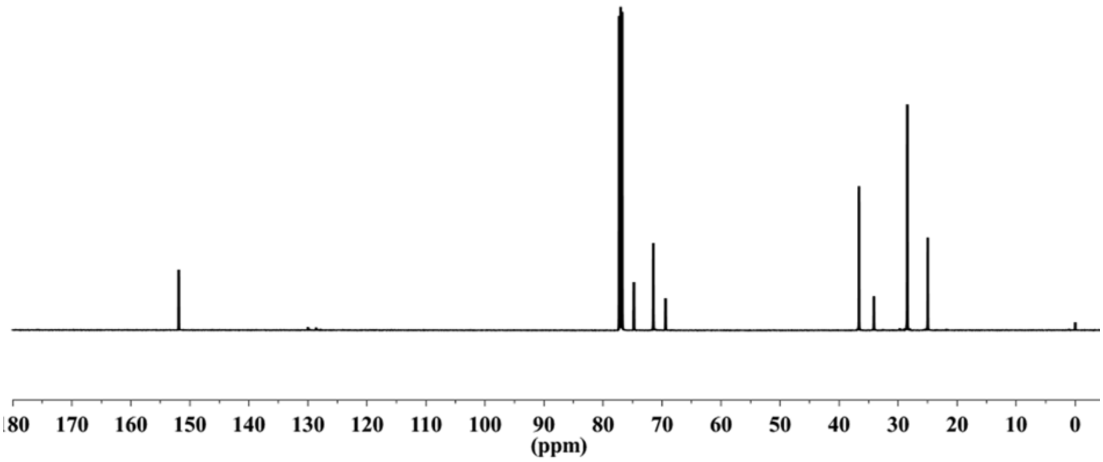


Figure 4.18 : ^{13}C NMR spectrum of P4 in $CDCl_3$ (500 MHz)

Figure 4.17. represents the ^{1}H NMR spectrum of P4. It was clearly seen that the ester unit protons CH_2CH are found between 4.18 and 4.07 ppm, and the aliphatic protons of cyclohexane are found between 2.02 and 1.07 ppm. In ^{13}C NMR spectrum which is given in 4.18., while the peaks of 151 and 74 ppm indicate the C=O and C≡C groups, the peaks between 71.3 and 25.1 ppm indicate the carbon atoms belonging the cyclohexanedimethanol.

For the preparation of P5; the reaction mechanism which is represented in Figure 4.19. is completely the same as general polyester synthesis procedure. Here, 1,4-benzenedimethanol was used as diol.

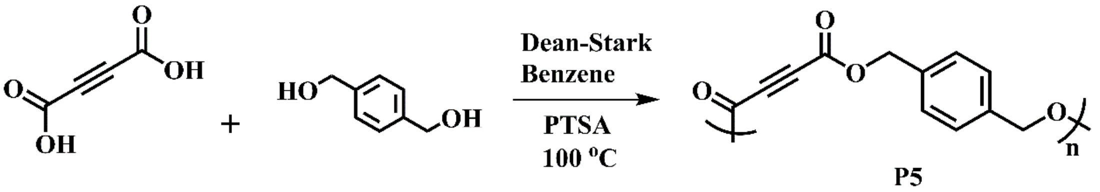


Figure 4.19 : Synthesis of P5 by using ADCA and 1,4-benzenedimethanol

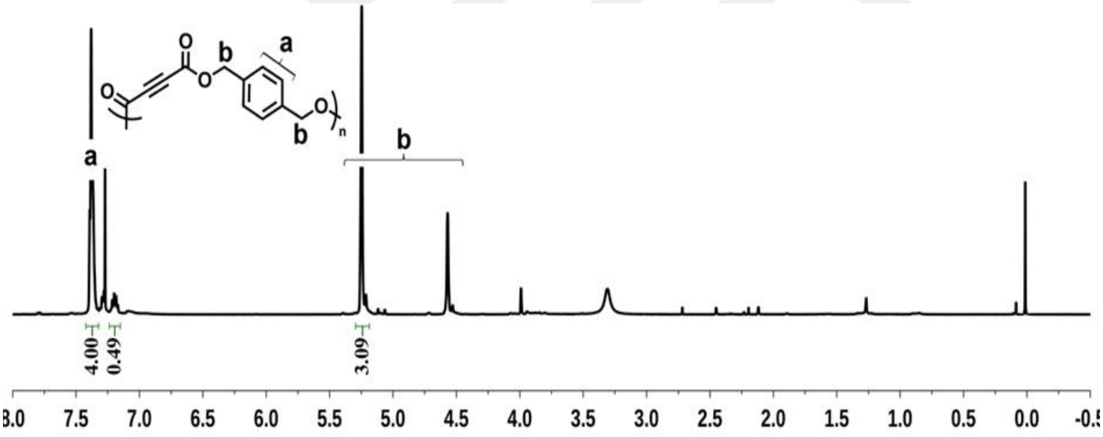


Figure 4.20 : ^{1}H NMR spectrum of P5 in $CDCl_3$ (500 MHz)

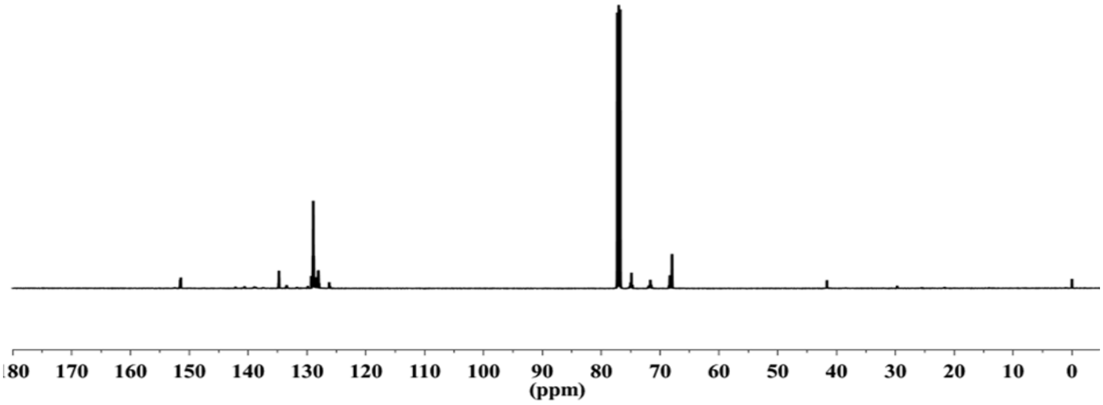


Figure 4.21 : ^{13}C NMR spectrum of P5 in $CDCl_3$ (500 MHz)

Figure 4.20. represents the ^{1}H NMR spectrum of P5, it was clearly seen that the aromatic protons of benzene ring (Ar*H*) are found at 7.35 ppm, the protons next to ester unit ($C{=}OOCH_2Ph$) are found between 5.23 and 4.57 ppm. Methylene protons ($C{=}OOCH_2CH_2O$) are detected at 3.74 ppm. In ^{13}C NMR spectrum which is represented in Figure 4.21., while the peaks of 151.1 and 74.7 ppm indicate C=O and C≡C groups, the peaks between 134.6 and 41.5 ppm indicate the carbon atoms of benzenedimethanol.

