ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

POST-MODIFICATIONS OF PERFLUOROPHENYL FUNCTIONALIZED ACYCLIC DIENE METATHESIS POLYMER

M.Sc. THESIS

Özgün DAĞLAR

Department of Chemistry

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Thesis Advisor: Prof. Dr. Gürkan HIZAL

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

PERFLOROFENİL FONKSİYONLU ASİKLİK DİEN METATEZ POLİMERİNİN MODİFİKASYONLARI

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ARALIK 2015

Özgün DAĞLAR, a M.Sc. student of ITU Graduate School of Science Engineering and Technology student ID 509141025, successfully defended the thesis entitled "POST-MODIFICATIONS OF PERFLUOROPHENYL FUNCTIONALIZED ACYCLIC DIENE METATHESIS POLYMERIZATION", which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my beloved family,

FOREWORD

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November 2015

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ABBREVIATIONS

^{1}H NMR	**:** Hydrogen Nuclear Magnetic Resonance Spectroscopy
^{13}C NMR	**:** Carbon Nuclear Magnetic Resonance Spectroscopy
^{19}F NMR	**:** Fluorine Nuclear Magnetic Resonance Spectroscopy
DCM	**:** Dichloromethane
DMF	**:** Dimethylformamide
GPC	**:** Gel Permeation Chromatography
IR	**:** Infrared
UV	**:** Ultra Violet
THF	**:** Tetrahydrofuran
FT-IR	**:** Fourier Transform Infrared Spectroscopy

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POST-MODIFICATIONS OF PERFLUOROPHENYL FUNCTIONALIZED ACYCLIC DIENE METATHESIS POLYMER

SUMMARY

ADMET polymerization is the process of obtaining α,ω-diene monomers which are produced by appropriate olefin metathesis catalysts. Generally, metathesis procatalyst is activated by the first reaction with the diene type monomer and metal alkylidene is formed. When the resulting metal alkiliden is reacted with another diene, a reformed dimer and methylidene type is produced in the environment.Metal methylidene acts as the real catalyst in this reaction. These reactions of the monomer or the polymer causes ethylene gas to be produced and it is disposed of by applying vacuum. Accordingly, due to the Le Chatelier's principle, this process shifts the reaction towards polymerization. In an ADMET polymerization concentration of the reaction environment has a key role in producing polymer chains. Polymerizations which take place in a diluted reaction environment causes the product to be mostly in oligomeric structure. This is due to the fact that the monomer -which has double bonds on each end- after gaining an oligomeric structure during growth stage, it reaches a level of flexibility where it attacks its own diene end in a diluted reaction environment and forms an oligomeric ring. Consequently, the monomer which is in the diluted environment chooses the ring closing metathesis(RCM) instead of the ADMET. In order to prevent this, it is more appropriate to make the polymerization as bulk instead of in a solvent.

Active ester reactions are popular types of reactions which are used in peptide synthesis in organic chemistry. It is known that active esters such as thiophenylesters, activated methyl esters and nitrthiophenyl esters are used in various synthesis reactions. Their use in polymer chemistry has become widespread and due to their high performance in mild reaction conditions, they became an important choice for polymer reactions. A frequently used active ester which is on the side chain of a synthesized polymer such as perfluorophenyl, helps to produce another completely different behaving polymer with an easily made substitution reaction. Obtaining modified polymers which show differences in solubility compared to the synthesized main polymer with the help of these modifications, provides many opportunities in medical applications. Especially when it is not very easy to synthesize the polymers with desired properties, active ester reactions proves to be a solution for these problems. Under normal cimcumstances, it can be very difficult or even impossible to modify a polymer, whereas if active esters are used as protective groups, modifications can be made and afterwards active ester functionality can be transformed into amide form with a pimary amine.

In this research, ADMET polymer which contains active ester was tested with different types of catalysts and solvent systems. Obtained results showed that, the G1 catalyst and bulk system are the best reaction conditions. Characterization of the synthesized polymer was made without using any solvent while using G1 catalyst.

Next, by reacting the resulting polymer with different amines without any need for an extra base, the easy leaving group of perfluorophenoxy were substituted with the used amines. In the second phase of the research, the obtained ADMET polymer was reacted with a base containing triple bond and made ready for a possible "azide-alkyne click" reaction. Then, the polymer was reacted with polyethylene glycol and it was characterized. All characterization processes are made by using GPC, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, DSC and FT-IR.

PERFLOROFENİL FONKSİYONLU ASİKLİK DİEN METATEZ POLİMERİNİN MODİFİKASYONLARI

ÖZET

Asiklik dien metatez (ADMET) polimerizasyonu, α,ω-dien monomerlerin uygun olefin metatez katalizörleriyle oluşacak polimerlerini elde etme yöntemidir. Genel olarak, metatez önkatalizi, dien tipi monomerle ilk reaksiyonu sonucunda aktiflenir ve metal aklilidenden elde edilir. Elde edilen metal alkilidenin, başka bir dien ile reaksiyonu sonucunda, yeniden şekillenmiş dimer ve metal metiliden türü ortamda oluşur. Metal metiliden bu reaksiyondaki gerçek katalizör görevindedir. Monomer ya da polimerin gerçekleştirdiği bu reaksiyonlar, etilen gazının oluşmasına neden olur ve bu gaz yüksek miktarda vakum uygulanarak ortamdan uzaklaştırılır. Bu işlem aynı zamanda, denge kuralı gereğince reaksiyonu polimerleşme yönüne kaydırır.

ADMET polimerizasyonunda, ortam konsantrasyonu polimer zincirinin oluşumunda anahtar faktör olarak yer alır. Çok seyreltik ortamlarda yapılacak polimerleşmede, elde edilecek ürün büyük oranda oligomerik yapıya sahip olmaktadır. Bunun nedeni; iki ucunda çift bağ bulunan monomerin, büyüme aşamasında oligomerik yapıya ulaştıktan sonra, yeterli esnekliğe kavuşup, seyreltik reaksiyon ortamında kendi dien ucuna atak ederek halka oluşturmasıdır. Buna göre de, seyreltik ortamdaki monomer ADMET yerine halka kapama metatezini (RCM) tercih eder. Bu duruma önlem olarak polimerleşmenin solvent içerisinde yapılması yerine, bulk olarak yapılması daha uygundur. Ve daha iyi sonuçlar elde edilmesini sağlamaktadır.

ADMET polimerizasyonunda kullanılan katalizörlerden en yaygın olan Grubbs katalizörleri, kendi içinde çeşitlendirilmektedir. Temel yapısının ihtiyaca göre fonksiyonlandırılması sonucu piyasada, temin edilebilecek farklı türde Grubbs katalizörleri mevcuttur. Kullanılacak farklı tipteki Grubbs katalizörleri; polimerleşme hızı, polimerleşme verimi, molekül ağırlığı gibi konularda farklı sonuçlar elde edilmesine neden olur.

Katalizör seçimi dışında polimerleşmeyi etkileyen diğer faktörler ise reaksiyon atmosferi ve sıcaklığıdır. Oda sıcaklığında da gerçekleşebilen reaksiyon, yüksek sıcaklıklarda gerçekleştirildiğinde polimerleşme hızı artar ve bu durum aynı zamanda daha yüksek molekül ağırlığında ürünler oluşmasına da olanak sağlar.

Oluşabilecek yan reaksiyonların engellenmesi konusunda ise reaksiyon atmosferi önemli bir yer tutmaktadır. İnert bir ortamda gerçekleşen reaksiyon, hem reaksiyon veriminin artmasına olanak sağlar, hem de yan ürün oluşumuna neden olacak, hatta polimerleşmeyi olumsuz yönde etkileyecek reaksiyonların gerçekleşmesinin minimum seviyelerde kalmasını sağlar. ADMET polimerleşmesi sonucunda oluşacak poliolefinler, çok yüksek molekül ağırlıklarına ulaşılabilmesi ve içeriğinde bulunan, fonksiyonlandırılmasını sağlayabilecek çift bağlardan ötürü önemli uygulama alanlarına sahiptir.

Polimerik yapılar çeşitli reaksiyonlarla türevlendirilse de bunlar arasında en çok ilgi çeken "click" reaksiyonlarıdır. 2001 yılında Sharpless ve çalışma arkadaşlarının "click" kimyası olarak adlandırdığı sentezler, hafif reaksiyon koşulu gerekesinimli, yüksek verimli ve hızlı gerçekleşen reaksiyonlar oldukları için polimer kimyasında yaygın kullanım alanlarına sahip olmaya başlamışlardır. Pek çok farklı yapıdaki organik bileşiklerin reaksiyonları ve modifikasyonları için kullanılan "click" reaksiyonları, kendi içinde farklı reaksiyona ayrılmaktadır. Bunların içinde bakır katalizli azid alkin siklokatılma reaksiyonları (CuAAC) ve aktif ester yer değiştirme reaksiyonları polimer kimyasında önemli bir yere sahiptir.

Organik azidler ve alkinler arasında Cu(I) katalizörlüğünde gerçekleşen "click" reaksiyonları (CuAAC), ısı ile gerçekleşen türeviyle karşılaştırıldığında farklı avantajlar sunmaktadır. Isıyla gerçekleşen siklokatılma, düşük verimle ve oluşan ürünlerin yapı izomeri karışımı şeklinde elde edilirken, Cu(I) katalizörlüğünde gerçekleşen reaksiyon; hafif reaksiyon koşulu gereksinimi, yüksek verim, reaksiyonun hızlı gerçekleşmesi, tek tip ürün oluşması gibi avantajlar sunmaktadır. Ayrıca reaksiyon sonucunda elde edilen ürünün saflaştırma işleminin kolay olması, yan ürün oluşmaması gibi etkenler de bu reaksiyonun çok tercih edilir bir "click" reaksiyonu olmasını sağlamaktadır.

Aktif ester reaksiyonları, organik kimyada peptit sentezinde kullanılan popüler bir reaksiyon çeşididir. Günümüzde, tiyofenilesterler, aktif metil esterler, nitrofenil esterler gibi bir çok farklı türdeki aktif esterin çeşitli sentezlerde kullanıldığı bilinmektedir. Uygulama alanlarının artmasıyla polimer kimyasında da dikkat çekici bir yere sahip olmaya başlayan aktif esterler, hafif reaksiyon koşullarında gösterdikleri verimle, polimer modifikasyonlar için önemli bir seçenek haline gelmiştir. Sentezlenen polimerin yan zinciri üzerinde yer alcak perflorofenil gibi sık kullanılan bir aktif ester, kolaylıkla gerçekleştirilebilecek bir yer değiştirme reaksiyonu sonucunda, tamamen farklı özellikler gösteren bir polimerin elde edilmesine imkan sağlamaktadır. Bu gibi değişikliklerle yapılabilecek modifikasyonlarda, sentezlenen ana polimerden farklı çözünürlük gösterebilecek modifiye polimerlerin elde edilebilmesi, medikal uygulamalar için önemli bir alternatif olabilmektedir.

Özellikle istenilen özelliklere sahip polimerlerin sentezinin her zaman kolaylıkla gerçekleştirelemeyecek olması nedeniyle, aktif ester reaksiyonları bu soruna bir çözüm olarak da ortaya çıkmaktadır. Normal koşullar altında spesifik bir polimer üzerindeki modifikasyonların çok zor gerçekleşebileceği hatta neredeyse imkansız olduğu durumlar, aktif esterlerin birer koruyucu grup olarak kullanılarak, modifikasyonların gerçekleştirilip daha sonrasında, aktif ester fonksiyonelitesinin, bir primer aminle kolaylıkla amid formuna döndürülebilmesiyle, çok kolay birer modifikasyon haline gelebilmektedir.

Bu çalışmada, aktif ester içeren ADMET polimerinin sentezi, farklı kataliz ve çözücü koşullarında denendi. Elde edilen sonuçlar, G1 katalizörü ve bulk sistemin en iyi reaksiyon koşulları olduğunu gösterdi G1 katalizörü varlığında çözücü kullanmadan sentezlenen polimer karaterize edildi. Daha sonra elde edilen polimer, farklı aminlerle, ekstra bir baza ihtiyaç duymaksızın reaksiyona sokularak, kolay ayrılabilen grup olan perflorofenoksi grubunun, kullanılan aminlerle yer değiştirmesi sağlandı. Çalışmanın ikinci aşamasında, elde edilen ADMET polimeri, 3'lü bağ içeren bir bazla reaksiyona sokularak, olası bir "azide-alkyne click" reaksiyonuna hazır hale getirildi. Daha sonra azid uçlu polietilen glikol ile reaksiyona sokulan polimer karakterize edildi. Tüm karakterizasyon işlemleri GPC, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, DSC ve FT-IR kullanılarak yapıldı.

1. INTRODUCTION

Researches and improvements on the olefin metathesis reactions have provided opportunities for organic and polymer chemists to work on more complicated structures [1]. Acyclic diene metathesis polymerization, one of the most important metathesis polymerizations, was firstly appeared during a Ph.D. oral examination in 1970 at the University of Florida. The document title was “Mechanistic Possibilities for the Skeletal Change Observed in Metal-Catalyzed Diene Rearrangement”. With the growing interest on metathesis reactions over the years, knowledge of metathesis has increased and with the discovery of the proper catalysts, ADMET polymerization has become one of the most interesting and unique polymerizations techniques ever made [2].

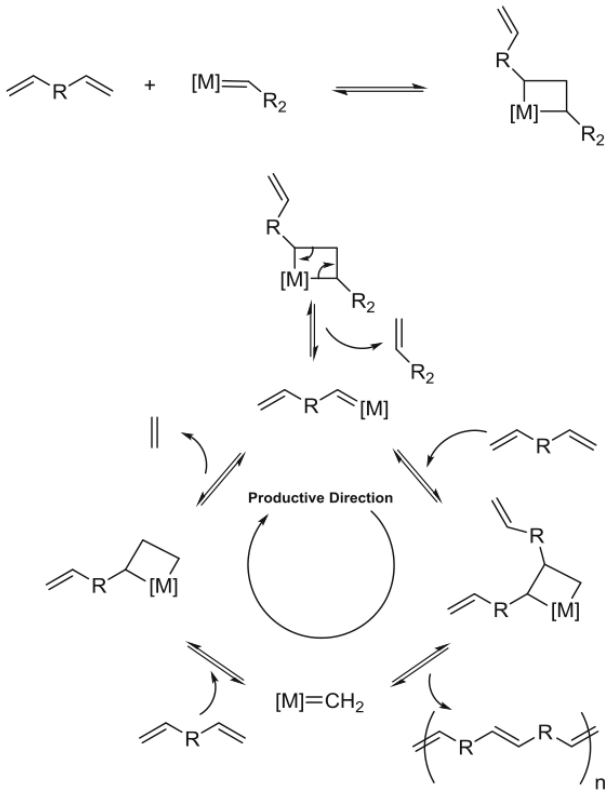


Figure 1.1 : The ADMET mechanism

Due to the nature of ADMET polymerization, acquired polymers have some distinctive properties compared to the other polymers obtained by the classical polymerization methods. Having unsaturated double bonds on the main chains, enables modifications to be made on these particular double bonds. By using proper pendant functionality on the side chain also provides another option to make modifications. For example, substituting the pendant group with the desired functionality could change the whole characther of the polymer. Especially while working on the biocompatible and biodegradable polymers, these types of modifications can be used on alternative drug delivery researches.

Use of active esters are very popular as peptide synthesis reactants in organic chemistry, but it is also a promising way to modify polymers with desired properties for polymer chemists. Gathered reports from these synthesis shows us, that the strongly electrophile group, bound to the carbonyl carbon can be substituted with nuchleophiles like amines and produce amides in suitable conditions. Esters with aromatic, substituted aromatic, aromatic heterocyclic and substituted aromatic heterocyclic alcohols covers these kind of esters [3].

As mentioned before, possibility to make changes on side chains of the polymer can move the research to another state. Previous successful attempts on application of active ester substitution reactions on polymers encouraged us to apply substitution reaction of active esters on ADMET polymer and consequent CuAAC click reaction. In this study, firstly we aimed to achieve an active ester functional ADMET polymer to synthesize and substitute this functionality with several types of amines effectively and with high conversion. To do that, perfluorophenyl functional diene monomer was synthesized as planned. After the ADMET polymerization, obtained polymer was reacted with amines and the structures were enlightened by characterization. In the second part of the study, the goal was changing the properties of polymer drastically. To achieve that, perfluorophenyl functional polymer was reacted with alkyne functional amine. By changing the structure, it became possible to modify the polymer with CuAAC click reactions. The solubility characteristic of the polymer changed after, reacting this structure with azide functional polyethylene glycol.

2. THEORETICAL PART

2.1 Step-Growth Polymerization

Chain-growth polymerization is one in which each polymer chain, after being started by a free radical initiator, a cationic catalyst or an anionic catalyst, grows rapidly, producing a high molecular weight polymer. After the propagation step, reaction chain is stopped by a termination or a chain transfer step. The initiation, propagation, and termination steps are distinctly different .

In step-growth type polymerizations, the molecular weight of the polymer chain builds grows slowly and there is only one mechanism for all formation steps. In step –growth polymerizations, distinct chain growth reaction steps are meaningless. A difunctional monomer or equal molar amounts of two different difunctional monomers are necessary at least to form a linear high molecular weight polymer. The polymerization reaction proceeds by individual reactions of the functional groups on the monomers. Thus, two monomers react to form a dimer. The dimer may now react with another dimer to produce a tetramer, or the dimer may react with more monomer to form a trimer. This process continues, each reaction of the functional groups proceeding essentially at the same reaction rate until over a relatively long period of time a high molecular weight polymer is obtained. In Figure 2.1 Differences between Step-Growth polymerization and Chain-Growth polymerization are shown.

Requirements For High Molecular Weight: There are three critical requirements for the step-growth polymerization to yield a high molecular weight linear polymer.First, a perfect stoichiometric balance of the two difunctional monomers must be introduced, or alternately a self-balancing reaction is necessary. Of course, when a single difunctional monomer can generate polymer, such as is the case of □ -aminocaproic acid, an internal balance (within the monomer) is provided.