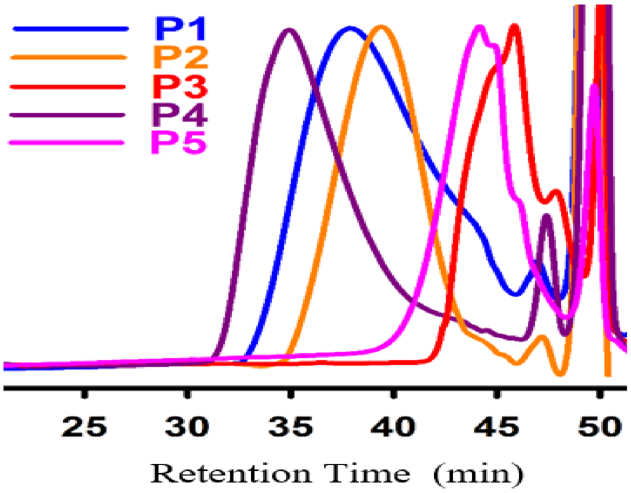


Figure 4.22 : Overlay of GPC traces of polyesters P1, P2, P3, P4 and P5

Figure 4.22. represents the overlay of GPC traces of polyesters. From the GPC traces of polyesters, it can be easily seen that the polyesters displayed monomodal distribution except for P3 and P5.They exhibit molecular weights ranging from 1650 to 12550 g/mol and polydispersity index between 3.18-1.39 as shown in Table 4.1.

Table 4.1 : Properties of polyesters obtained from ADCA and various diols.

Polymer Type	M_n,GPC[a] (g/mol)	M_w,GPC[a] (g/mol)	Mw/Mn[a]
P1	6050	11800	1.95
P2	5250	7700	1.46
P3	1250	2150	1.70
P4	3950	12550	3.18
P5	1200	1650	1.39

[a] GPC calibrated on the basis of linear PS standards in THF at 30 ˚C.

4.4 Functionalization of Polyester via 1,3-Dipolar Cycloaddition Reaction

In the second part of the study, polyesters were functionalized by using 1,3-dipolar cycloaddition reactions. All polyester types were reacted with azide terminated compound (2) in 1,4-dioxane at 40 ˚C for 24h to give triazole ring in the backbone of the polyesters. General functionalization reaction for polyesters are given as in Figure 4.23 and all related ^{1}H NMR spectra are given below.

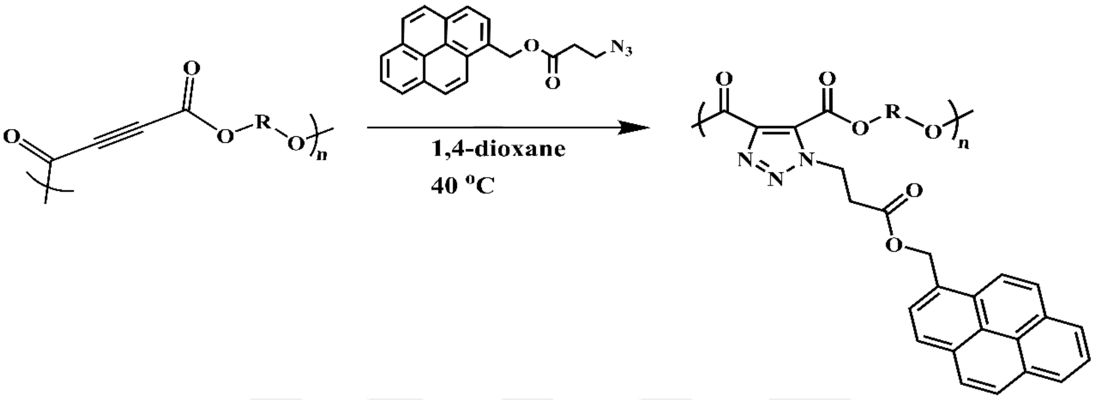


Figure 4.23 : General functionalization procedure of polyesters via 1,3-Dipolar cycloaddition

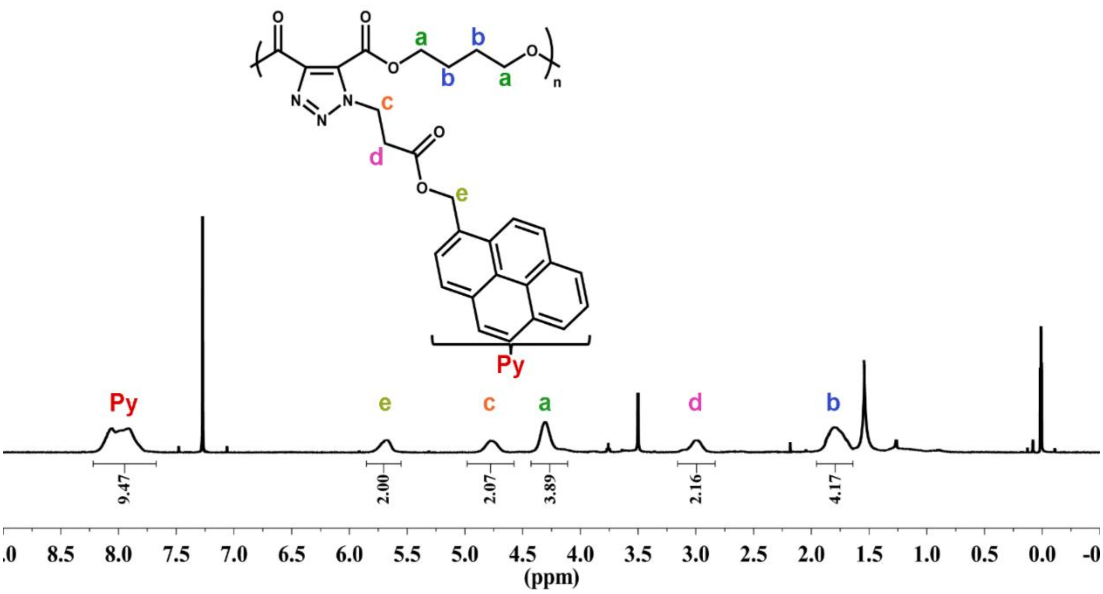


Figure 4.24 : ^{1}H NMR spectrum of functionalized P1 (P1-py)

Figure 4.24. represents the ^{1}H NMR spectrum of P1-py; it was clearly seen that the aromatic protons of the pyrene moiety (Ar*H*) are detected at 7.96 ppm. Methylene protons next to pyrene moiety are detected at 5.66 ppm. The OCH_2 protons of polyester

backbone are found at 4.29 ppm and 1.77 ppm**.** While methylene protons linked to triazole ring are detected at 4.77 ppm, the protons next to ester carbonyl are detected 2.99 ppm. Due to the shifting of signal value for these protons compared to previous compound (2), it can be said that the functionalization reaction was carried out succesfully.

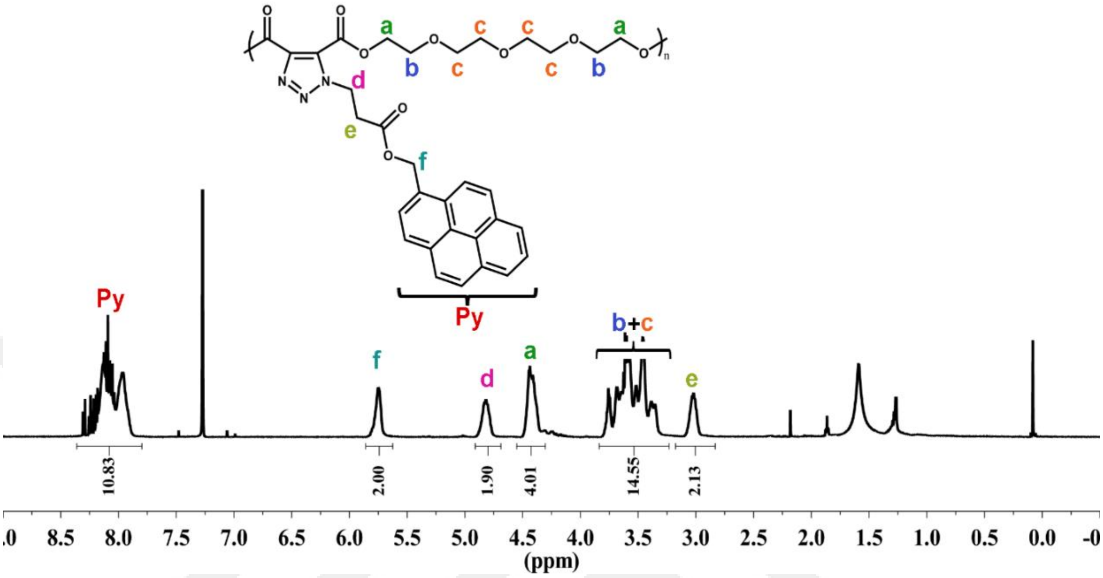


Figure 4.25 : ^{1}H NMR spectrum of functionalized P2 (P2-py)

Figure 4.25. represents the ^{1}H NMR spectrum of P2-py ; it was clearly seen that the aromatic protons of the pyrene are detected at 8.09 ppm. Methylene protons next to pyrene moiety are detected at 5.74 ppm. The protons next to ester units are found at 4.40 ppm, the methylene groups are found at 3.76 ppm and the protons of the tetraethylene’s interior ethylene groups are found at 3.60 ppm. While methylene protons linked to triazole ring are detected at 4.84 ppm, the protons next to ester carbonyl are detected 3.02 ppm. Due to the shifting of signal value for these protons compared to ^{1}H NMR spectrum previous compound (2), it can be said that the functionalization reaction was carried out succesfully.

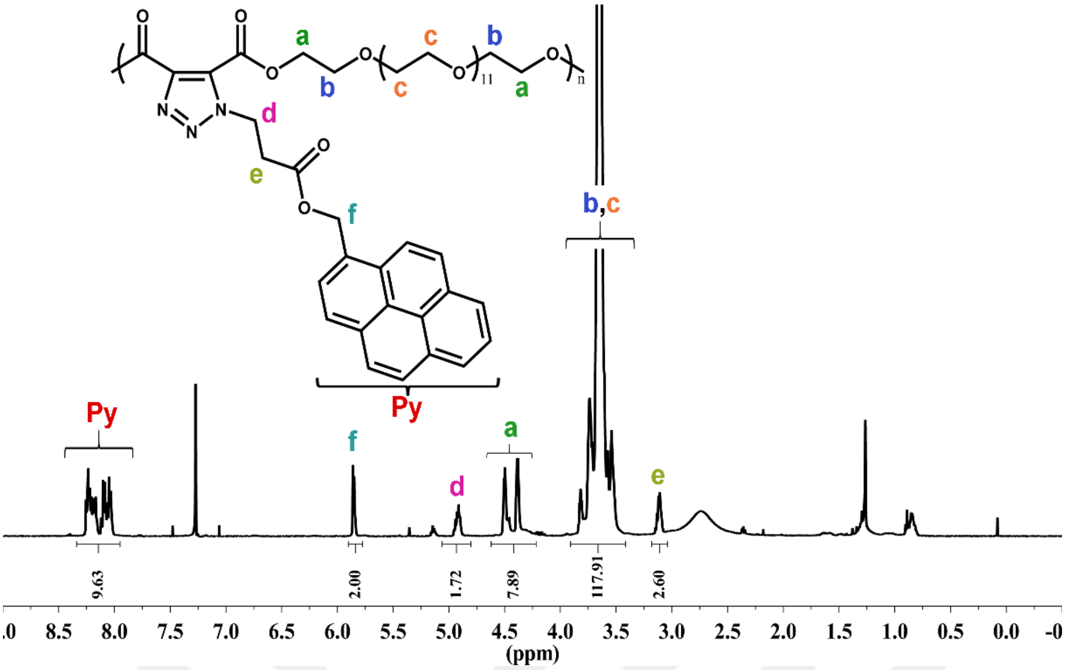


Figure 4.26 : ^{1}H NMR spectrum of functionalized P3 (P3-py)

Figure 4.26. represents the ^{1}H NMR spectrum of P3-py ; it was clearly seen that the aromatic protons of the pyrene are detected at 8.08 ppm. Methylene protons next to pyrene moiety are detected at 5.90 ppm. The protons next to ester units are found at 4.40 ppm, the methylene groups and the protons of interior methylene protons are found at 3.76 ppm. While methylene protons linked to triazole ring are detected at 4.84 ppm, the protons next to ester carbonyl are detected 3.02 ppm. Due to the shifting of signal value for these protons compared to ^{1}H NMR spectrum previous compound (2), it can be said that the functionalization reaction was carried out succesfully.