Step-Growth versus Chain-Growth Polymerization

	Step-Growth	Chain-Growth
• Reactions	One reaction is responsible for polymer formation.	Initiation, propagation, and termination reactions have different rates and mechanisms.
• Polymer Growth	Any two molecular species present can react; slow, random growth takes place.	The growth reaction takes place by the addition of one unit at a time to the active end of the polymer chain.
• Polymer Molecular Weight	Molecular weight rises steadily throughout the reaction. High conversion is required for high molecular weight polymer.	High molecular weight polymer is formed immediately.
• Monomer Concentration During Polymerization	Monomer disappears in the early stages of the polymerization. At an average degree of polymerization of 10, less than 1 weight percent of the monomer remains.	Monomer concentration decreases steadily throughout the reaction.
• Composition of the Polymerization Reaction	A relatively broad, calculable distribution of molecular species are present throughout the course of the polymerization.	Mixture contains only monomer, high molecular weight polymer and only about 10^{-8} part of growing chains. This is true shortly after initiation and at the end of the polymerization (except for the growing chain concentration) since 100% conversion of monomer usually is not achieved.

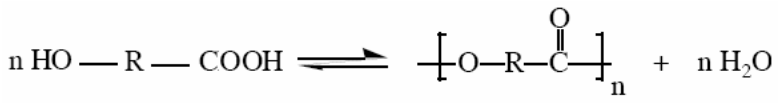
Figure 2.1 : Compraison of Step-Growth and Chain-Growth polymerization

Second, a high degree monomer purity is necessary. It is evident that in the case of □ -aminocaproic acid, if the decarboxylation product, n-pentylamine, is present, then internal balance is no longer achieved. Likewise, the presence of a trace of monocarboxyric acid iq adipic will lead to a stoichiometric imbalance. Furthermore, these monofunctional monomers act as caps to the polymer chain. Once the monocarboxylic acid has underagone amide formation, no further reaction is possible at the end of the chain.Third, the reaction responsible for the polymerization must be a very high yield reaction with the absence of side reactions. Of the large number of reactions known to organic chemists today, only four are utilized in the synthesis of step-growth polymers in large amounts [4]. These four polymers meet the requirements of high yield reactions and cost feasibility. Polyesters, polyamides, polycarbonates and polyethers.

2.1.1 Polyesters

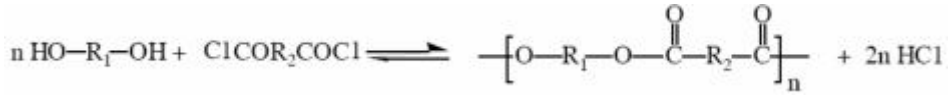
Polyesters are very popular and one of the most versatile synthetic copolymers. They are produced in high volumes like more than 30 billion pounds a year worldwide [5-7]. They are widely used commercially as fibres, plastics, composites and for coatings applications too. In their polymer backbones,they possess carboxylate ester functionalities as an integral component.

- Esterification of hydroxy acid



- Esterification of diol and diacid

- Esterification of diol and diacid chloride



- Lactone polymerization

2.2 Olefin Metathesis

Olefin metathesis is a metal-catalyzed transformation, which acts on carbon carbon double bonds and rearranges them via cleavage and reassembly [8-11]. While the reaction itself was discovered in the mid-1950s, its now generally accepted mechanism was not proposed until 1971 [12]. First introduced mechanism by Chauvin shows that, the coordination of an olefin to a metal carbene catalytic species leads to the reversible formation of a metallacyclobutane (Figure 1.1). This intermediate then proceeds by cycloreversion via either of the two possible paths: 1) non-productive—resulting in the re-formation of the starting materials or 2) product-forming—yielding an olefin that has exchanged a carbon with the catalyst's alkylidene. Since all of these processes are fully reversible (Figure 2.2), only statistical mixtures of starting materials as well as all of possible rearrangement products are produced in the absence of thermodynamic driving forces.

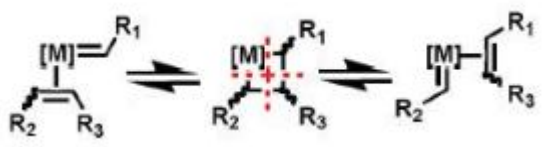


Figure 2.2 : General mechanism of olefin metathesis.

Fortunately for the organic and polymer chemistry communities, the olefin metathesis reaction's thermodynamic equilibrium can be easily influenced. There are two major approaches that are commonly employed to drive the reaction towards the desired products. One tactic is to rely on Le Chatelier's principle by continuously removing one of the products from the reaction system in order to shift the equilibrium in favor of the other product. This method is especially effective in the case of cross metathesis (CM) [13] reactions involving terminal olefins, ring-closing metathesis (RCM) [14-15] and acyclic diene metathesis polymerization (ADMET) [16-20], because the volatile ethylene gas by-product formed in these processes can be easily removed (Scheme 1.2). The other approach capitalizes on the ring strain of cyclic olefins such as cyclooctenes and norbornenes. The energy released during the ring-opening of these compounds is sufficient to drive forward reactions such as ring-opening cross metathesis (ROCM) [21-22] and ring-opening metathesis polymerization (ROMP) [23-24] (Figure 2.3). In addition, in some instances, substrate concentration (which often distinguishes ADMET from RCM) or the catalysts' sensitivity to olefin substitution can also be taken advantage of to influence product selectivity. All of these methods are currently successfully employed in the synthesis of a large variety of small, medium, and polymeric molecules, as well as novel materials [25-29].

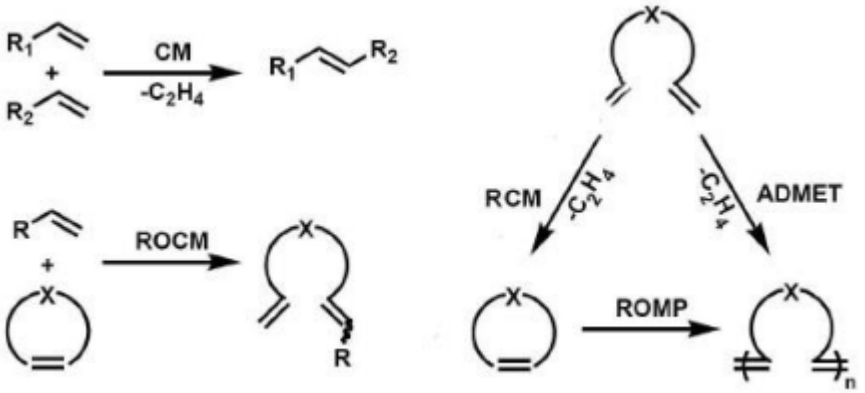


Figure 2.3 : Types of olefin metathesis reactions

Once an olefin metathesis mechanism consistent with the experimental evidence was established, rational catalyst design became possible. Consequently, several welldefined, single-species catalysts based on different transition metals such as titanium [30], tungsten [31-32], molybdenum [33], rhenium [34], osmium [35], and ruthenium [36-37] evolved from the original metathesis-active but ill-defined multi-

component mixtures. However, even today, the early transition metal catalysts, although very active, are also sensitive to many functional groups found in organic molecules, as well as moisture and air -a drawback that significantly limits their synthetic applications-. For example, a metathesis catalyst with a tungsten center will preferentially react with olefins in the presence of esters and amides, but it will ignore all of these functionalities in favor of ketones, aldehydes, alcohols, acids or water. On the other hand, the late transition metal, ruthenium-based catalysts proved to be very tolerant towards polar functional groups and water, albeit at the expense of activity, early in olefin metathesis research [38]. Overall, both Mo and Ru metathesis catalysts gained the most prominence and popularity due to their versatility, as they provided a good balance between activity and functional group tolerance (Figure 2.4).

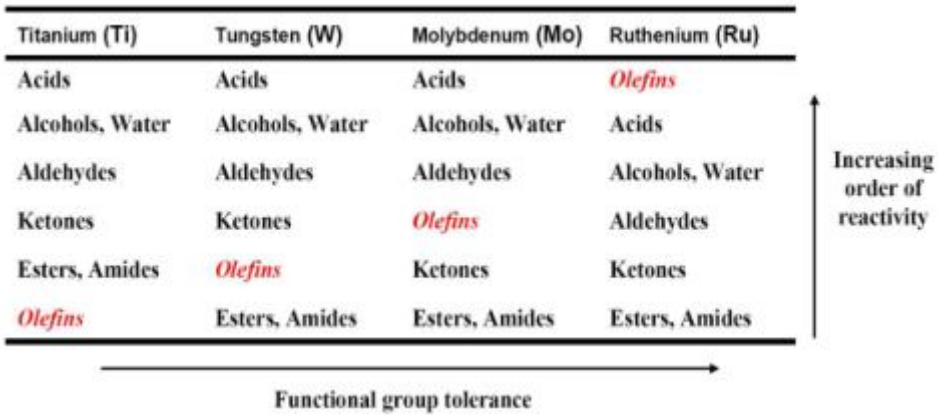


Figure 2.4 : Functional group tolerance of olefin metathesis catalysts.

The exceptional selectivity of ruthenium for C–C double bonds secured continuous interest for this line of catalysts despite the low activity of the early versions, relative to the molybdenum catalysts of the time. For example, the activity of bistriphenylphosphine (PPh_3) predecessors of catalyst 1 (Figure 2.4) was limited to ROMP of strained monomers, yet the catalyst performed remarkably well in polar media such as alcohols. Cross metathesis of acyclic olefins are more likely to occur more stable and have more group tolerance, when compared to earlier ruthenium ligands, phosphine ligands (PPh_3) changed with cyclohexyl groups (PCy_3), resulting in more active 1st generation Grubbs catalyst [39]. Furthermore, the substitution of one of the phosphine ligands for an even more electrondonating N-heterocyclic carbene (NHC) resulted in a series of 2nd generation catalysts, such as 230 and the phosphine-free [40] which now rival Mo catalysts in activity (Figure 2.5). While

both 2 and 3 maintain the excellent selectivity for olefins typical of ruthenium catalysts, they have somewhat slower rates of initiation than the first generation catalysts, limiting their application in polymer synthesis. Alternatively, NHC catalyst [41] which bears a bispyridine ligand in place of a phosphine (Figure2.5), has a sufficiently rapid initiation rate to promote ROMP of norbornenes with all of the attributes of a living polymerization. Moreover, the continuing emergence of new catalysts serves to further improve the metathesis reaction to be applicable to asymmetric, [42] sterically demanding, [43] or aqueous [44-45]transformations.

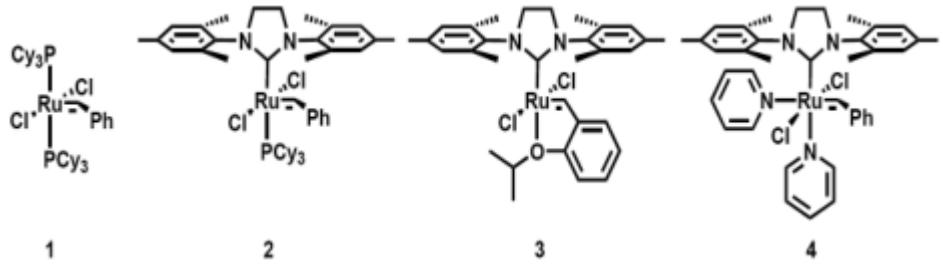


Figure 2.5 : Ruthenium-based olefin metathesis catalysts

One specific example of the improved reactivity of 2nd generation ruthenium catalysts, such as 2 and 3, is their ability to react with electron-deficient B,C-unsaturated carbonyls, which are inert to 1. As a result, excellent cross metathesis selectivity can be achieved in the reactions with such substrates [46-47]. While both types of catalysts will successfully homodimerize “easy,” electron-rich, unsubstituted olefins, such as terminal aliphatic alkenes, even the active NHC-catalysts have very limited ability, if any, to cross a pair of “difficult,” electron-deficient olefins, such as acrylates. Nevertheless, unlike 1, NHC-catalysts will promote selective cross metathesis between an “easy” and a “difficult” olefin. Therefore, a mixture of compounds, each functionalized with either a terminal alkene or an acrylate, will produce homodimers of the “easy” alkenes exclusively when exposed to 1, and mixed “easy”-“difficult” cross products when exposed to 2 or 3. Importantly, although homodimerization of “easy” olefins occurs in the presence of either 2 or 3, the disubstituted, electron-rich product of this cross is still qualified as “easy” and can proceed through secondary metathesis with acrylates and the NHC- catalyst to form a thermodynamically more stable cross product. In fact, this cross metathesis selectivity of 2nd generation ruthenium catalysts has already been creatively exploited in the synthesis of small molecules [48], macrocycles [49], and alternating A,B polymers [50].

2.2.1 ADMET

Acyclic diene metathesis (ADMET) polymerizations follow a step growth mechanism to produce strictly linear polymers with unsaturated polyethylene backbones [51] As with all other olefin-metathesis reactions, ADMET proceeds through the exchange of substituents of two reacting olefins in an equilibrium reaction, a transalkylidenation. In the case of ADMET polymerizations, this exchange results in the release of ethylene (Figure 2.6), which can be removed from the equilibrium reactionmby the application of vacuum or a constant flow of an inert gas to obtain high conversions and high-molecular-weight polymers [51]. This loss of ethylene during ADMET polymerizations might be considered as unsustainable as it is not atom economic, but it should be possible to collect the produced ethylene in large-scale operations to use it as feedstock for other processes und thus circumvent this problem.

Figure 2.6 : ADMET polymerization

In particular, the introduction of ruthenium-based metathesis initiators in the 1990s allowed an unmatched functional group tolerance [52] and led to the development of the first- generation catalyst from Grubbs [53-54]. The observation that the introduction of a N-heterocyclic carbene (NHC) to the catalyst leads to metathesis initiators with improved activity [55-57] as well as stability led to the development of the second- generation catalysts from Grubbs [58-59] and Hoveyda [60] that are widely applied today in organic synthesis as well as polymer chemistry [51, 61-64].Therefore, the ADMET polymerization technique has not only led to the preparation of well- defined, branched polyolefins (from branched monomers) that would not be accessible by other methods [65-66] but has also opened ways to prepare polyolefins with a number of different functional groups [67-70]. Even if the preparation of a large variety of different polymers is possible through ADMET polymerization as discussed above, relatively little is known about the use of ADMET polymerizations for the preparation of telechelics or even block copolymers. As for any other step growth polymerizations, this is however, possible. For instance, methoxydimethylsilane- and chlorodimethylsilane-

terminated telechelic polyoctoenomer oligomers were prepared using ruthenium as well as molybdenum metathesis catalysts, and it was observed that the number-averaged molecular weight (Mn) values of the prepared telechelics was dictated by the initial ratio of the monomer to the chain stopper [71](Figure 2.7).

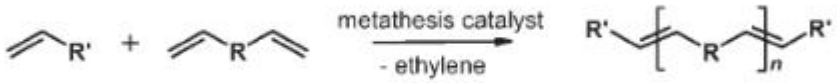


Figure 2.7 : ADMET polymerization with chain stoppers.

2.3 Click Chemistry

In 2001, Sharpless and coworkers introduced "click" chemistry, a new approach inorganic synthesis that involves a collection of almost perfect chemical reactions. Sharpless describes click chemistry as tailored to generate substances quickly and reliably by joining small units together.Click chemistry can be summarized with only one sentence: Molecules that are easy to make. Sharpless also introduced some criteria in order to fulfill the requirements of click reactions, which reactions are modular, wide in scope, high yielding, create only inoffensive by-products, reactions are stereospecific, simple to perform and that require benign or easily removed solvent [72].

Nowadays there are several processes have been identified under this term in order to meet these criteria. Nucleophilic ring opening reactions; non-aldol carbonylchemistry; thiol additions to carbon–carbon multiple bonds (thiol-ene and thiol-yne); and cycloaddition reactions fulfill Sharpless's criteria (Figure 2.8) [73]. Among those selected reactions, copper (I)-catalyzed azide-alkyne (CuAAC), active ester reactions and Diels-Alder (DA) cycloaddition reactions have gained much interest among the chemists not only the synthetic ones but also the polymer chemists. From this point of view, these reactions will shortly be summarized.

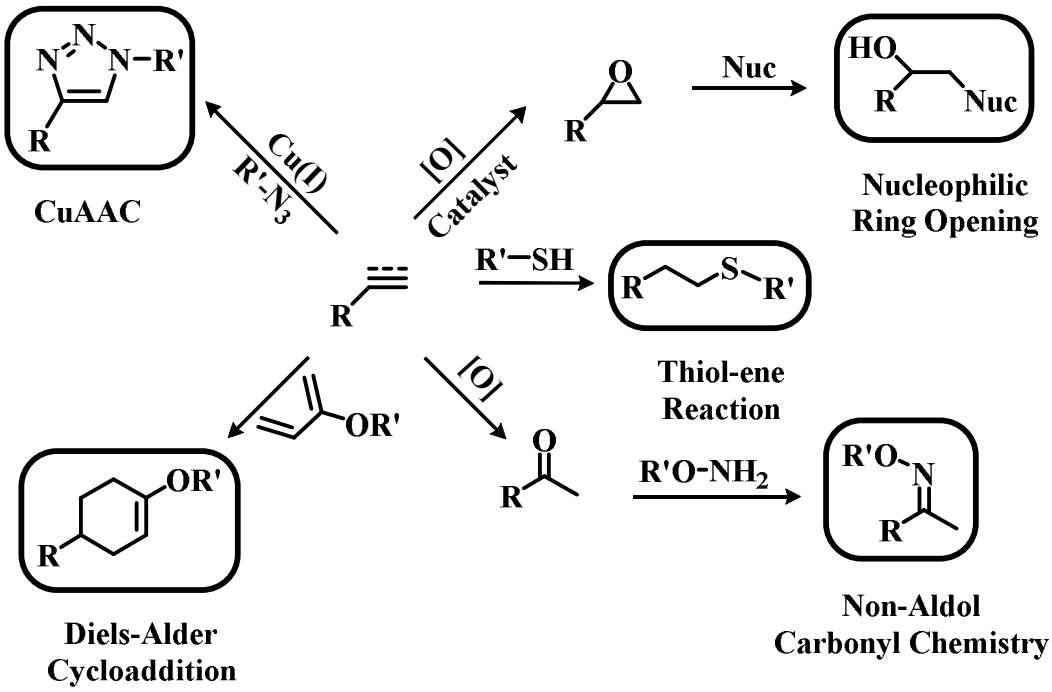


Figure 2.8: General representation of popular click reactions.