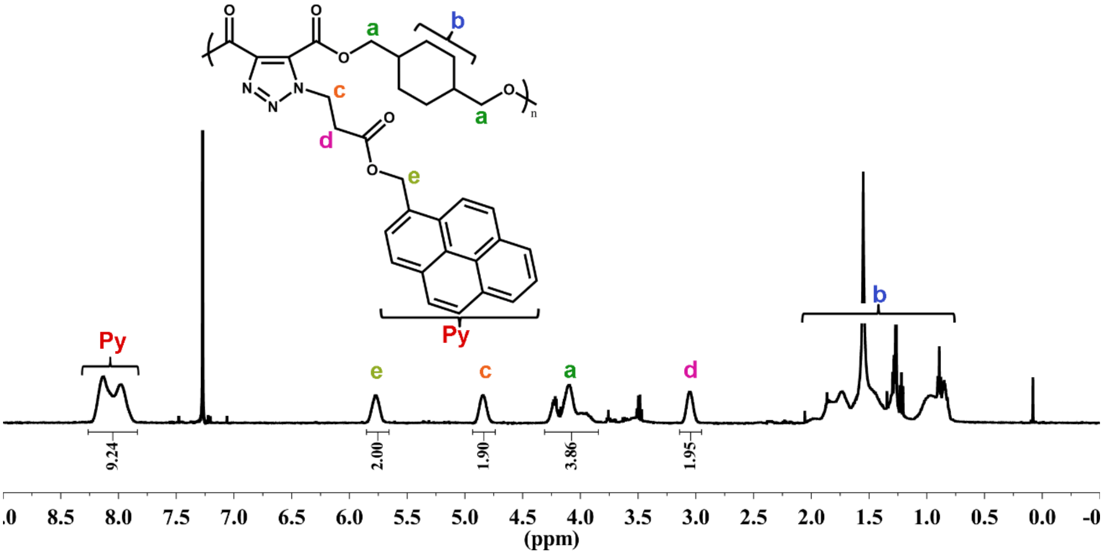


Figure 4.27 : ^{1}H NMR spectrum of functionalized P4 (P4-py)

Figure 4.27. represents the ^{1}H NMR spectrum of P4-py ; it was clearly seen that the aromatic protons of the pyrene are detected at 8.02 ppm. Methylene protons next to pyrene moiety are detected at 5.78 ppm. Ester unit protons $C\mathit{H}_2CH$ are found between 4.18 and 4.07 ppm, and the aliphatic protons of cyclohexane are found between 1.90 and 0.89 ppm.While methylene protons linked to triazole ring are detected at 4.84 ppm, the protons next to ester carbonyl are detected 3.04 ppm. Due to the shifting of signal values for these protons compared to ^{1}H NMR spectrum previous compound (2), it can be said that the functionalization reaction was carried out succesfully.

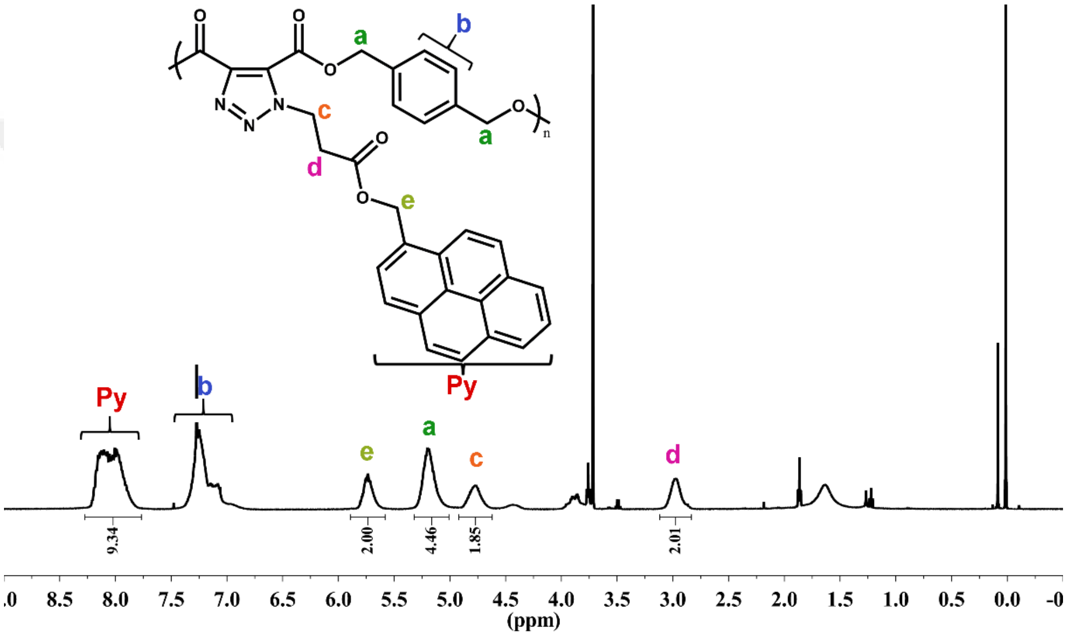


Figure 4.28 : ^{1}H NMR spectrum of functionalized P5 (P5-py)

Figure 4.28. represents the ^{1}H NMR spectrum of P5-py; it was clearly seen that the aromatic protons of the pyrene are detected at 8.09 ppm. Methylene protons next to pyrene moiety are detected at 5.90 ppm. The aromatic protons of benzene ring are found at 7.3 ppm and the methylene protons next to ester unit are detected at 5.21 ppm . While methylene protons linked to triazole ring are detected at 4.84 ppm, the protons next to ester carbonyl are detected 3.04 ppm. Due to the shifting of signal values for these protons compared to ^{1}H NMR spectrum previous compound (2), it can be said that the functionalization reaction was carried out succesfully.

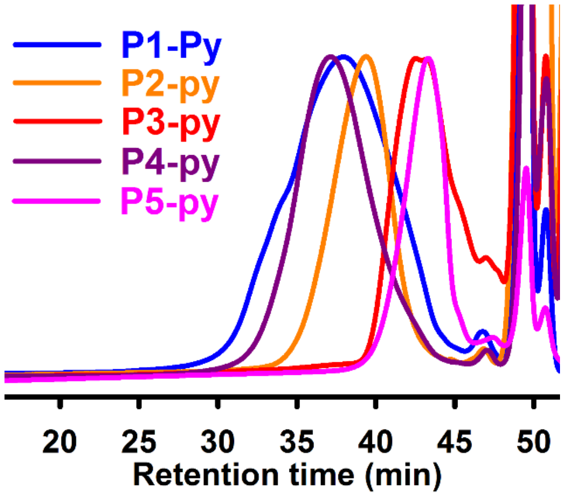


Figure 4.29 : Overlay of GPC traces of functinalized polyesters.

Figure 4.29. represents the GPC traces of pyrene functionalized polyesters, it can be easily seen that the polyesters exhibit molecular weights ranging from 2100 to 37700 g/mol and polydispersity index between 3.18-1.39 as shown in Table 4.2.