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

The thermal reaction between organic azides and alkynes has been known for more than a century, the first 1,2,3-triazole being synthesized by A. Michael from phenyl azide and diethyl acetylenedicarboxylate in 1893. The reactionhas been investigated in detail by Huisgen and coworkers in the middle of the 20th century in thecourse of their studies of the larger family of 1,3-dipolar cycloaddition reactions [74]. The Huisgen 1,3-dipolar cycloaddition reaction of alkynes and organic azideshas gained considerable the most attention of any click reaction since 2001, CuAAC was realized independently by Fokin and Sharpless, and Meldal in 2002 [75, 76]. The conventional Huisgencycloaddition of azides and alkynes is not appropriate the criterion of a clickreaction, because of the high temperature necessity (>110 °C) and the lack ofregiospecificity which produce products with a racemic mixture of 1,4-triazole and 1,5-triazole products as seen in Figure 2.9 [77]. The copper catalyzed reaction allows to proceed much faster under muchmilder conditions and produces only one isomer which is 1,4-regiosomer triazole [72, 77]. Thegreat success of the Cu (I) catalyzed reaction is actually a virtually quantitative, veryrobust, insensitive, general, and orthogonal ligation reaction.

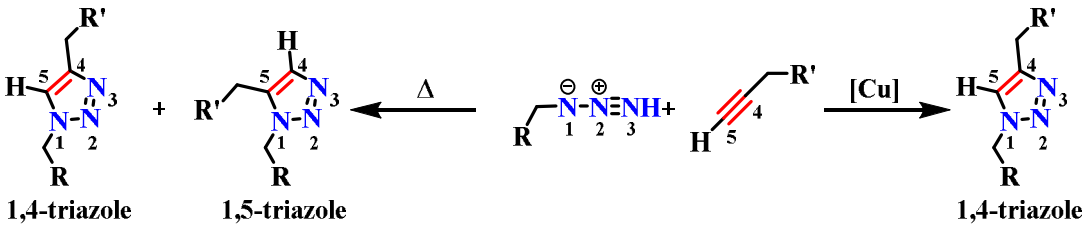


Figure 2.9: Huisgen's 1,3-dipolar cycloaddition and CuAAC.

When the mechanism is catalyzed, Cu (I) can easily overcome the activation barrier as a result of this difference the CuAAC reaction rate is increased by a factor of 10^7 relative to the Huisgen 1,3-dipolar cycloaddition, so it considerably fast at and below room temperature [78-79]. Thereaction is not significantly affected by the steric and electronic properties of the functionalgroups attached to the azide and alkyne centers, and the CuAAC is fairly general with a broad range of alkynes and azides [80].

In fact, the discovery of Cu (I) as catalyst has a great importance which efficiently and regiospecifically combines terminal alkynes and azides under mild conditions. On the other hand, Fokin and Sharpless reported that only1,5-disubstituted 1,2,3-triazole was obtained from terminal alkynes when the catalystswitched from Cu(I) to ruthenium(II) [81].

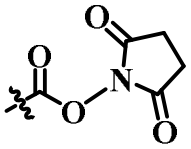
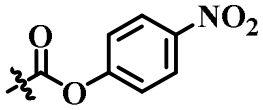
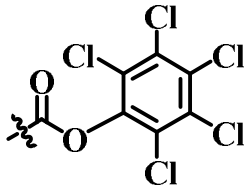
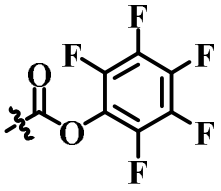
Although CuAAC reaction was initially postulated in general for organic synthesis, this strategy has also an enormous potential in polymer chemistry.The importance of CuAAC in polymer chemistry is the synthesisof functionalized polymers and the construction of polymers with well-defined architectures. Since the first report ofclick chemistry in polymer science which is published by Hawker, Sharpless and coworkers, theconstruction of well-defined and complex macromolecular architectures via clickchemistry has been used in many study and the number of publications in this field has increased dramatically within the years [82].

2.3.2 Active esters

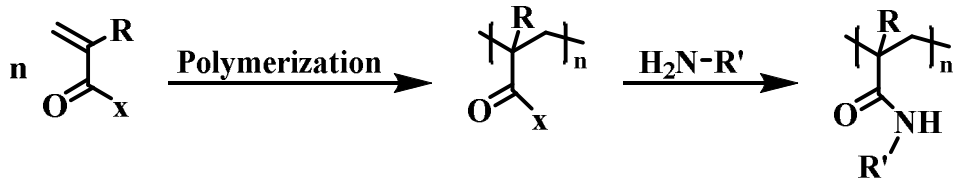
Active esters are very popular in the field of peptide synthesis in organic chemistry [83].This methodology has been much applied mainly to form peptidebonds under mild conditions in both liquid and solid phase synthesis. Many different active esters have been presented: thiophenylesters [84], activated methyl esters [85] and nitrothiophenyl esters [86].New active esters were investigated after grooving interest, e.g.;*O*-acyl derivatives of hydroxylaminessuch as N-hydroxysuccinimide

esters and many different aryl esters with electron withdrawing substituents inthe aromatic ring (Table 2.1). One of these esters, the pentachlorophenyl esters introduced by Kupryszewski which excel a high reactivity, but suffer fromthe steric effect of the bulky activating groups [87]. On the other hand, these esters have less potential to be used in solid phase peptide synthesis. A logical cure for this drawback wasthe replacement of the five chlorine atoms by fluorine. This change results a very powerful active ester with less sterichindrance that retains its reactivity even in the matrix used for solid phase peptide synthesis [88].

Table 2.1: Common active esters.

Name	Structure
N-Hydroxysuccinimide ester	
4-nitrothiophenyl ester	
Pentachlorophenyl ester	
Pentaflorophenyl ester	

Functional polymers are usually prepared by polymerization of the desired functional monomers, however, the preparation of the corresponding monomers and/or their polymerization is often difficult or even impossible, especially when complex structures are desired. If prepolymers with reactive chemical functions in the side chain are utilized, in many cases these problems can be evaded; such as by protecting and de-protecting the functionality.As described above active esters are an ideal starting point in this kind of drawbacks. Because these reactive groups can be transformed into amide groups by polymer analogous reaction with primary or secondary amines in a quantitative and simple way, as shown in Figure 2.10 [91].



x: active ester

Figure: 2.10: Poly(active ester) as starting material.

Most examples of polymeric active esters that have been reported so far have focused on the modification of polymeric active esters either with primary amines or with peptides or metalbinding ligands, which would have been difficult to introduce via direct polymerization [90]. As a result of, active ester polymers react fast and quantitatively with primary or secondary amines to form the corresponding poly(acrylamide) derivatives allows an opportunity to obtain macromolecules with specialized functionalities [91]. The research for alternative active ester monomers and resulting polymers of these active ester monomers are still challenging. Pentafluorophenyl esters proved to be very effective in peptide chemistry and in polymer chemistry [89].

3. EXPERIMENTAL WORK

3.1 Materials

Poly(ethylene glycol monomethyl ether) (PEG-OH) (M_n=550 g/mol, Acros) was dried over anhydrous toluene by azeotropic distillation.Tetrahydrofuran (THF, 99.8%, J.T. Baker) was dried and distilled from benzophenone-Na. N,N-dimethylformamide (DMF, 99.8%, Aldrich) was dried and distilled under vacuum over CaH_2. Dichloromethane (CH_2Cl_2, 99%, J. T. Baker) was dried and distilled over and P_2O_5. 1,2-Dichlorobenzene (ODCB)(99%, Aldrich), diethyl ether (99.7%, Aldrich),methanol (99.8%, Aldrich) were used without further purification. Ethyl acetate (EtOAc) and hexane were in technical grade and distilled prior to use. N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) was distilled over NaOH before use. N,N'-Dicyclohexylcarbodiimide (DCC, 99%, Aldrich), 4-dimethylaminopyridine (DMAP, 99%, Acros),CuBr (99.9%, Aldrich),octylamine (99%, Aldrich),allylamine (98%, Aldrich), furfurylamine (99+%, Acros), propargylamine (98%, Aldrich), benzylamine (98%, Acros), pentafluorophenol (99%, Aldrich),5-hexenoic acid (98%, Aldrich), sodium azide (99.5%, Aldrich), hydrochloric acid (37%, Aldrich), Grubbs Catalyst 1st Generation (G1) (97%, Aldrich), Hoveyda-Grubbs Catalyst 2nd Generation (GH-II) (97% Aldrich), butyl vinyl ether (contains 0.01% potassium hydroxide as stabilizer, 98%) were used as received. All other reagents were purchased from Aldrich and used as received without further purification.

3.2 Instrumentation

^{1}H (500 MHz), ^{13}C(125 MHz) and ^{19}F NMR ((470.4 MHz) spectra were recorded in $CDCl_3$ with $Si(CH_3)_4$ as internal standard, using an Agilent VNMRS 500 instrument.The conventional Gel Permeation Chromatography (GPC) measurements were carried out with an Agilent instrument (Model 1100) consisting of a pump, refractive index, and UV detectors. 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) were used in series. The effective molecular weight ranges were 2000-4.000.000, 50-100.000, 500-30.000, and 500–20.000, respectively. THF was used as eluent at a flow rate of 0.3 mL/min at 30°C. 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).The differential scanning calorimetry (DSC) measurements were performed on a DSC Q1000 (TA Instruments) with a heating rate of 10°C /min under nitrogen. All data were collected from a second heating cycle, and the glass transition (T_g) temperatures were determined as a midpoint of thermograms.FT-IR spectra were recorded on an Agilent Technologies Cary 630 FTIR instrument over the range 4000–500 cm^{-1}.

3.3 Synthetic Procedures

3.3.1 Synthesis of 2,2,5-trimethyl-1,3-dioxane-5-carboxylic acid (1)

The 2,2-bis(hydroxymethyl)propionic acid (16.0 g, 119.2 mmol) along with p-TSA (0.9 g, 4.64 mmol), and 2,2-dimethoxypropane (22.4 mL, 178.8 mmol) dissolved in 80 mL of dry acetone, and stirred 2h at room temperature. In the vicinity of 2h, while stirring continued the reaction mixture was neutralized with 12 mL of totally NH 4 OH (25%), and absolute ethanol (1:5), filtered off by-products and subsequent dilution with dichloromethane (240 mL), and once extracted with distilled water (80 mL). The organic phase dried with Na 2 SO 4 concentrated to white solid after evaporation of the solvent (Yield=14.8 g 71%). ^{1}H NMR ($CDCl_3$, δ) 4.17 (d, 2H, CC*H*$_2$O), 3.67 (d, 2H, CC*H*$_2$O), 1.45 (s, 3H, C*CH*$_3$), 1.42 (s, 3H, C*CH*$_3$), 1.21 (s, 3H, C=OC(CH$_2$O)$_2$*CH*$_3$).

3.3.2 Synthesis of perfluorophenyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate (2)

2,3,4,5,6-pentafluorophenol (3,3 g, 17.9 mmol) was dissolved in 130 mL CH_2Cl_2 and **1** (3,74 g, 21,5 mmol), and DMAP (1,10 g, 9 mmol) were added to the mixture in that order. After stirring 5 min at room temperature, DCC (4,44 g, 21,5 mmol) dissolved in 20 mL of CH_2Cl_2 was added in N_2 atmosphere. Reaction mixture was stirred overnight at room temperature and urea byproduct was filtered. After evaporating the solvent, remaining product was purified by column chromatography with hexane/ethyl acetate (9:1) mixture (Yield=3.9 g; 64%). ^{1}H NMR ($CDCl_3$, δ) 4.32 (d, *J*=11.9 Hz, 2H, CC*H*$_2$O), 3.81 (d, *J*=11.8 Hz, 2H, CC*H*$_2$O), 1.49 (s, 3H,

CC*H*$_3$) 1.44 (s, 3H, CC*H*$_3$), 1.35 (s, 3H, C=OC(CH$_2$O)$_2$C*H*$_3$). ^{19}F NMR (CDCl$_3$, δ) -153.08 (d, *J*=17.6 Hz, 2F, o-*F*), -157.14 (t, *J*=21.7 Hz, 1F, p-*F*), -161.88 (t, *J*=20.0 Hz, 2F, m-*F*).

3.3.3 Synthesis of perfluorophenyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate (3)

Perfluorophenyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate (3.85 g, 11.3 mmol) was dissolved in a mixture of 50 mL of THF, 50 mL of distilled water and 4 mL of 1 M HCl. The reaction mixture was stirred for 2 h at room temperature. Obtained product extracted with 100 mL of CH_2Cl_2 and 50 mL of water for four times, and combined organic phases were dried with Na_2SO_4. Solvent was evaporated under reduced pressure and white solid product obtained (Yield=3.25 g; 96%). ^{1}H NMR (CDCl$_3$, δ) 4.07 (d, *J*=11.0 Hz, 2H, C*H*$_2$OH), 3.88 (d, *J*=10.9 Hz, 2H, C*H*$_2$OH), 1.31 (s, 3H, C=OC(CH$_2$O)$_2$*CH*$_3$). ^{19}F NMR (CDCl$_3$, δ) -152.74 (d, *J*=17.3 Hz, 2F, o-*F*), -157.47 (t, *J*=21.6 Hz, 1F, p-*F*), -162.09 (t, *J*=21.7 Hz, 2F, m-*F*).

3.3.4 Synthesis of 2-methyl-2-((perfluorophenoxy)carbonyl)propane-1,3-diyl bis(hex-5-enoate)(4)

Perfluorophenyl diol (**3**) (3.18 g, 10.60 mmol,1 equiv) was dissolved in 100 mL CH_2Cl_2 and stirredunder nitrogen. To this solution were added 5-hexenoic acid (2.77 mL,23.32 mmol, 2.2 equiv) and DMAP (1.30 g, 10.60 mmol, 1 equiv) in that order. The mixture was stirred 5 min at room temperature, DCC (4.81 g, 23.32 mmol, 2.2 equiv) was dissolved in 20 mL of $CH_2Cl_2$and added to this mixture. Reaction mixture was stirred overnight at room temperature. After filtering the urea byproduct the solvent was evaporated and the remaining product was purified by column chromatography over silica gel eluting with ethyl acetate/hexane (19:1) to give **4** as a colorless viscous oil. (Yield=3.30 g,63%).^{1}H NMR (CDCl$_3$, δ) 5.77 (m, 2H, CH$_2$=C*H*CH$_2$CH$_2$CH$_2$C=O), 5.02 (m, 4H, C*H*$_2$=CHCH$_2$CH$_2$CH$_2$C=O), 4.36 (m, 4H, C*H*$_2$OC=O), 2.38 (t, 4H, CH$_2$=CHCH$_2$CH$_2$C*H*$_2$C=O), 2.10 (m, 4H, CH$_2$=CHCH$_2$C*H*$_2$CH$_2$C=O), 1.75 (m, 4H, CH$_2$=CHCH$_2$C*H*$_2$CH$_2$C=O), 1.47 (s, 3H, CC*H*$_3$).^{19}F NMR (CDCl$_3$, δ) -153.12 (d, 2F, o-*F*), -157.16 (t, 1F, p-*F*), -161.89 (t, 2F, m-*F*).^{13}C NMR (CDCl$_3$, δ) 172.88, 169.17, 137.42, 115.51, 65.02, 47.15, 33.16, 32.95, 23.82, 17.83.

3.3.5 Synthesis of tosylated PEG (5)

Me-PEG-OH (M_n=550 g/mol) (5 g, 9.09 mmol) was dissolved in 150 mL of $CH_2Cl_2$and TEA (12.66 mL, 90 mmol) was added to this solution. The mixture was cooled to 0°C and toluene-4-sulfonyl chloride (tosyl chloride) (8.66 g, 45 mmol) in CH_2Cl_2 were added dropwise (30 min) to the reaction mixture.Than the reaction mixturewas stirred overnight at room temperature. First, it was extracted with cold 4 M HCl,then with distilled water and dried over Na_2SO_4. The organic phase was evaporated and white solid was further purified by column chromatography over silica gel eluting with firstly CH_2Cl_2 and secondly with MeOH/ CH_2Cl_2 (1/6) to give **5** as colorless viscous liquid. (Yield=5.8 g, 91 %). ^{1}H NMR ($CDCl_3$, δ) 7.80 and 7.34 (8H, PEG-$OSO_2C_6H_4CH_3$), 4.15 (2H, OCH_2CH_2-$OSO_2C_6H_4CH_3$), 3.63 (OCH_2CH_2 repeating unit of PEG), 3.37 (3H, CH_3-$PEGOSO_2C_6H_4CH_3$) 2.44 (3H, PEG-$OSO_2C_6H_4CH_3$).

3.3.6 Synthesis of azide end functional PEG (PEG-azide) (6)

Tosylated-PEG, **5** (5.8 g, 8.24 mmol) was dissolved in DMF (20 mL) and sodium azide (NaN_3) (5.36 g, 82.3 mmol) was added to this solution. After stirring the reaction mixture overnight at room temperature, CH_2Cl_2 and water were added and the organic layer was extracted three times with water and dried over Na_2SO_4. Solvent was removed under reduced pressure and **6** afforded as colorless viscous liquid (Yield=4.51 g, 95 %). ^{1}H NMR ($CDCl_3$, δ) 3.63 (m, OCH_2CH_2 repeating unit of PEG), 3.36 (5H, CH_3-PEG-$N_3$and CH_2O-N_3).

3.3.7 Acyclic Diene Metathesis (ADMET) polymerization of 4 (P1)

Into a flame-dried 25 mL flask was charged with activated ester functionalized monomer(**4**)(0.90 g,1.83 mmol) in CH_2Cl_2(2 mL), and the solution was stirred for 5 min at room temperature under nitrogen. G1(15.0 mg, 0.0183 mmol)was then added to this solution under nitrogen atmosphere. After the addition of the catalyst, very slow to moderate bubbling of ethylene was observed. The reaction mixture was stirred at room temperature under nitrogen flow until the solvent completely removed. The reaction mixture was then exposed to intermittent vacuum to remove ethylene until the viscosity increased and the increased viscosity prevented stirring.

After which time the reaction temperature was started to increase gradually to 40 ^{o}C, then 60 ^{o}C and finally to 80 ^{o}C and the polymerization was pursued overnight until no more bubbling was observed. The reaction mixture was cooled to room temperature and the catalyst quenched by adding ethylvinyl ether (0.5 mL in 5 mL CH_2Cl_2), fallowed by 30 min stirring at room temperature. The reaction mixture was precipitated in methanol (100 mL) and decanted. This dissolution–precipitation procedure was repeated two times. After decantation, the recovered polymer was dissolved in $CHCl_3$ and evaporated to dryness (Yield=0.72 g, 80%, $M_{n,\ GPC}$=21200 g/mol, M_w/M_n=1.74, relative to PS standards).^{1}H NMR ($CDCl_3$, δ) 5.40 (br, =C*H*$CH_2CH_2CH_2C$=O), 4.37 (m, C*H*$_2$OC=O), 2.35 (m, =$CHCH_2CH_2CH_2C$=O), 2.03 (br, =$CHCH_2CH_2CH_2C$=O), 1.70 (m, =$CHCH_2CH_2CH_2C$=O), 1.47 (s, CC*H*$_3$).^{19}F NMR ($CDCl_3$, δ) -153.09 (d, 2F, o-*F*), -157.22 (t, 1F, p-*F*), -161.95 (t, 2F, m-*F*).^{13}C NMR ($CDCl_3$, δ) 172.89, 169.16, 130.08, 129.51, 65.07, 47.22, 33.24, 31.78, 26.69, 26.48, 24.47, 17.77.

3.3.8 Activated ester substitution reaction of P1 and benzylamine (P2)

ADMET polymer **(P1)** (0.10 g, 0.215 mmol of activated ester, 1 equiv) and benzylamine (0.047 mL, 0.430 mmol,2 equiv per activated ester) were dissolved in 3 mL of DMF. Subsequently, the solution was bubbled with nitrogen for 10 min and stirred at room temperature for 24 h. After that time, the polymer solution was precipitated in 30 mL of diethyl ether and the solvent was removed by decantation. The residual solid was dissolved in THF and consequently precipitated in diethyl ether. The purified polymer was finally dried at 40°C in a vacuum oven for 24 h (Yield=0.065 g, 78%, $M_{n,\ GPC}$=17700 g/mol, M_w/M_n=1.33, relative to PS standards).^{1}H NMR ($CDCl_3$, δ) 7.4-7.2 (m, Ar*H*), 6.44 (br, N*H*),5.36 (bs, =C*H*$CH_2CH_2CH_2C$=O), 4.45 (d, Ar-C*H*$_2$), 4.23 (s, C*H*$_2$OC=O), 2.26 (m, =$CHCH_2CH_2CH_2C$=O), 1.98 (br, =$CHCH_2CH_2CH_2C$=O), 1.63 (m, =$CHCH_2CH_2CH_2C$=O), 1.27 (s, CC*H*$_3$).^{13}C NMR ($CDCl_3$, δ) 172.99, 172.20, 138.19, 130.11, 129.54, 128.68, 127.53, 66.41, 46.19, 43.62, 33.40, 31.80, 27.65, 26.47, 24.50, 17.92.

3.3.9 Activated ester substitution reaction of P1 and octylamine (P3)

ADMET polymer **(P1)**(0.10 g, 0.215 mmol of activated ester, 1 equiv) and octylamine (0.071 mL, 0.430 mmol,2 equiv per activated ester) were dissolved in 3

mL of DMF. Subsequently, the solution was bubbled with nitrogen for 10 min and stirred at room temperature for 24 h. After that time, DMF was evaporated from the reaction mixture. Obtained product was dissolved in THF and precipitated in 30 mL of hexane and the solvent was removed by decantation. The residual solid was re-dissolved in THF again and precipitated in hexane. The purified polymer was finally dried at 40°C in a vacuum oven for 24 h (Yield=0.055 g, 62%, $M_{n,\,GPC}$= 6100 g/mol, M_w/M_n=1.50 , relative to PS standards).^{1}H NMR ($CDCl_3$, δ) 6.07 (br, N*H*),5.39 (bs, =C*H*$CH_2CH_2CH_2C$=O), 4.22 (s, CH_2OC=O), 3.27 (m, NHCH_2CH_2), 2.32 (m, =$CHCH_2CH_2$CH_2C=O), 2.02 (br, =CHC$H_2CH_2CH_2$C=O), 1.68 (m, =$CHCH_2$CH_2CH_2C=O), 1.50 (bs, $NHCH_2$CH_2), 1.4–1.2 (m, CCH_3 and CH_2 of octyl), 0.89 (m, C$H_3$$(CH_2)_7$NH).^{13}C NMR ($CDCl_3$, δ)173.03, 172.13, 130.10, 129.54, 66.85, 66.38, 46.12, 39.73, 33.48, 31.79, 29.51, 29.23, 26.89, 26.50, 24.73, 24.58, 22.63, 17.98, 14.08.

3.3.10 Activated ester substitution reaction of P1 and allylamine (P4)

ADMET polymer **(P1)** (0.10 g, 0.215 mmol of activated ester, 1 equiv) and allylamine (0.032 mL, 0.430 mmol, 2 equiv per activated ester) were dissolved in 3 mL of DMF. Subsequently, the solution was bubbled with nitrogen for 10 min and stirred at room temperature for 24 h. After that time, DMF was evaporated from the reaction mixture. Obtained product was dissolved in THF and precipitated in 30 mL of hexane and the solvent was removed by decantation. The residual solid was re-dissolved in THF again and consequently precipitated in hexane. The purified polymer was finally dried at 40°C in a vacuum oven for 24 h (Yield=0.032 g, 44%, $M_{n,\,GPC}$= 14000 g/mol, M_w/M_n=1.49, relative to PS standards).^{1}H NMR ($CDCl_3$, δ) 6.20 (br, N*H*),5.84 (m, CH_2=C*H*CH_2NH) 5.39 (bs, =C*H*$CH_2CH_2CH_2$C=O), 5.16 (m, CH_2=$CHCH_2$NH), 4.24 (s, CH_2OC=O), 3.91 (m, CH_2=CHCH_2NH), 2.32 (m, =$CHCH_2CH_2$CH_2C=O), 2.02 (br, =CHC$H_2CH_2CH_2$C=O), 1.68 (m, =$CHCH_2$CH_2CH_2C=O), 1.27 (s, CCH_3).^{13}C NMR ($CDCl_3$, δ)173.01, 172.14, 134.05, 130.12, 129.55, 116.18, 67.96, 66.37, 46.19, 41.97, 33.45, 31.80, 26.49, 25.61, 24.56, 17.96.

3.3.11 Activated ester substitution reaction of P1 and furfurylamine (P5)

ADMET polymer **(P1)** (0.10 g, 0.215 mmol of activated ester, 1 equiv) and furfurylamine (0.038 mL, 0.430 mmol, 2 equiv per activated ester) were dissolved in

3 mL of DMF. Subsequently, the solution was bubbled with nitrogen for 10 min and stirred at room temperature for 24 h. After that time, the polymer solution was precipitated in 50 mL of diethyl ether and the solvent was removed by decantation. The residual solid was dissolved in THF and consequently precipitated in diethyl ether. The purified polymer was finally dried at 40°C in a vacuum oven for 24 h (Yield=0.061 g, 75%, $M_{n,\ GPC}$= 15100 g/mol, M_w/M_n=1.52, relative to PS standards).^{1}H NMR ($CDCl_3$, δ) 7.35 (s, C*H* of furan), 6.45 (br, N*H*),6.33 (s, C*H* of furan),6.23 (s, C*H* of furan), 5.37 (bs, =C*H*$CH_2CH_2CH_2$C=O), 4.44 (d, furan-C*H*$_2$NH), 4.22 (s, C*H*$_2$OC=O), 2.29 (m, =CHCH_2CH_2C*H*$_2$C=O), 2.00 (br, =CHC*H*$_2CH_2CH_2$C=O), 1.65 (m, =CHCH_2C*H*$_2CH_2$C=O), 1.26 (s, CC*H*$_3$).^{13}C NMR ($CDCl_3$, δ) 172.99, 172.13, 151.09, 142.17, 130.12, 129.56, 110.52, 107.44, 66.29, 46.16, 36.72, 33.41, 31.82, 26.48, 24.49, 17.90.

3.3.12 Activated ester substitution reaction of P1-2 and propargylamine(P6)

Freshly prepared ADMET polymer (**P1-2**) ($M_{n,\ GPC}$= 30800 g/mol, M_w/M_n=1.90)(0.20 g, 0.430 mmol of activated ester, 1 equiv) and propargylamine (0.055 mL, 0.0860 mmol,2 equiv per activated ester)were dissolved in 5 mL of DMF. Subsequently, the solution was bubbled with nitrogen for 10 min and stirred at room temperature for 24 h. After that time, the polymer solution was precipitated in 50 mL of diethyl ether and the solvent was removed by decantation. The residual solid was dissolved in THF and consequently precipitated in diethyl ether. The purified polymer was finally dried at 40°C in a vacuum oven for 24 h (Yield=0.070 g, 48%, $M_{n,\ GPC}$= 20000 g/mol, M_w/M_n=1.68, relativeto PS standards).^{1}H NMR ($CDCl_3$, δ) 6.43 (br, N*H*),5.40 (bs, =C*H*$CH_2CH_2CH_2$C=O), 4.24 (s, C*H*$_2$OC=O), 4.06 (m, CH≡CC*H*$_2$NH), 2.34 (m, =CHCH_2CH_2C*H*$_2$C=O), 2.28 (s, C*H*≡CCH_2NH), 2.03 (br, =CHC*H*$_2CH_2CH_2$C=O), 1.69 (m, =CHCH_2C*H*$_2CH_2$C=O), 1.27 (s, CC*H*$_3$).^{13}C NMR ($CDCl_3$, δ)173.05, 172.12, 130.14, 129.58, 125.51, 79.40, 71.81, 66.19, 46.14, 33.44, 31.81, 30.32, 29.48, 26.49, 24.53, 17.87.

3.3.13 Copper(I) catalyzed azide-alkyne cycloaddition (CuAAC) reaction of side chain propargylfunctionalized ADMET polymer (P6) and PEG-N_3(P7)

P6(0.069 g,2.04 mmol of alkyne, 1equiv) andPEG-N_3 (0.176 g; 2.45mmol1.2equiv per alkyne) were dissolved in 4 mL of DMF, and the mixture was transferred to a 10 mL of Schlenk tube.CuBr (0.0293 g; 2.04 mmol) and PMDETA (0.043 mL, 2.04

mmol, 1 equiv) were added to the solution, and the reaction mixture was degassed by three freeze-pump-thaw (FPT) cycles, left in vacuum and stirred for 24 h at room temperature. After the specified time, solution was diluted with THF, filtered through a column filled with neutral alumina to remove copper complex and precipitated in diethyl ether and solvent was removed by decantation. The dissolution-precipitation procedure was repeated two times. The recovered polymer was dried in a vacuum oven at 40°C for 24 h (Yield=0.086 g, 46%, $M_{n,\ GPC}$=2250 g/mol, M_w/M_n=1.12, relative to PS standards).^{1}H NMR ($CDCl_3$, δ)7.74 (s, C*H* of triazole),5.37 (s, =C*H*$CH_2CH_2CH_2C$=O), 4.6–4.4 (d, triazole-C*H*$_2$NH and OCH_2C*H*$_2$-triazole), 4.21 (s, C*H*$_2$OC=O), 3.87 (br, OC*H*$_2CH_2$-triazole), 3.70–3.6(m, C*H*$_2$C*H*$_2$O of PEG), 3.39 (s, OC*H*$_3$ of PEG), 2.29 (br, =$CHCH_2CH_2$C*H*$_2$C=O), 2.08 (br, =CHC*H*$_2CH_2CH_2$C=O), 1.63 (m, =$CHCH_2$C*H*$_2CH_2$C=O), 1.25 (s, CC*H*$_3$).^{13}C NMR ($CDCl_3$, δ)173.04, 172.56, 144.14, 130.11, 129.55, 123.36, 73.93, 70.55, 69.40, 66.27, 59.01, 50.25, 46.03, 35.16, 33.42, 31.82, 26.49, 24.54, 17.80.

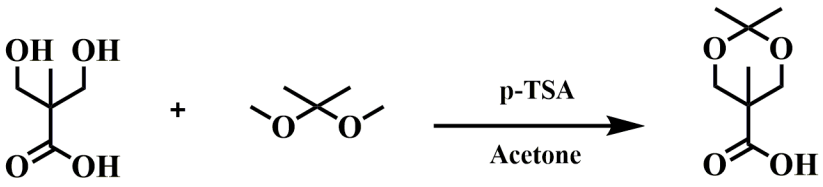
4. RESULTS AND DISCUSSION

ADMET polymerization is an effective way to polymerize α,ω-diene monomers. After the developments of ADMET catalysts like Grubbs catalyst, this polymerization method started to become more popular. Its unique nature of polymerization and the created polymers that have double bonds on their backbones and active ester functionality on their side chains present us effective modifications that can be made from these sites.

Using active ester compounds on polymer side chains, made it possible to apply modifications easily. For substitution reactions, several amine compounds have been used. As an active ester compound, 2,3,4,5,6-pentafluorophenol has been used in these experiments. To synthesize the monomer, firstly pentafluorophenyl ester functional diol was synthesized. After that, in order to optimize the monomer for ADMET polymerization, the diol compound reacted with 5-hexenoic acid. Several polymerization attempts were made to the ADMET monomer with various catalyst and reaction conditions. Considering the results of the attempted reaction conditions, G1 was chosen as the catalyst system. After the attempts of substitution reactions of benzylamine, octylamine, allylamine and furfurylamine with the active ester compound resulted with success, this time propargylamine was used for further modifications. With the preparation of the azide end-functional PEG, these two compounds became ready for CuAAC click reaction and these compounds were combined succesfully.

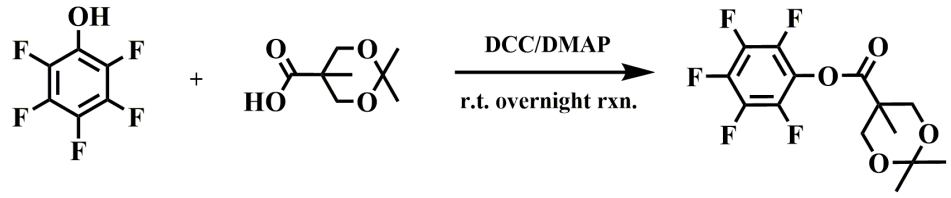
4.1 Preparation of Active Ester Functional ADMET Monomer

Ester functional ADMET monomer were synthesized within four steps. First 2,2,5-trimethyl-1,3-dioxane-5-carboxylic acid **(1)** was synthesized by the reaction of 2,2-bis(hydroxymethyl)propionic acid with 2,2-dimethoxypropane in dry acetone in the presence of *p*-toluene sulfonic acid as catalyst. Reaction equation is given below (Equation 4. 1).



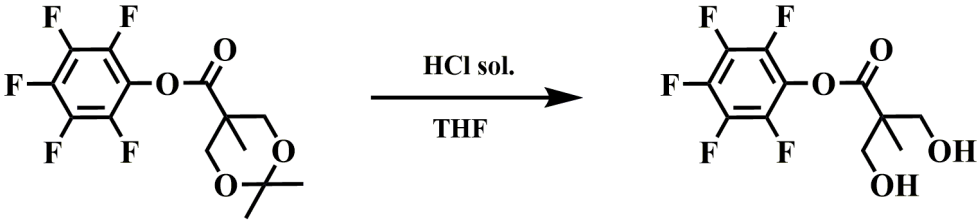
(4.1)

The second reaction to obtain monomer is esterification reaction between **(1)** and 2,3,4,5,6-pentafluorophenol. The reaction was carried out using DCC as a coupling agent and catalytic amount of DMAP as catalyst to give perfluorophenyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate**(2)**(Equation 4.2).



(4.2)

On the next step, hydrolysis of compound **(2)** was taken placed in THF using 1 M HCl to produce 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate**(3).** The reaction was stirred in room temperature for 2 h. Process is given below. (Equation 4.3).



(4.3)

The ^{1}H NMR and ^{19}F NMR spectrums of the **1**, **2** and **3** are shown in Figure 4.1 and Figure 4.2. From the ^{1}H NMR spectrum, the peaks in the range between 4.33 and 3.67 ppm are assigned to methylene protons. The peaks in the range between 1.48 and 1.31 ppm are identified to methyl protons, when hydrolysis of **2** have conducted the peaks at 1.48 and 1.43 ppm disappeared. From the ^{19}F NMR spectrum, F signals of F substituted phenyl group were found at -152 (o-*F*), -157 (p-*F*) and -162 (m-*F*) ppm. The data derived from the ^{1}H NMR and ^{19}F NMR spectrums confirmed that preparation of perfluorophenyl diol carried out successfully.

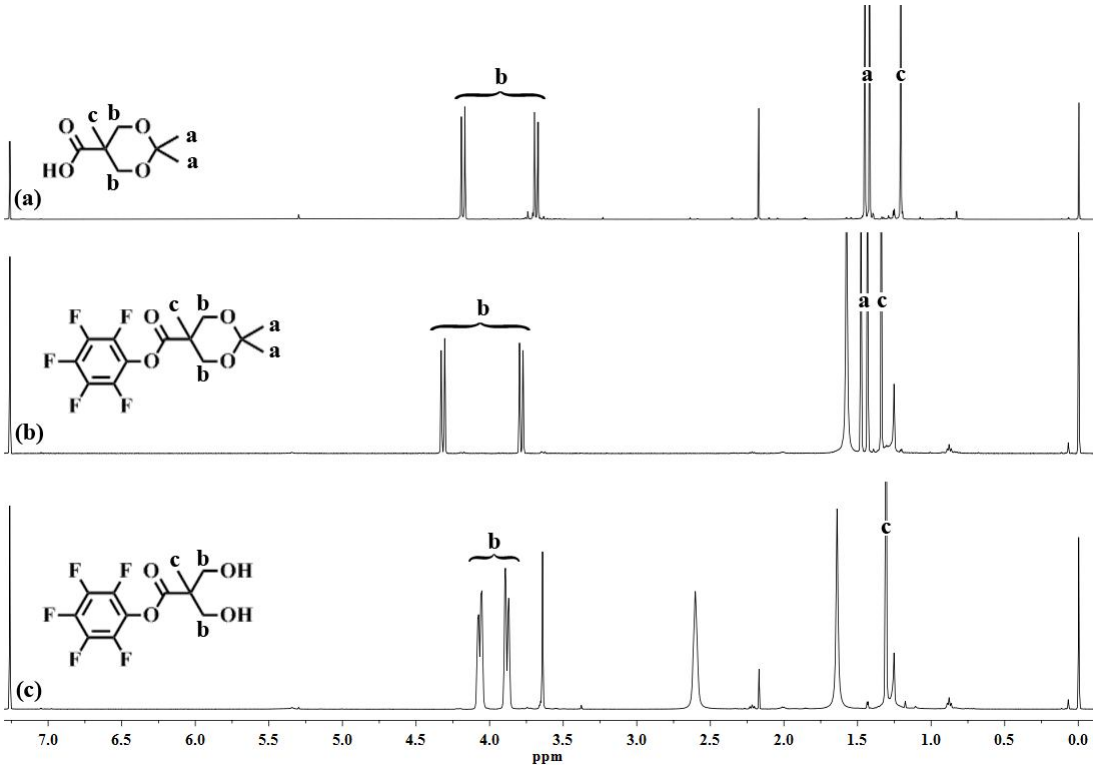


Figure 4.1 : ^{1}H NMR spectra of: **a)** 2,2,5-trimethyl-1,3-dioxane-5-carboxylic acid **(1)**,**b)**perfluorophenyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate **(2)**, **c)** perfluorophenyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate (perfluorophenyl diol) **(3)**, in $CDCl_3$.