Table 4.2 : Properties of various functionalized polyesters.

Polymer Type	M_n,GPC[a] (g/mol)	M_w,GPC[a] (g/mol)	*M*w/*M*n[a]
P1-py	6700	37700	5.48
P2-py	6300	7800	1.23
P3-py	2600	3250	1.26
P4-py	9100	21200	2.32
P5-py	1800	2100	1.19

[a]GPC calibrated on the basis of linear PS standards in THF at 30 ˚C.

4.5 Modification of Carbon Nanotubes with Pyrene Functionalized Polyesters

After the addition of both pyrene functionalized polyesters and MWCNTs into the sufficient amount of solvent , the mixture was sonicated during 30 min under nitrogen atmosphere for 10 days to allow formation of π- π stacking interactions between nanotube surface and polyesters as shown in Figure 4.30-4.35.

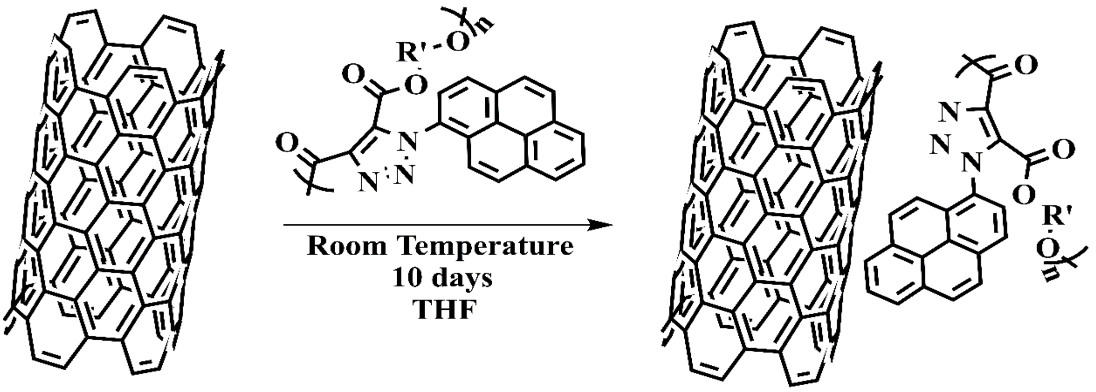
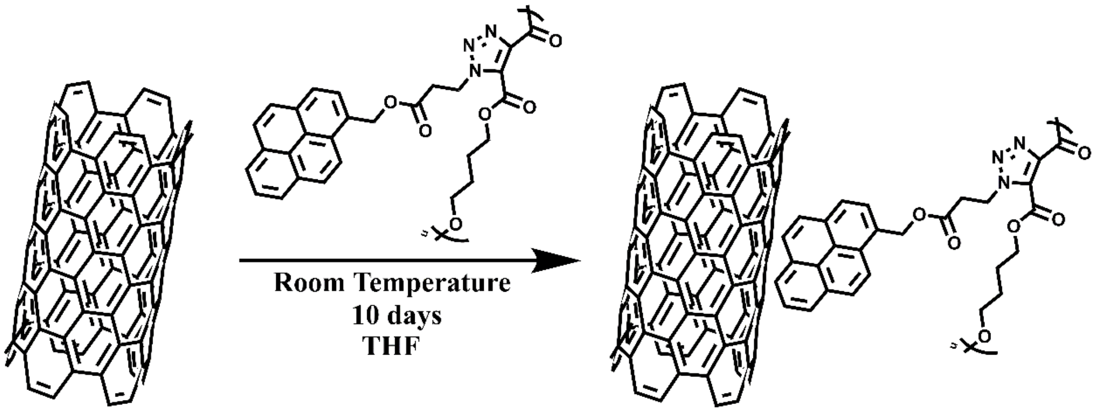
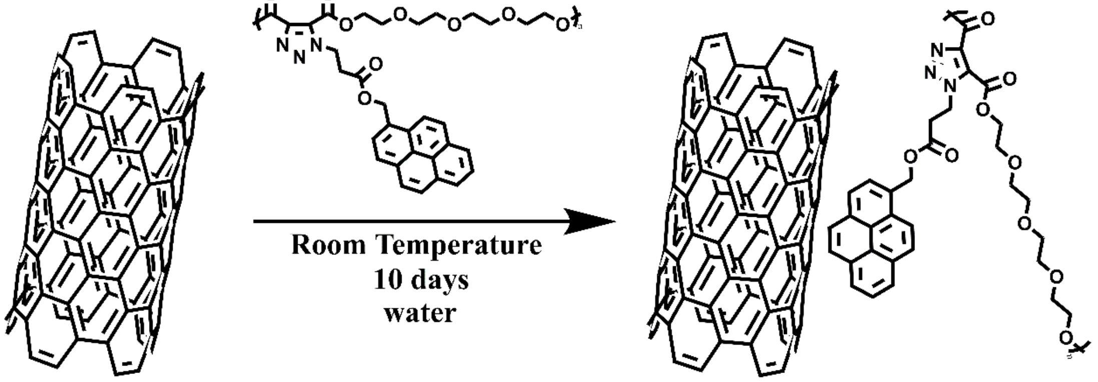


Figure 4.30 : General representation for formation of π-π stacking interaction between nanotube surface and polyesters.