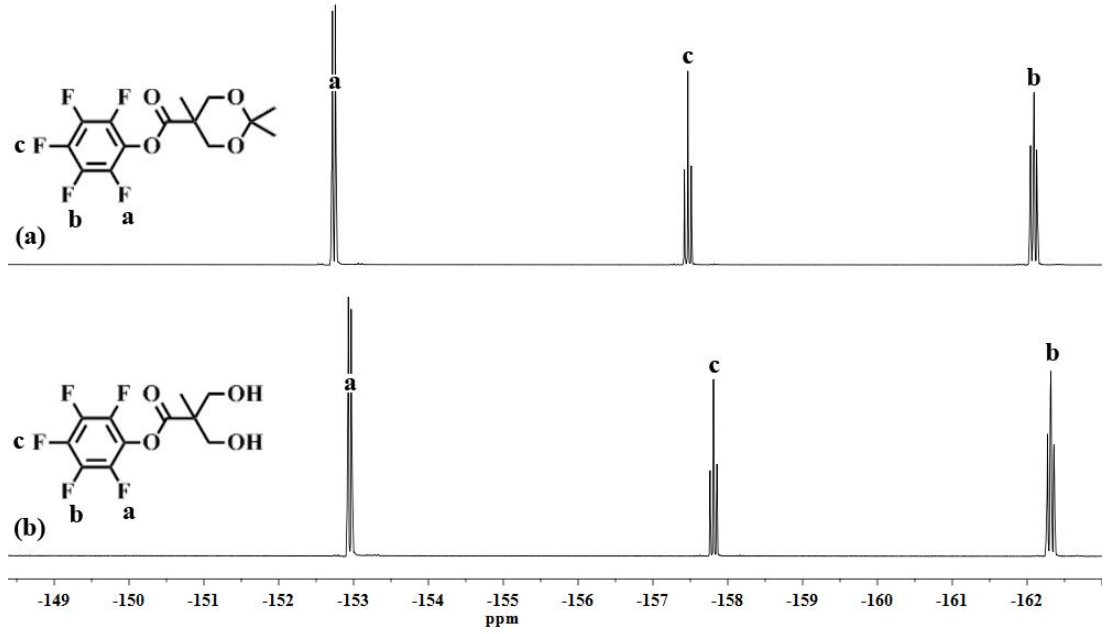
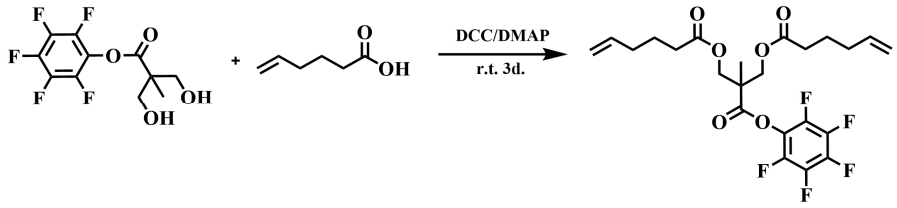


Figure 4.2 : ^{19}F NMR spectra of: **a)** perfluorophenyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate **(2)**, **b)** perfluorophenyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate (perfluorophenyl diol) **(3)**, in $CDCl_3$.

At the final step, synthesized pefluorophenyl diol**(3)**, was reacted with 5-hexenoic acid to give another esterification product, 2-methyl-2-((perfluorophenoxy)carbonyl)propane-1,3-diyl bis(hex-5-enoate)**(4)**. Reaction was carried out by using DCC and catalytic amount of DMAP. Reaction process shown below (Equation 4.4).



(4.4)

According to ^{1}H NMR spectrum of 4, Figure 4.3 proves that the monomer were synthesized succesfully. Disappearance of characteristic peaks of **3** at 4.33 and 3.67 ppm and appearance as a new peak around 4.36 ppm shows that the diol structure changed. Methyl peak of diol was expected to remain unchanged and it appeared at 1.47 ppm as estimated. The three distinctive peaks between 2.38 and 1.75 ppm are assigned to the protons of the main polymer chain. The peaks at the 5.77 and 5.02 ppm are assigned to the CH_2=C*H*$CH_2CH_2CH_2C$=O and C*H*$_2$=$CHCH_2CH_2CH_2C$=O in this order.

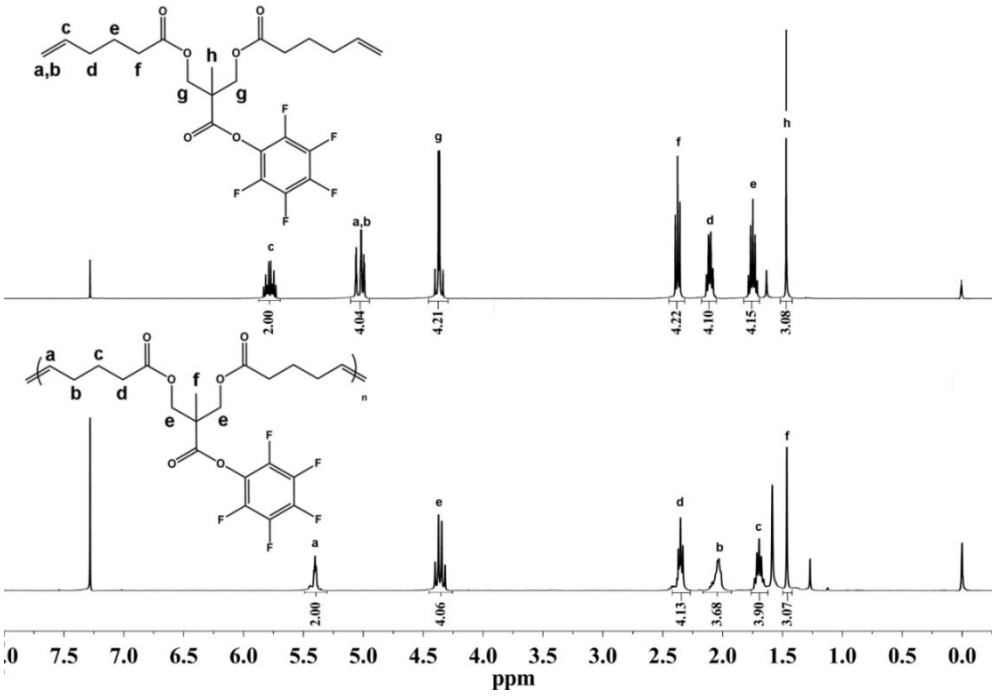
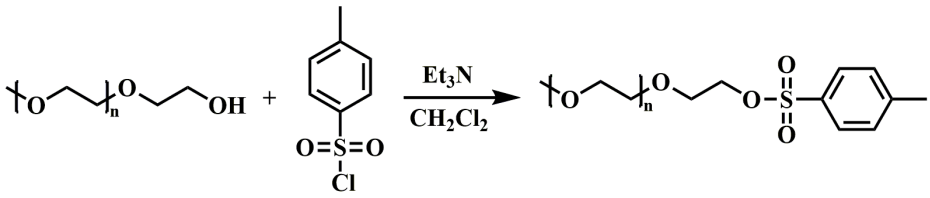


Figure 4.3 :^{1}H NMR spectra of activated ester functionalized monomer (**4**) (**up**) and ADMET polymer **(P1)** of **4**(**bottom**) in $CDCl_3$.

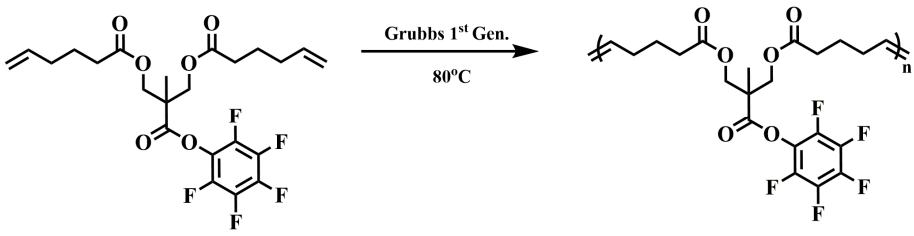
4.2 Preparation of Azide End Functional PEG

Poly(ethylene glycol) monomethyl ether was first tosylated using toluene-4-sulfonyl chloride and converted to azide by reacting NaN_3 in DMF at room temperature (Equation 4.5). After purification steps azide end functional PEG obtained as colorless viscous liquid.



(4.5)

4.3 Preparation of Active Ester Functional ADMET Polymer



(4.6)

^{1}H NMR confirmed the expected structure of ADMET polymer**(P1)**. ^{1}H NMR spectra comparison of **P1** and **4** (Figure 4.3) shows that the protons of the diene functionality disappeared after reaction and also CH_2=C*H*$CH_2CH_2CH_2$C=O proton peak of the compound shifted from 5.77 to 5.40 ppm after polymerization.

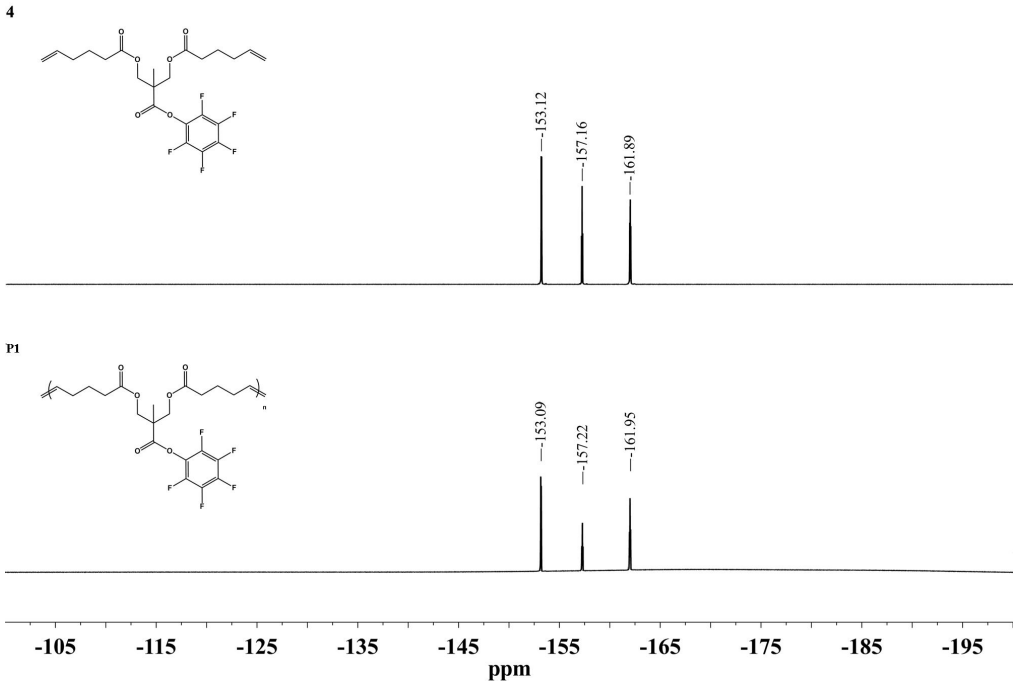


Figure 4.4 : ^{19}F NMR spectra of activated ester functionalized monomer (**4**) (**up**) and ADMET polymer **(P1)** of **4**(**bottom**) in $CDCl_3$.

^{19}F NMR spectrum of **P1** (Figure 4.4) showed that the *m*-F at -161.95 ppm, *p*-F at -157.22 ppm and *o*-F at 153.09 ppm appeared after the reaction. These results proved that the pentafluorophenyl containing polymer was successfully synthesized. Also ^{13}C NMR spectrum of **P1** confirmed the structure (Figure 4.5).

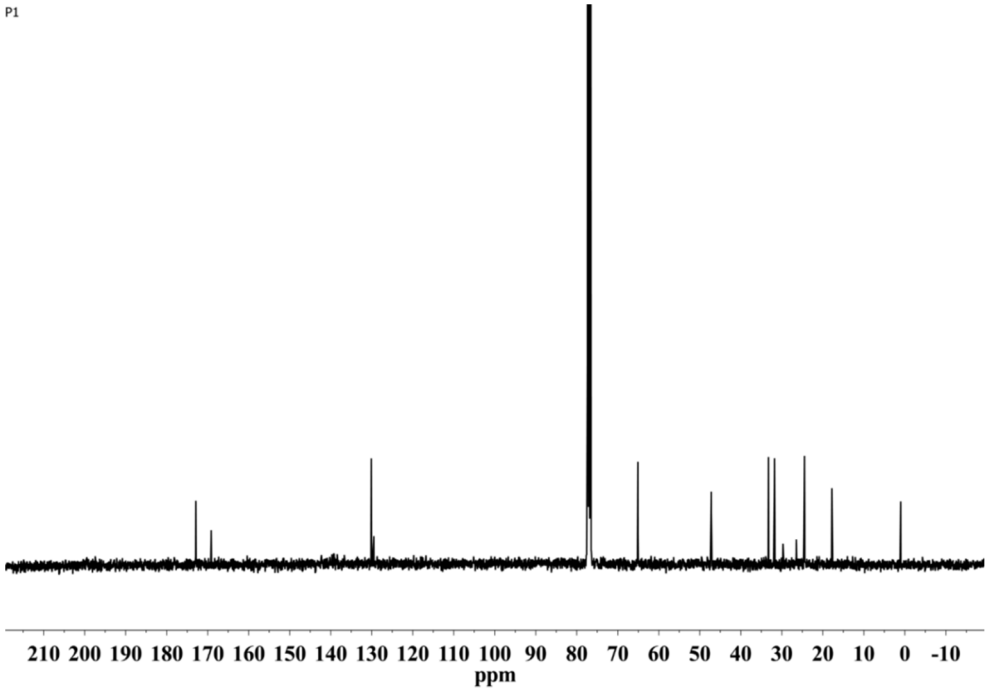


Figure 4.5 : ^{13}C NMR spectrum of **P1** in $CDCl_3$.

After several attempts on the polymerization process, to achieve best results and efficient reaction conditions, different reaction conditions were tested(Table 4.1). After these attempts, results showed that the most suitable reaction condition was bulk polymerization at 80°C using Grubbs 1st Gen. catalyst.

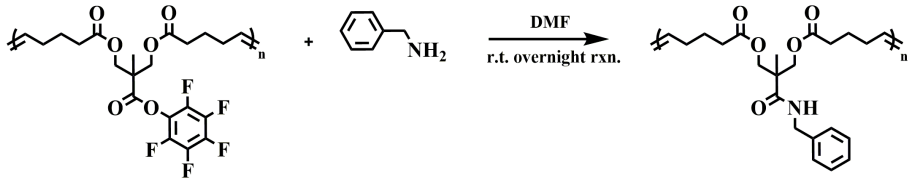
Table 4.1: Results of model ADMET polymerizations to test the catalyst performance.

Run	M_n[e]	M_w[e]	M_w/M_n[e]
1[a]	21200	36800	1.74
2[b]	13000	18900	1.45
3[c]	-	-	-
4[d]	-	-	-

[a]Reaction was performed at 80 °C employing G1 as catalyst.
[b]Reaction was performed at 80 °C employing GH-II as catalyst.
[c]Reaction was performed at 80 °C in ODCB employing G1 as catalyst.
[d]Reaction was performed at 80 °C in ODCB employing GH-II as catalyst.
[e]Obtained by GPC calibrated on the basis of linear PS standards in THF at 30 °C.

4.4 Active Ester Substitution Reactions

In the first step, four types of amines were used to substitute with active perfluorophenyl group of **P1**. First attempt was made with benzylamine at room temperature, as an overnight reaction(Equation 4.7).



(4.7)

Both ^{1}H NMR and ^{19}F NMR confirmed that the active ester substitution reactions were successfully made. Proton peaks between 7.4 and 7.2 ppm were identified as Ar*H* of the benzyl group, and also Ar-CH_2 peak appeared at 4.45 ppm. Around 6.44 ppm, N*H* peak was also seen(Figure 4.6). The absence of peaks on ^{19}F NMR spectrum proved that 100% conversion was obtained(Figure 4.7). FT-IR spectrum also showed, N-H streching around 3500-3200 cm^{-1} and C=O streching of amide

structure around 1700-1650 cm^{-1}(Figure 4.9). ^{13}C NMR spectrum also confirmed the structure (Figure 4.8).

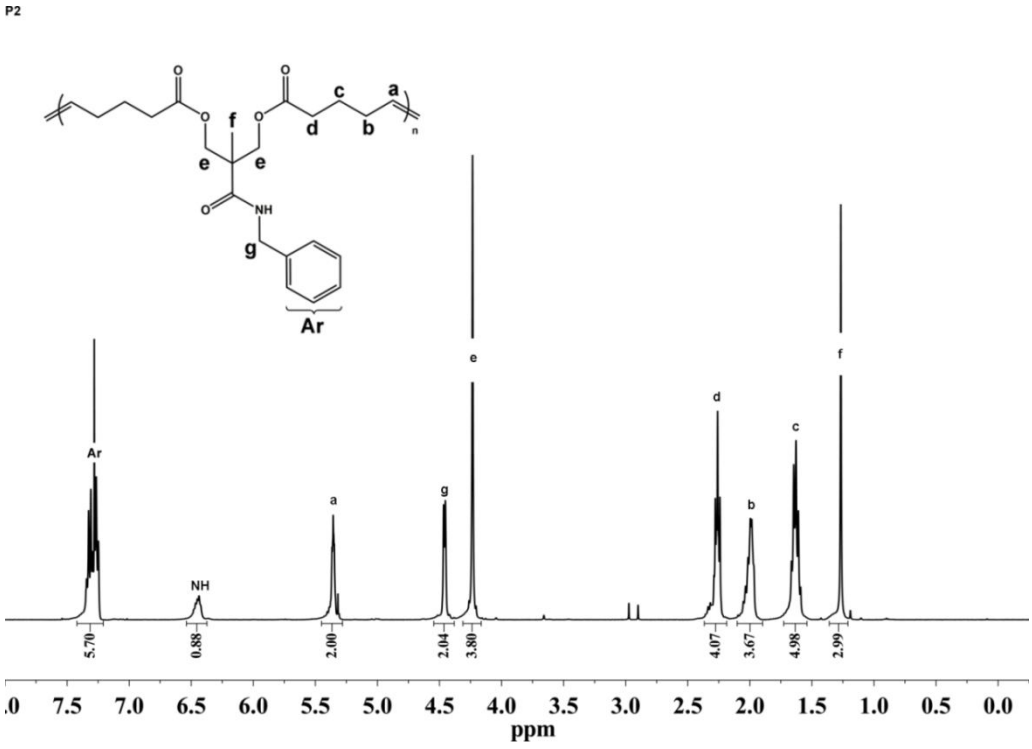


Figure 4.6 : ^{1}H NMR spectrum of **P2** in $CDCl_3$.

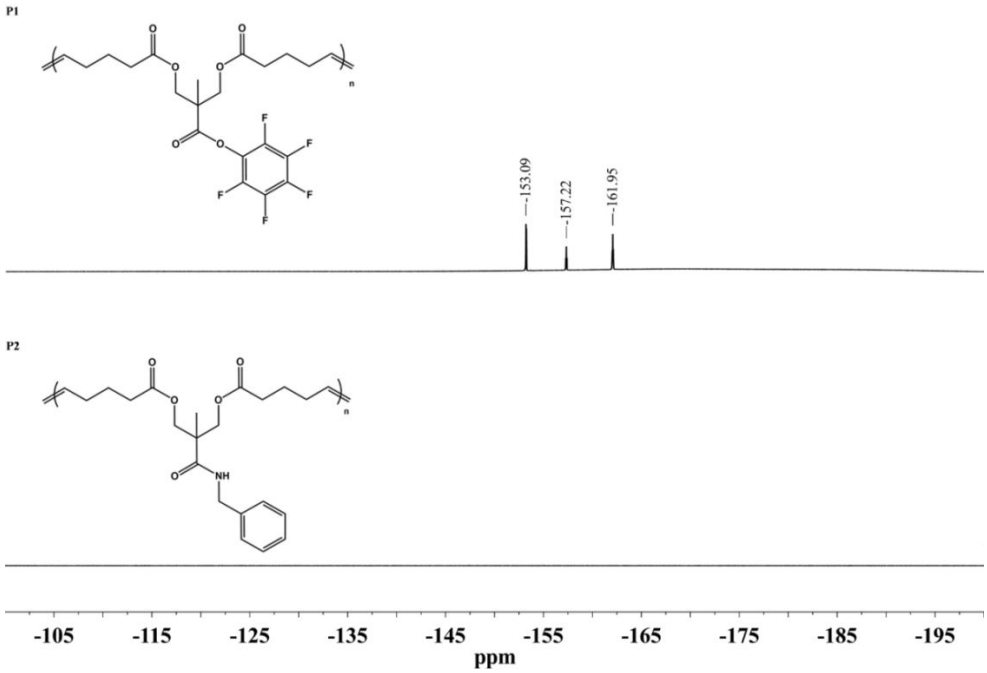


Figure 4.7 : ^{19}F NMR spectra of **P1** before (**up**) and after (**bottom**) the activated ester substitution reaction with benzylamine (**P2**) in $CDCl_3$.

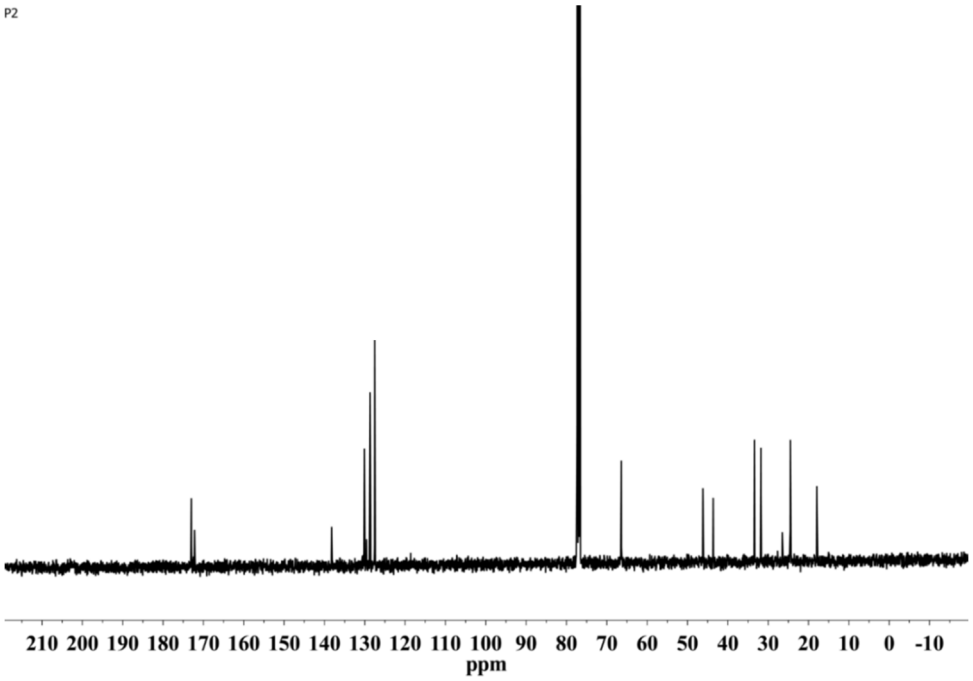


Figure 4.8 : ^{13}C NMR spectrum of **P2** in $CDCl_3$.

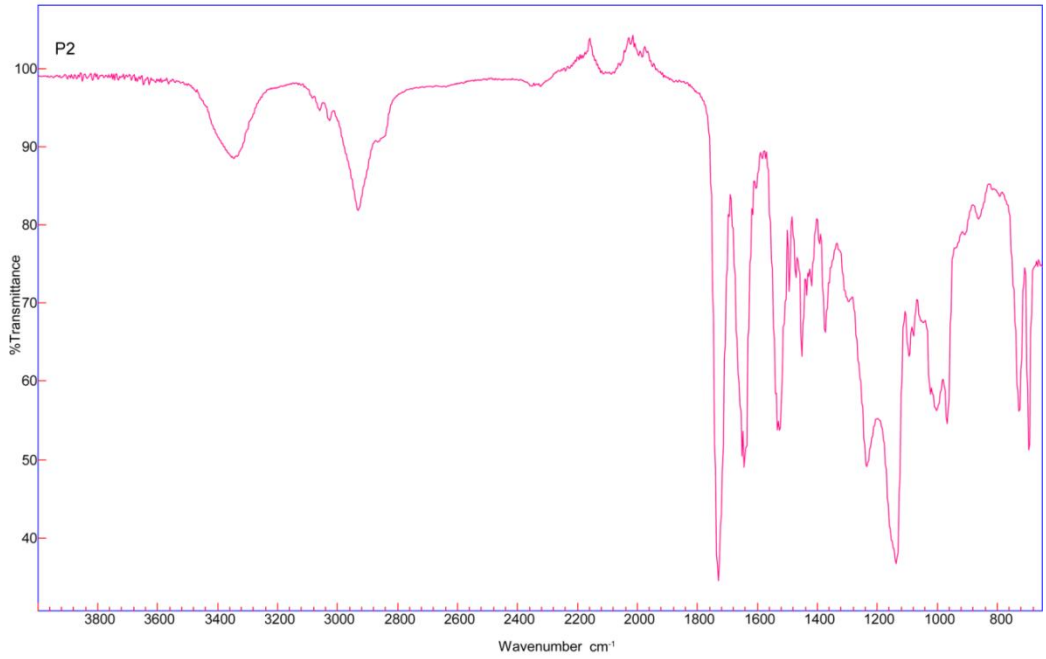
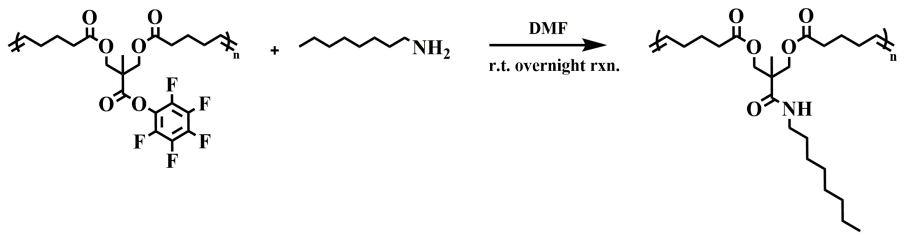


Figure 4.9 :FTIR spectrum of **P2**.

Second attempt was made with octylamine at room temperature, as an overnight reaction(Equation 4.7).



(4.7)

Both ^{1}H NMR and ^{19}F NMR confirmed that the active ester substitution reactions were successfully made. Proton peaks were identified as NHCH_2CH$_2$ at 3.27, NHCH$_2$CH_2 at 1.5, CH_2 of octyl at 1.3 and CH_3(CH$_2$)$_7$NH at 0.89 ppm. Around 6.07 ppm, N*H* peak was also seen(Figure 4.10). The absence of peaks on ^{19}F NMR spectrum showed, 100% conversion was obtained(Figure 4.11). FT-IR spectrum also confirmed, N-H streching around 3500-3200 cm^{-1} and C=O streching of amide structure around 1700-1650 cm^{-1}(Figure 4.13). ^{13}C NMR spectrum also confirmed the structure (Figure 4.12).

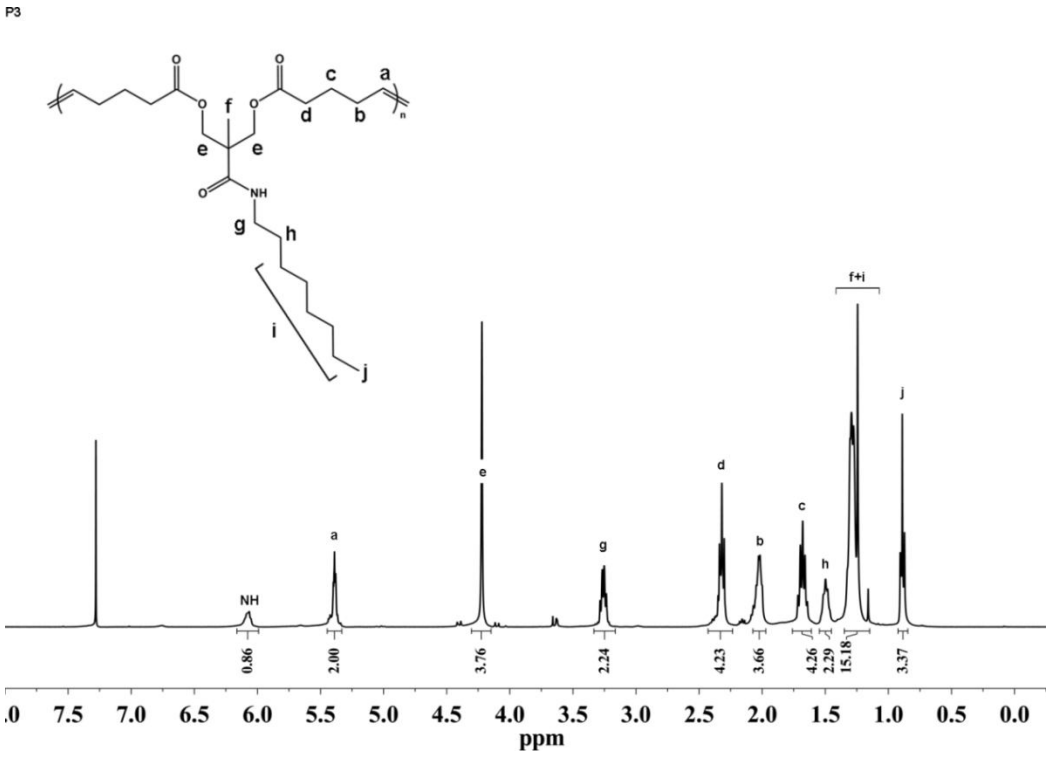


Figure 4.10 :^{1}H NMR spectrum of **P3** in $CDCl_3$.

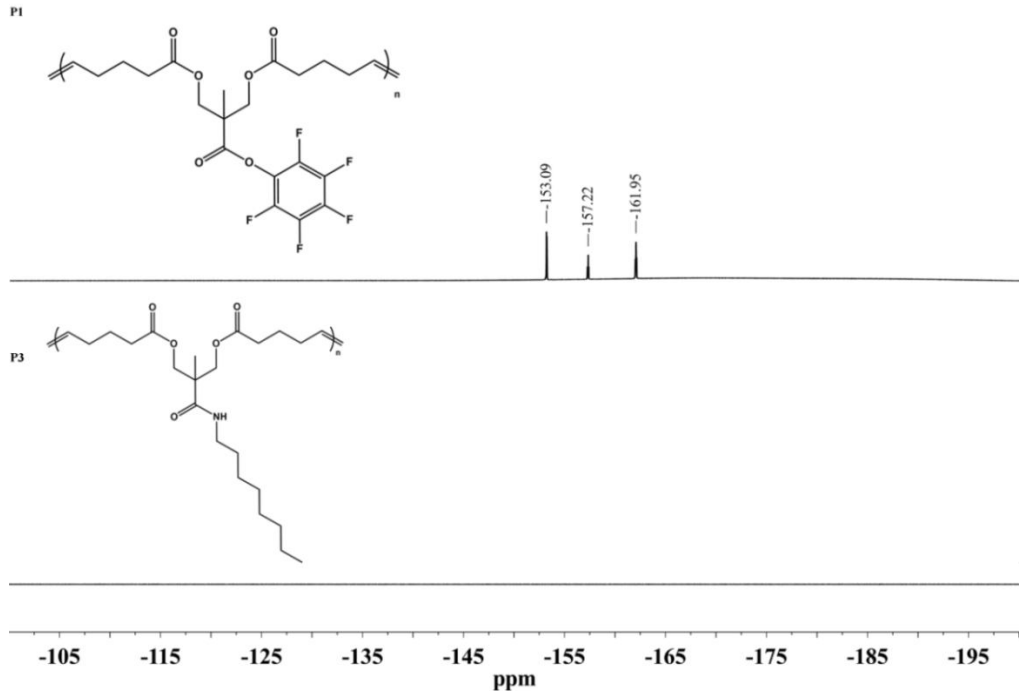


Figure 4.11 : ^{19}F NMR spectra of **P1** before(**up**) and after (**bottom**) the activate ester substitution reaction with octylamine (**P3**) in $CDCl_3$.

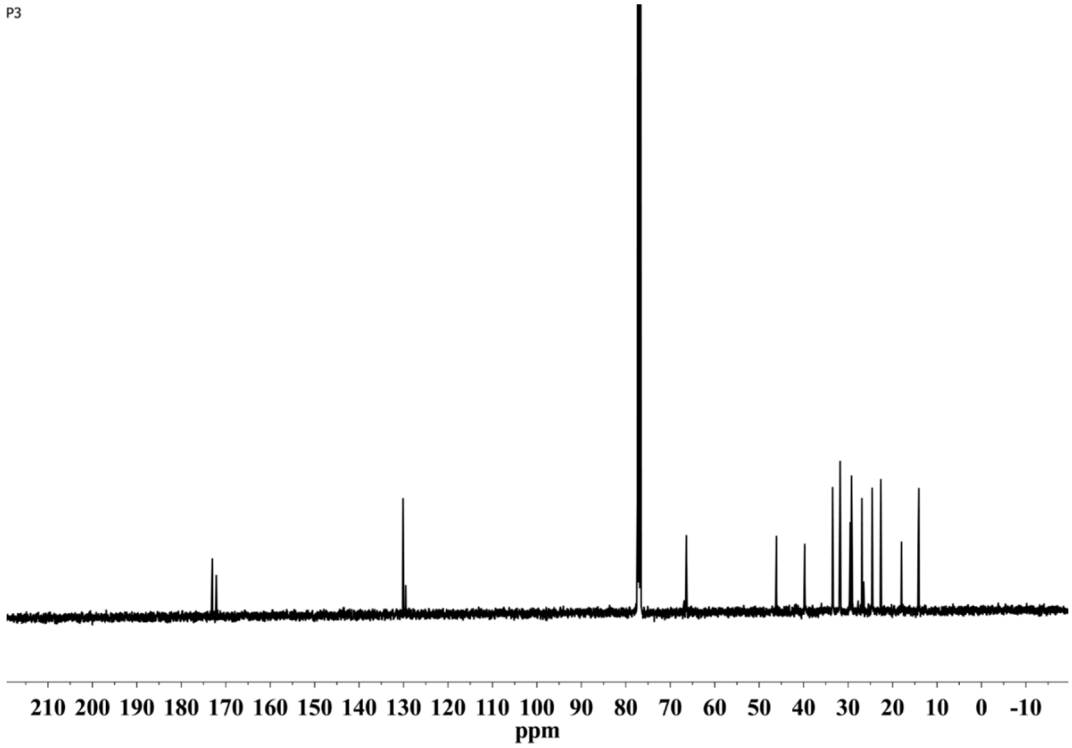


Figure 4.12 : ^{13}C NMR spectrum of **P3** in $CDCl_3$.