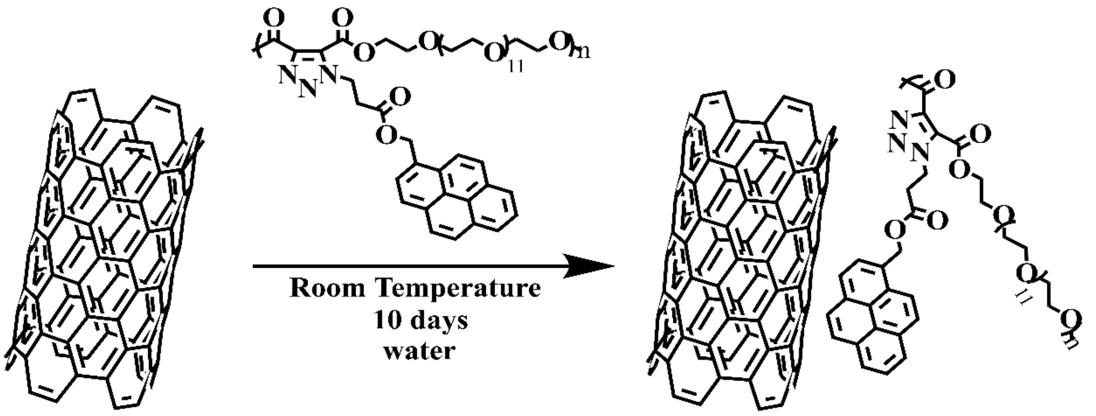
CNT-1

Figure 4.31 : Formation of CNT-1 by using pyrene functionalized P1



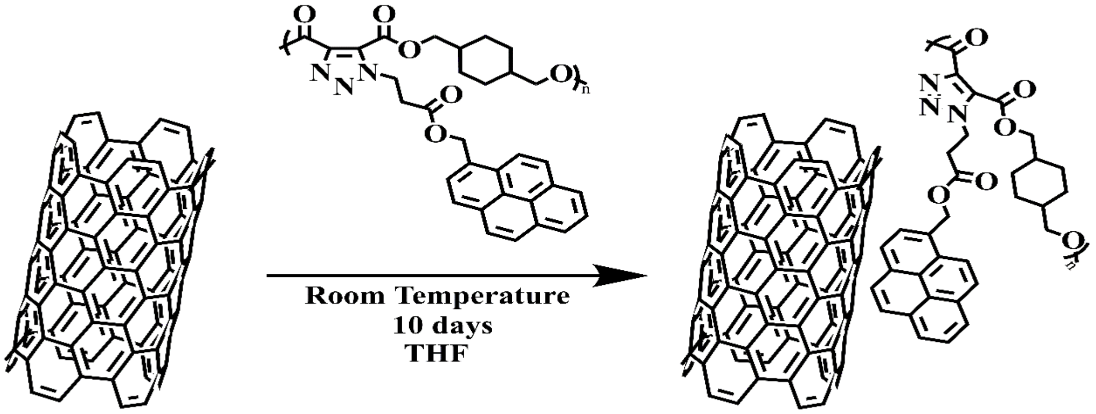
CNT-2

Figure 4.32 : Formation of CNT-2 by using pyrene functionalized P2



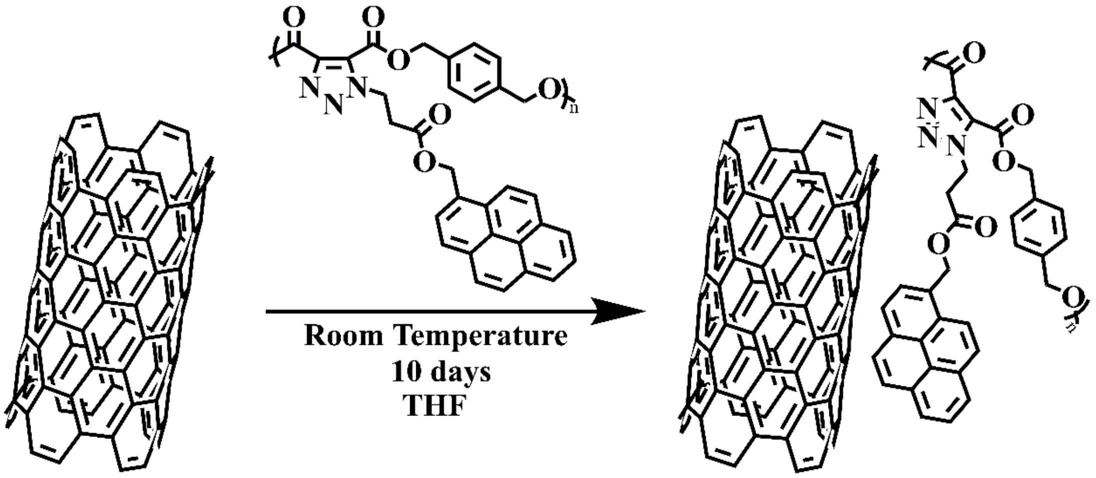
CNT-3

Figure 4.33 : Formation of CNT-3 by using pyrene functionalized P3



CNT-4

Figure 4.34 : Formation of CNT-4 by using pyrene functionalized P4



CNT-5

Figure 4.35 : Formation of CNT-5 by using pyrene functionalized P5

After the modification of MWCNTs with pyrene functionalized polyesters, various instrumental analysis techniques such as FTIR, UV, TGA, TEM were applied as characterization techniques to evaluate the properties, structure and behaviours of the modified nanotubes.

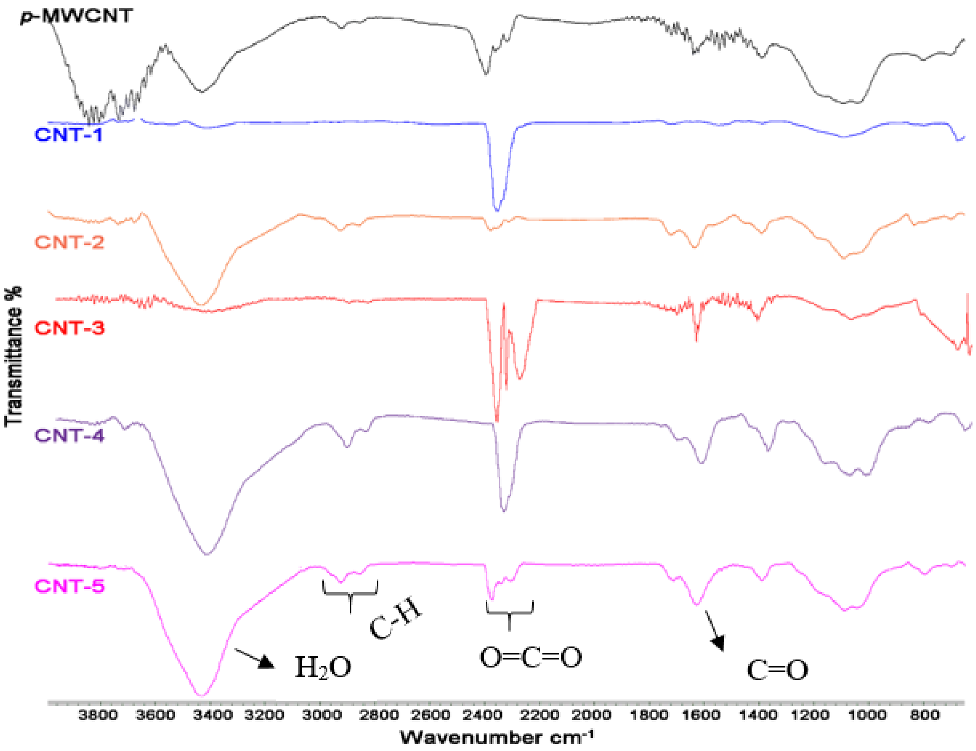


Figure 4.36 : FT-IR results of CNTs modified with functionalized polyesters.

CNT samples were prepared as pellets by using KBr to measure specific wavenumbers of the functional groups in nanotube structure by using FT-IR spectroscopy. The concentration of the CNT samples in KBr was taken into account to obtain meaningful informations from IR spectra. According to the FT-IR results given in Figure 4.36, It can be clearly seen that both p-MWCNT and modified CNTs contain water in their structure due to the presence of signals between 3700-3100 cm^{-1}. Apart from large amount of H_2O absorption, CO_2 was also determined because of the signals between 2400-2100 cm^{-1}. The signals in the range of 3000 and 2800 cm^{-1} indicate the stretches of C-H groups which are found in nanotube surfaces in plenty amount. Carbonyl groups also exist in nanotube structure the signal approximately at 1780 cm^{-1} represents the C=O stretching. Although FT-IR spectroscopy is one of the most commonly used instrumental analysis techniques, adequate and informative comments can not be easily made about the modification of nanotubes with polymer chains. The main indication for the modification of nanotubes belongs to the fingerprint region having wavenumber of 1500-500 cm^{-1}. Since the aromatic groups are also signified in 1600-1500 cm^{-1} wavenumbers, the alterations in this region may indicate the presence of additional aromatic groups coming from pyrene moiety in the polyester structure. Therefore, it can be an evidence for the formation of non-covalent attachment between nanotube surface and polymer chains.

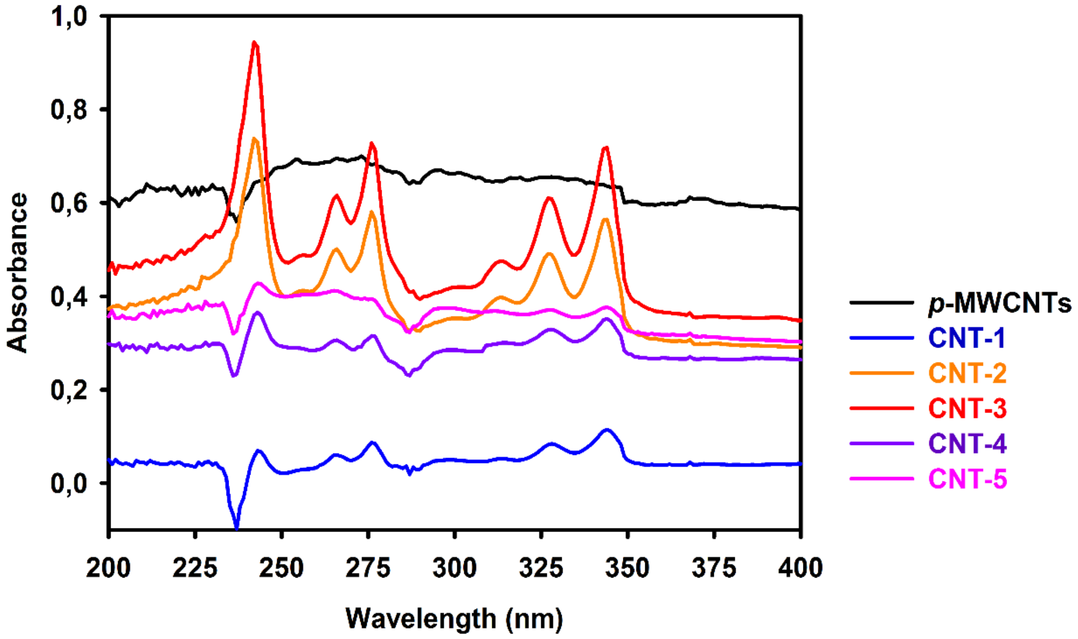


Figure 4.37 : UV results of CNTs modified with functionalized polyesters.

The samples for UV measurement were prepared by using 0.5 mg CNT in 5 mL THF. According to UV results given in Figure 4.37, it can be easily seen that there was no absorption in the case of p-MWCNT. However, the peaks similar to pyrene group were observed in modified CNT samples. Since the attachment between nanotube surface and polymer chains took place in non-covalent manner, the pyrene structure had been maintained as it can be clearly seen from the UV results. The absorptions in the range of both 300-350 nm and 275-250 nm display the presence of pyrene moiety in the polyesters which was interacted with carbon nanotube, non-covalently.

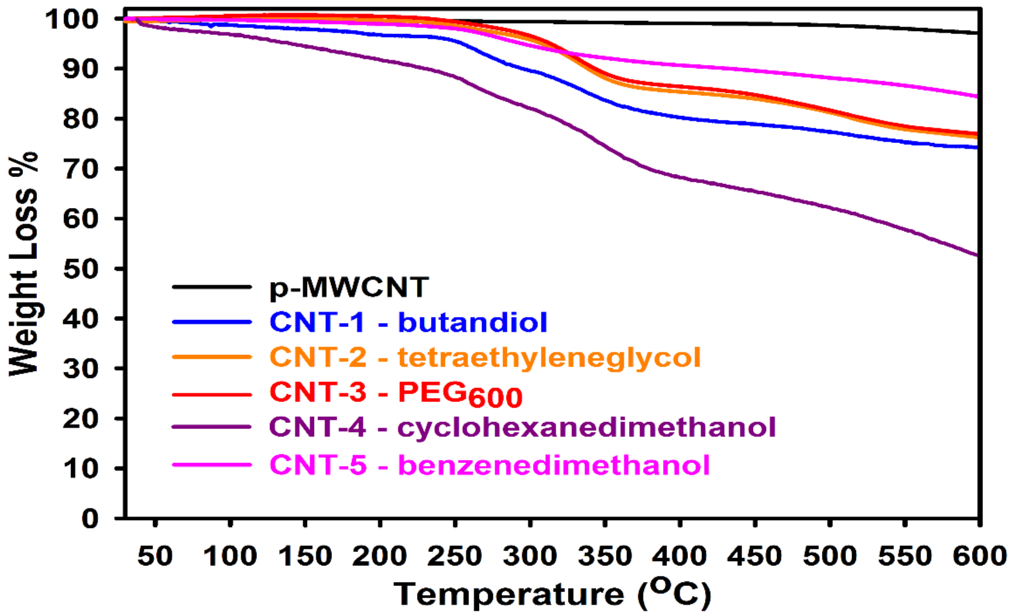


Figure 4.38 : TGA results of CNTs modified with functionalized polyesters.

Thermogravimetric analysis (TGA) was performed in the temperature range of 30-600 ˚C, with a heating rate of 10 ˚C/min under nitrogene to enlighten the thermal stabilities of CNTs modified with polyesters and to obtain a quantitative result on the amount of polymer interacted with the MWCNTs. According to the TGA results given in Figure 4.38., the nonmodified MWCNTs (p-MWCNT) start to decompose at around 500 ˚C until a weight loss of 2 %. The decomposition of polymer samples occur between 200-450 ˚C in several steps and their degradation occurs at approximately the same temperatures. The weight loss for CNT-1, CNT-2, CNT-3, CNT-4 and CNT-5 are observed as 25 %, 22 %, 22 %, 45 % and 15 % as shown in Table 4.3. at higher temperatures, respectively. When compared functionalized MWCNTs to p-MWNTs, it can be observed that the presence of organic molecules in the structure decreases the degradation temperature of the structure.