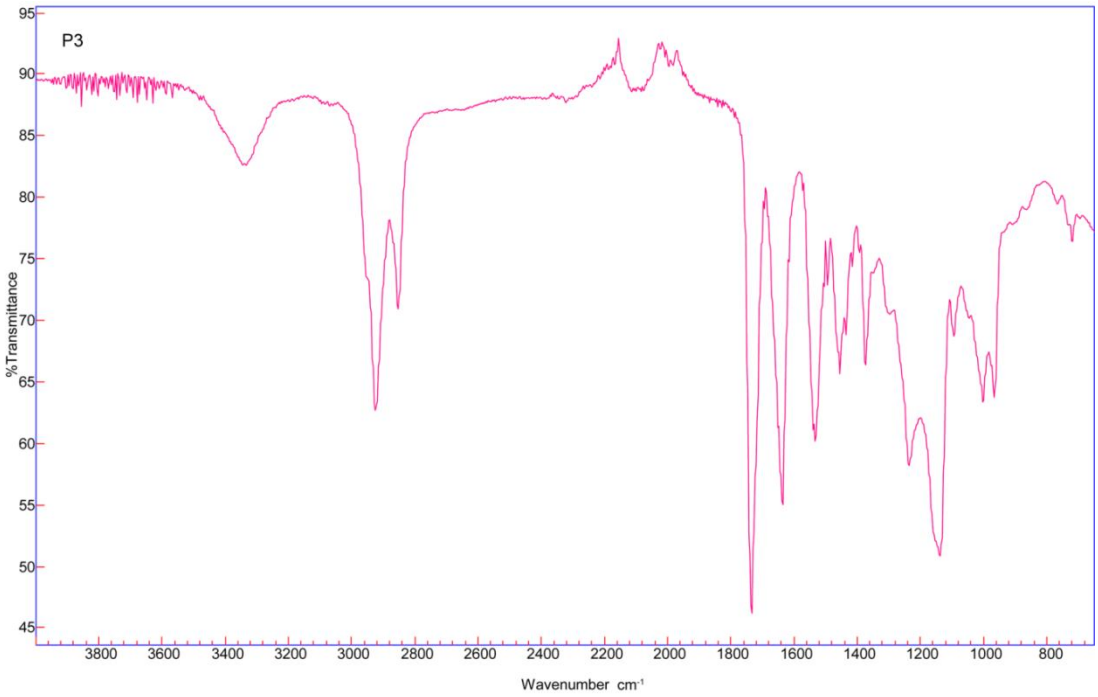
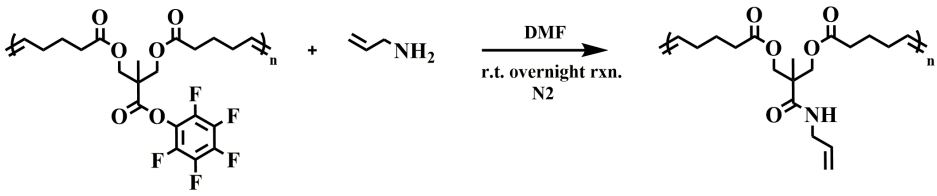


Figure 4.13 :FTIR spectrum of **P3**.

The third attempt was performed with allylamine at room temperature, as an overnight reaction(Equation 4.8). Reaction conditions remained the same as the previous attempts on the **P1**, but only the substituted amine was changed with allylamine.



(4.8)

Both ^{1}H NMR and ^{19}F NMR confirmed that the active ester substitution reactions were successfully made. Proton peaks were identified as $NHCH_2CH{=}CH_2$ at 5.84, $NHCH_2CH{=}CH_2$ at 5.16 and $NHCH_2CH{=}CH_2$ at 3.91 ppm. Around 6.20 ppm, N*H* peak was also seen(Figure 4.14). The absence of peaks on ^{19}F NMR spectrum showed, 100% conversion was obtained(Figure 4.15). FT-IR spectrum also showed, N-H streching around 3500-3200 cm^{-1} and C=O streching of amide structure around 1700-1650 cm^{-1}(Figure 4.17). ^{13}C NMR spectrum also confirmed the structure (Figure 4.16).

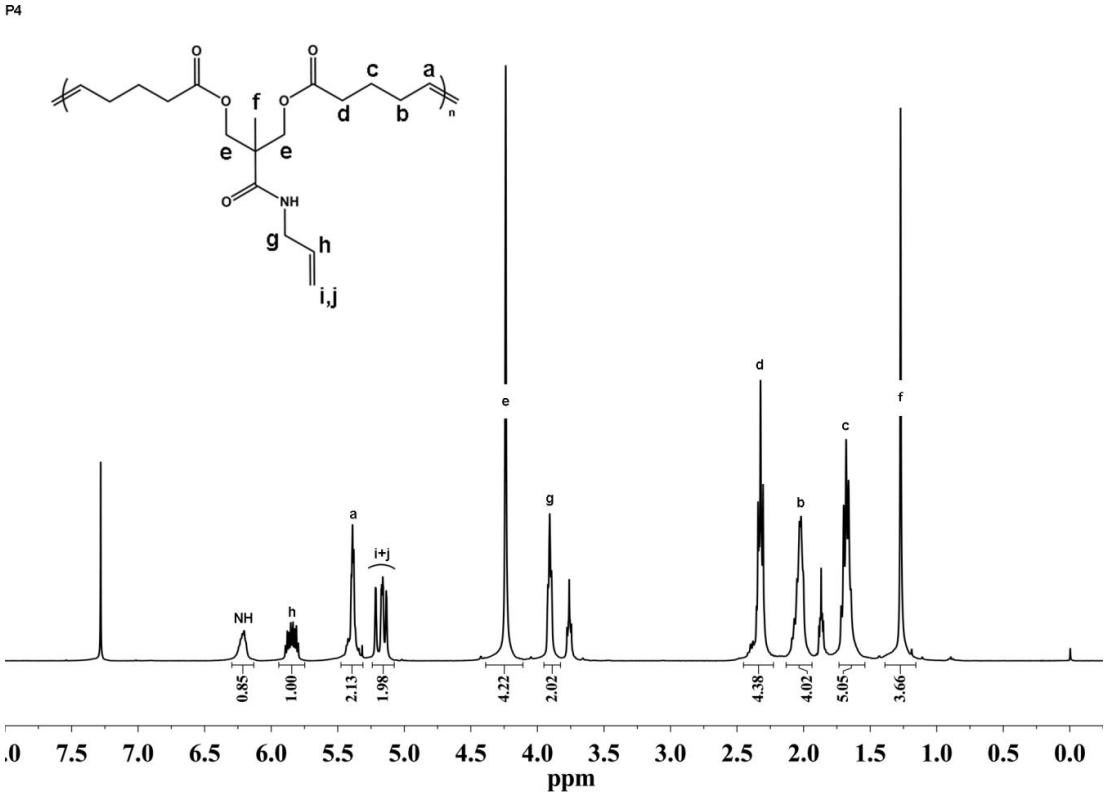


Figure 4.14 : ^{1}H NMR spectrum of **P4** in $CDCl_3$.

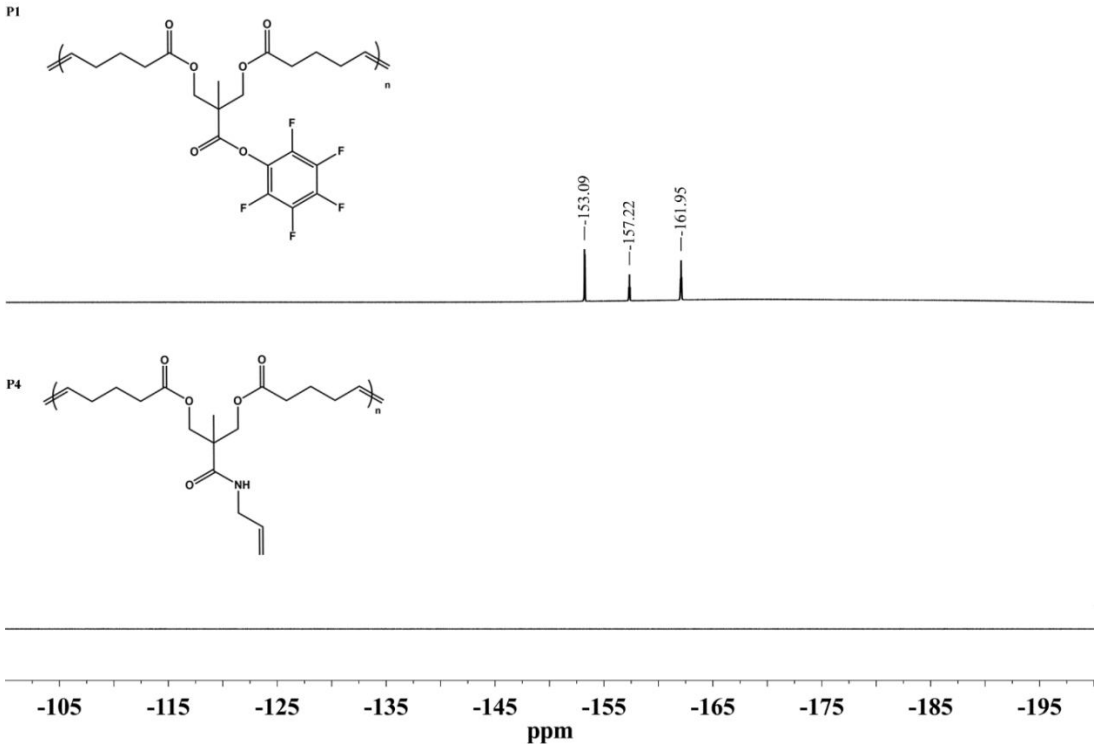


Figure 4.15 : ^{19}F NMR spectra of **P1** before (**up**) and after (**bottom**) the activate ester substitution reaction with allylamine (**P4**) in $CDCl_3$.

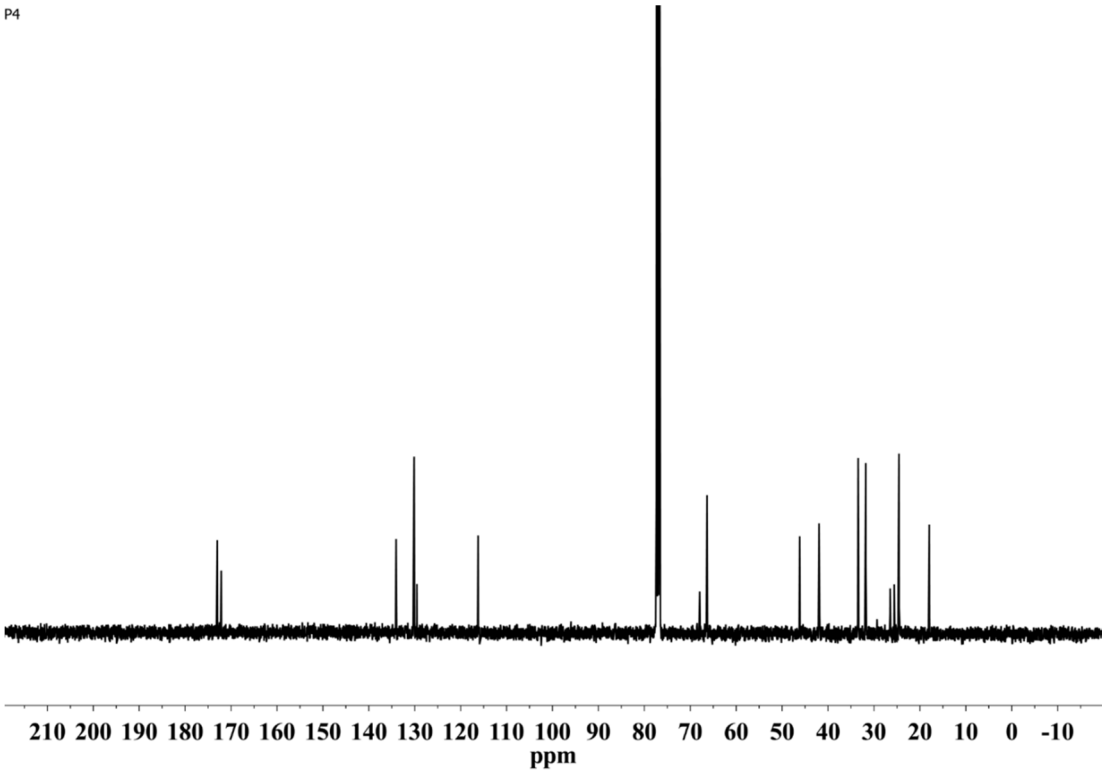


Figure 4.16 : ^{13}C NMR spectrum of **P4** in $CDCl_3$.

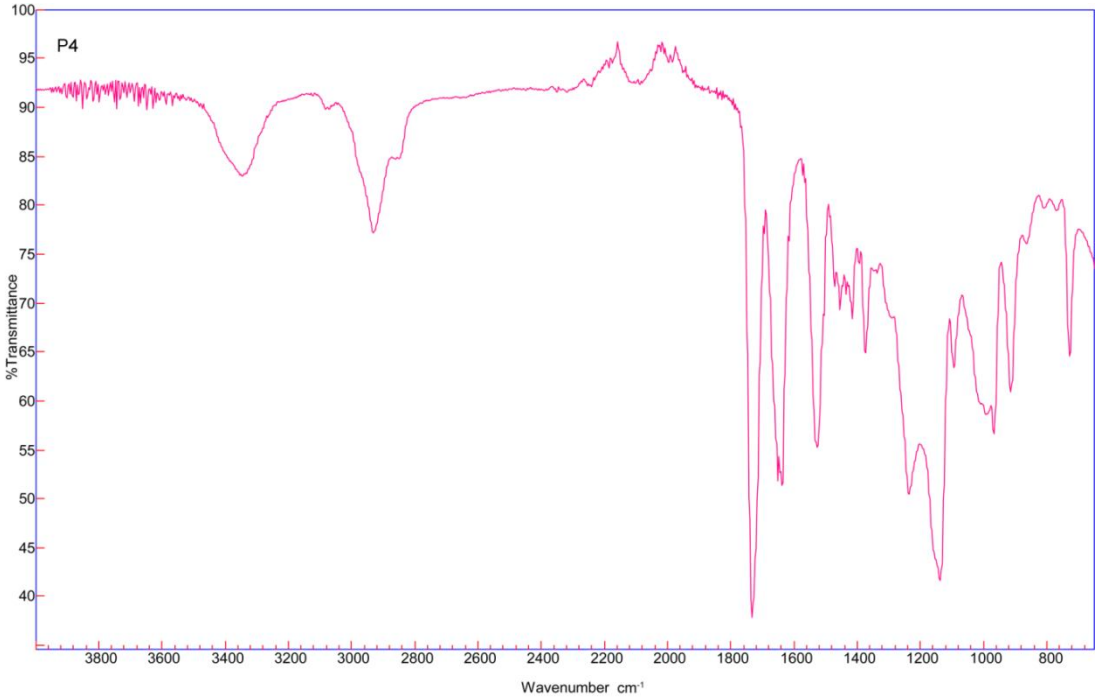
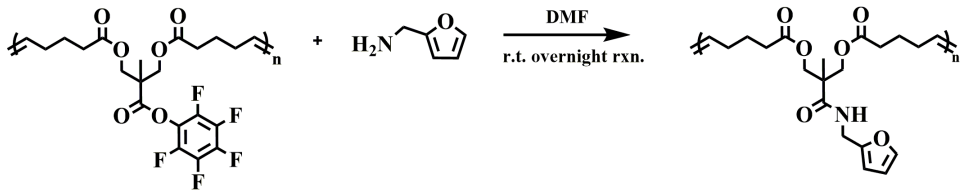


Figure 4.17 :FTIR spectrum of **P4**.

The final attempt was made with furfurylamine at room temperature, as an overnight reaction(Equation 4.9).



(4.9)

Both ^{1}H NMR and ^{19}F NMR confirmed that the active ester substitution reactions were successfully made. Proton peaks at 7.35, 6.33 and 6.23 ppm were identified as C*H* peaks of furan group, and also NHCH_2-furan peak appeared at 4.44 ppm. Around 6.45 ppm, N*H* peak was also seen(Figure 4.18). The absence of peaks on ^{19}F NMR spectrum showed, 100% conversion was obtained(Figure 4.19). FT-IR spectrum also showed, N-H streching around 3500-3200 cm^{-1} and C=O streching of amide structure around 1700-1650 cm^{-1}(Figure 4.21). ^{13}C NMR spectrum also confirmed the structure (Figure 4.20).

GPC results of the all five polymers are shown below(Figure 4.22) and according to these results, almost every value acquired from Table 4.2 was obtained as expected. Figure 4.23 gives the DSC results of the polymers. According to the glass transition temperature values of the polymers, resulting polymer of the reaction between **P1** and octylamine is the only exception, since the hydrodynamic behaviour of the octylamine.

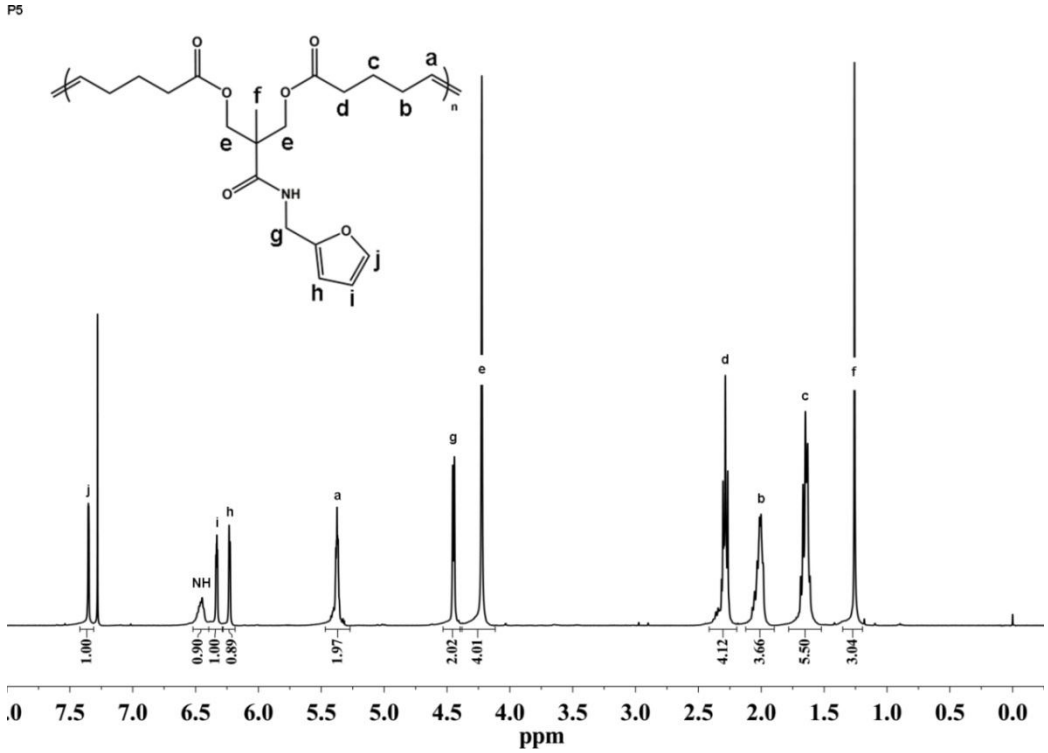


Figure 4.18 : ^{1}H NMR spectrum of **P5** in $CDCl_3$.