Table 4.3 : Evaluation of TGA curves belong to CNTs.

CNTs Type	Weight Lose
p-MWCNT	2 %
CNT-1	25 %
CNT-2	22 %
CNT-3	22 %
CNT-4	45 %
CNT-5	15 %

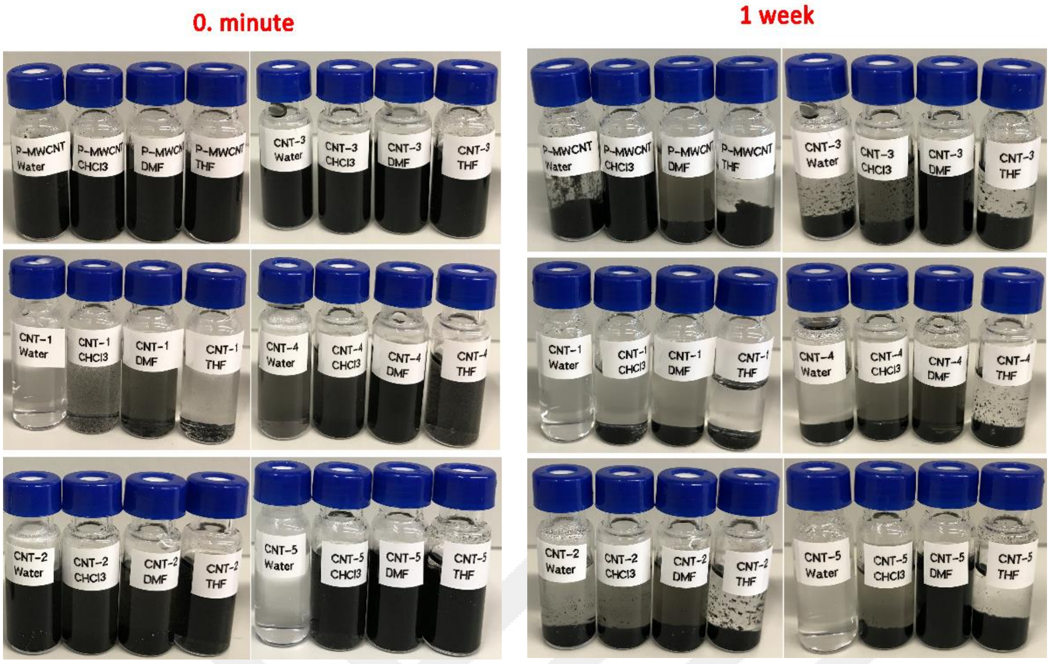


Figure 4.39 : Photograph of p-MWCNT and modified CNTs in different solvents.

The dispersibility of p-MWCNT and modified CNTs in different solvents with different polarities was investigated as shown in Figure 4.39. 0.5 mg of CNTs were sonicated in 2 mL solvent for 20 minutes to prepare the dispersions of CNTs. According to the photographs taken at the beginning of the dispersion, that is at 0. minute; nearly all types of CNTs exhibited stability without aggregation in water, $CHCl_3$, DMF and THF except for the CNT-1. An immediate aggregation took place in the case of CNT-1 in THF. These dispersions of CNTs had changed remarkably in a week. Aside from the p-MWCNT in $CHCl_3$, CNT-3 in DMF, CNT-4 in DMF, CNT-2 in DMF and CNT-5 in DMF, it can be clearly seen that all samples exhibited aggregation.

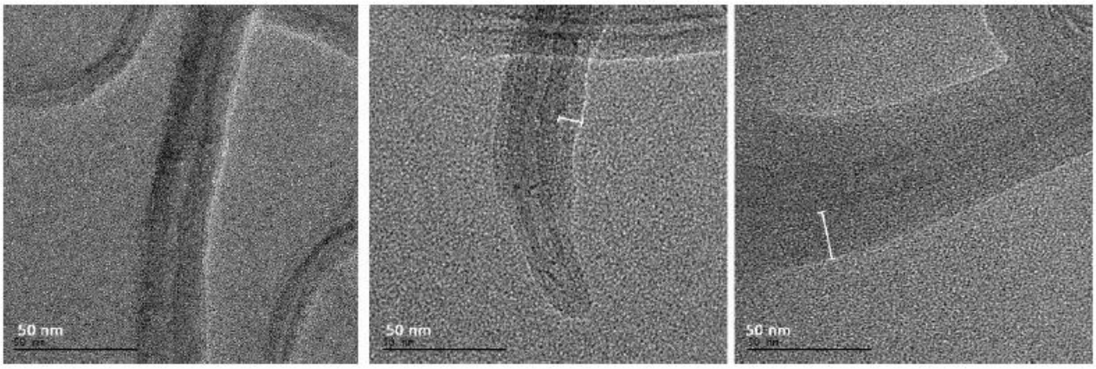


Figure 4.40 : HR-TEM micrographs of p-MWCNT, CNT-1 and CNT-3.

The change in morphological structure of carbon nanotubes had been observed , after the functionalization of nanotubes with P1-py and P3-py polymers. According to the results given in Figure 4.40, the comparison of the p-MWCNT and functionalized nanotubes can be easily done as the nanotube surface was wrapped by the pyrene functionalized polymers with the thickness of 13 nm for CNT-1 and 18 nm for CNT-3.

5. CONCLUSION

In this study, various polyesters containing alkyne unit in their main chain had been synthesized by using different diols via condensation polymerization. Due to the presence of reactive alkyne unit in the structure, polymers had been further functionalized with an ester compound having pyrene moiety in its structure by using 1,3-dipolar cycloaddition reaction mechanism. The reaction had been carried out at mild conditions to obtain desired products. Then, these polyesters having pyrene moiety in their structure were used for the modification of carbon nanotube surface in a non-covalent attachment manner in both THF and water as a solvent. After 10 days of mixing, the formation of π-π stacking between nanotube surface and polymer chain was observed through various characterization techniques.

It should be noted that the solubility and the dispersion of the nanotubes can be increased by wrapping of nanotube surface with polymers via non-covalent attachment. The presence of aromatic moieties such as pyrene in the polymer structure has an increasing effect on the solubility of the nanotubes due to the formation of physical attachment between nanotube surface and polymer chain. This formation had been observed by using instrumental analysis techniques. According to the results, the nanotube samples having an attachment with polymer chains exhibit higher dispersion and solubility. Therefore, it is really important to make the nanotube soluble in solvent to enhance the usage areas in various engineering applications.

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