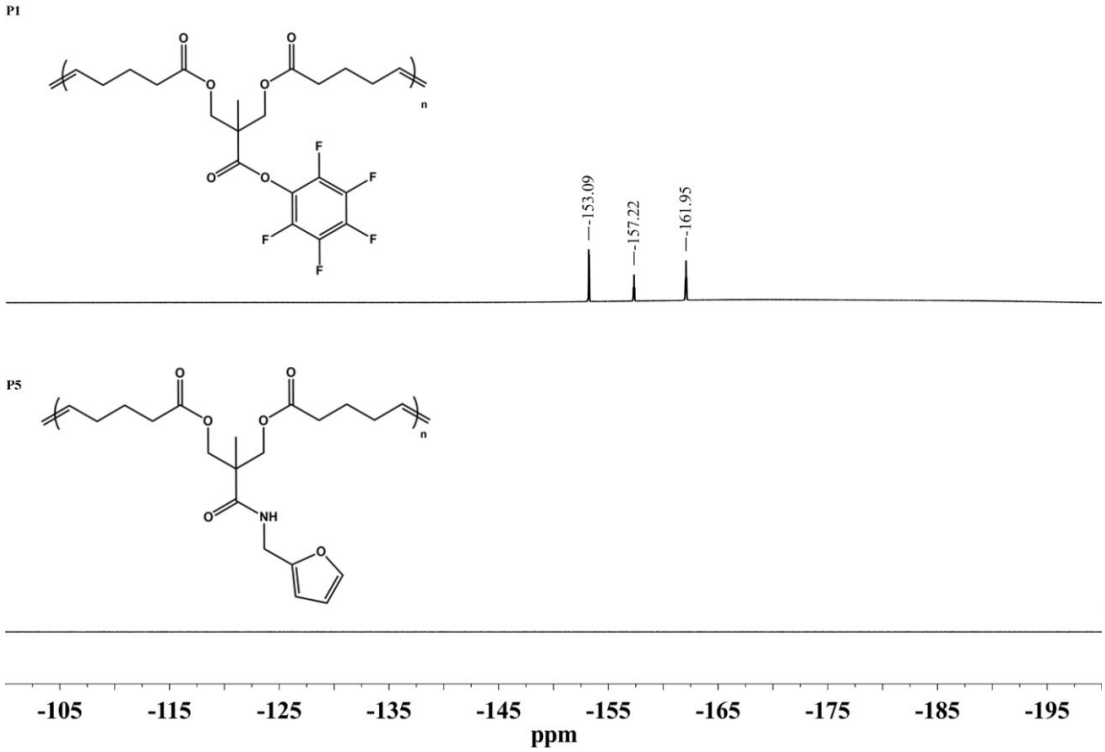


Figure 4.19 : ^{19}F NMR spectra of **P1** before (**up**) and after (**bottom**) the activate ester substitution reaction with furfurylamine (**P5**) in $CDCl_3$.

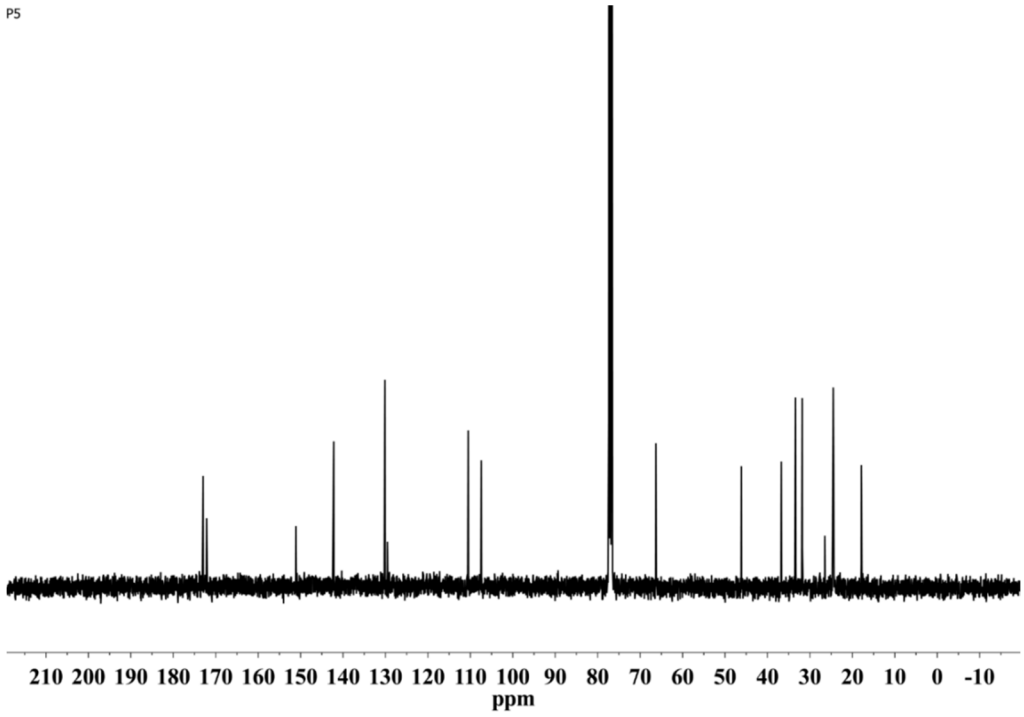


Figure 4.20 : ^{13}C NMR spectrum of **P5** in $CDCl_3$.

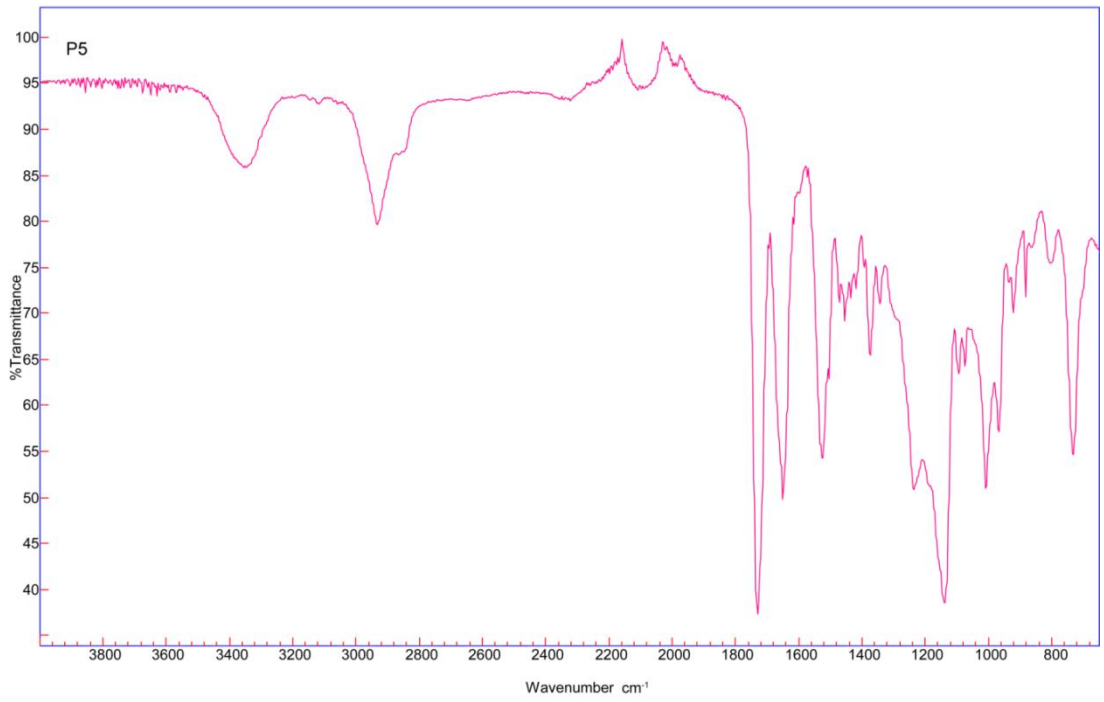


Figure 4.21 :FTIR spectrum of **P5**.

Table 4.2: Characterizations of activated ester functional polymer and subsequent post-functionalized polymers after active ester substitution reactions.

Polymer	M_n[e]	M_w[e]	M_w/M_n[e]	T_g[f]
P1	21200	36800	1.74	-19 °C
P2[a]	17700	23550	1.33	-4 °C
P3[b]	6100	9100	1.50	-33 °C
P4[c]	14000	20850	1.49	-20 °C
P5[d]	15100	22900	1.52	-12 °C

[a]Benzyl side chain.[b]Octyl side chain. [c]Allyl side chain. [d]Furfuryl side chain. [e]Obtained by GPC calibrated on the basis of linear PS standards in THF at 30 °C.[f]Measured by DSC.

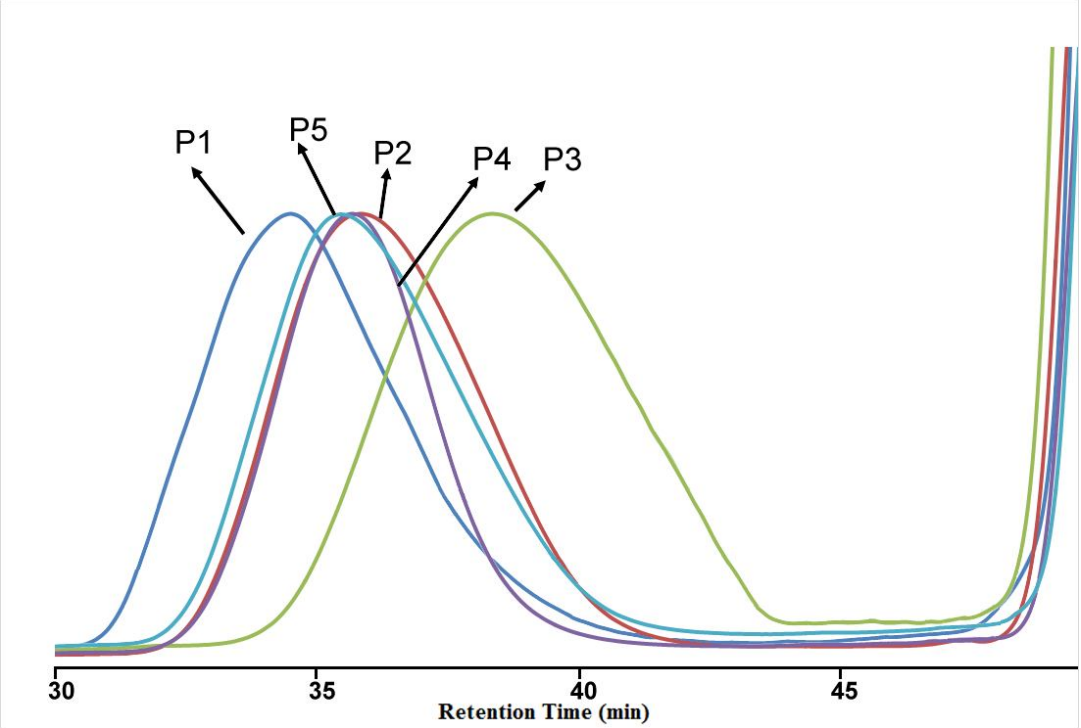


Figure 4.22 : Overlay GPC traces of **P1**, **P2**, **P3, P4** and **P5** in THF at 30°C.

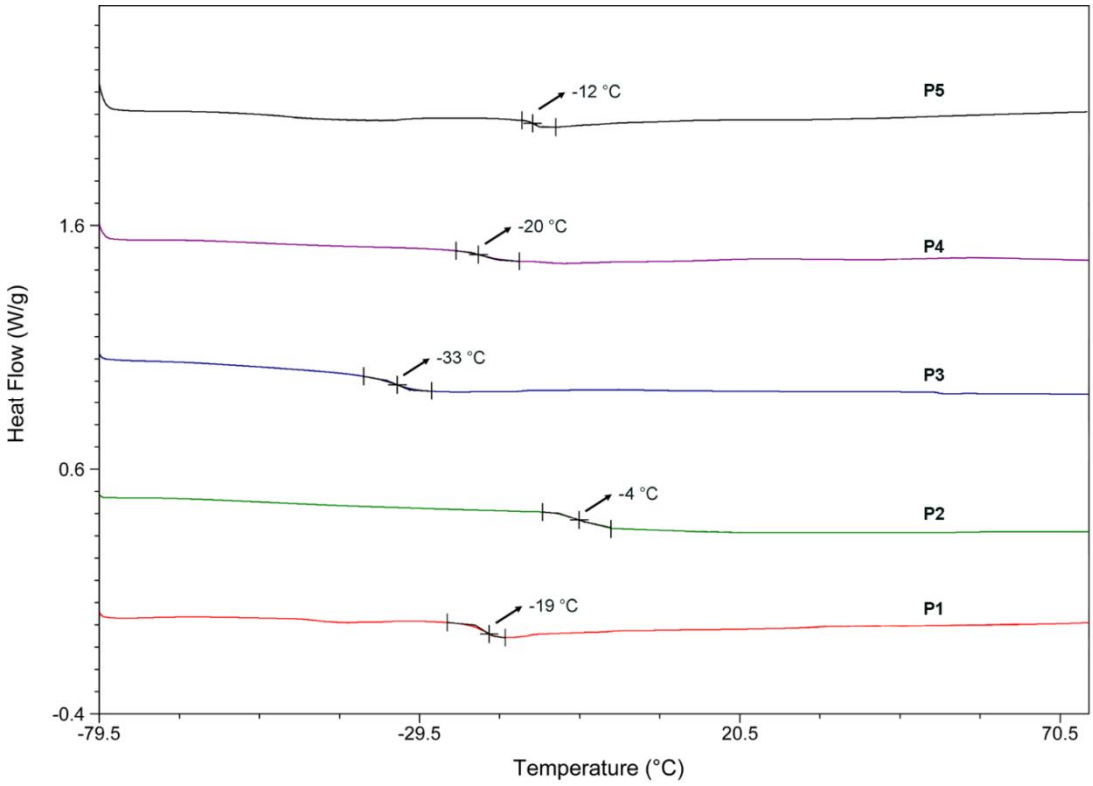
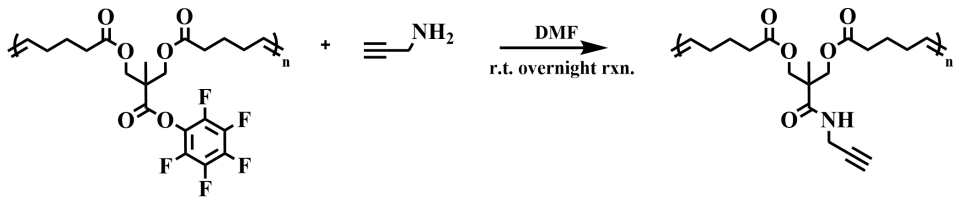


Figure 4.23 :DSC overlay of P1, P2, P3, P4 and P5.

4.5 Preparation of Clickable ADMET Polymer

To prepare a polymer which is suitable for a click reaction, **P1** was reacted with propargylamine in DMF at room temperature as an overnight reaction(Equation 4.10).



(4.10)

^{1}H NMR and ^{19}F NMR confirmed that the active ester substitution reactions were successfully made as previous substitution attempts. The characteristic proton peaks of the **P1** remained at the ^{1}H NMR spectrum with slightly shifts, but expected proton peaks appeared at 4.06 ppm and 2.28 ppm(Figure 4.24). Also absence of the F peaks of the perfluorophenyl compound confirmed the substitution(Figure 4.25). FT-IR spectrum showed, N-H streching around 3500-3200 cm^{-1} and C=O streching of amide structure around 1700-1650 cm^{-1}In addition to that, C-C triple bond streching

caused by the propargylamine observed around 2100 cm^{-1}(Figure 4.27). ^{13}C NMR spectrum also confirmed the structure (Figure 4.26).

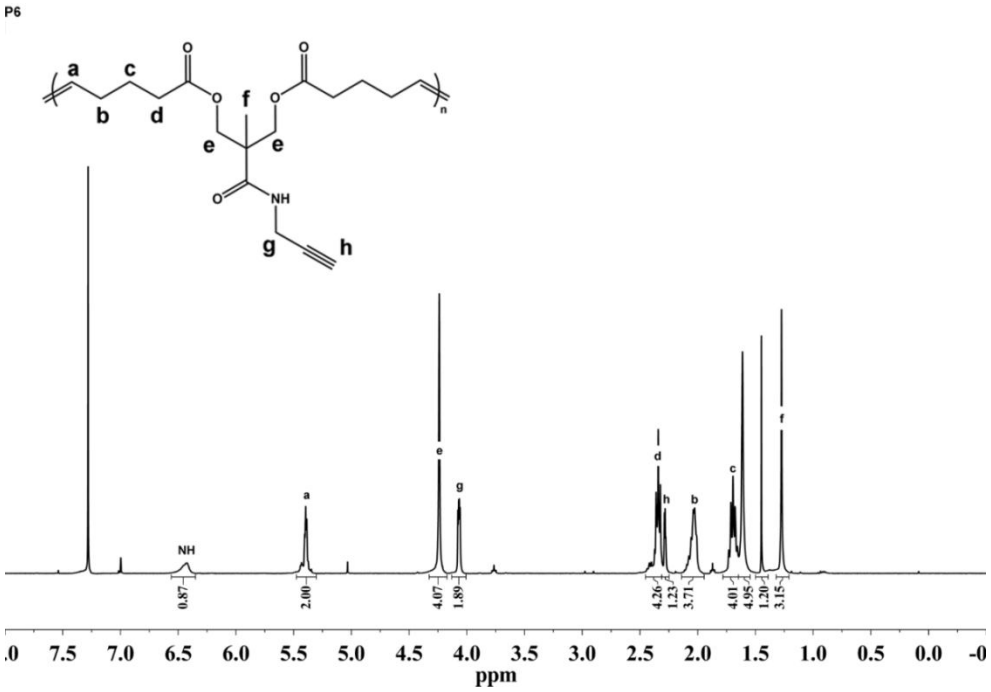


Figure 4.24 : ^{1}H NMR spectrum of **P6** in $CDCl_3$.

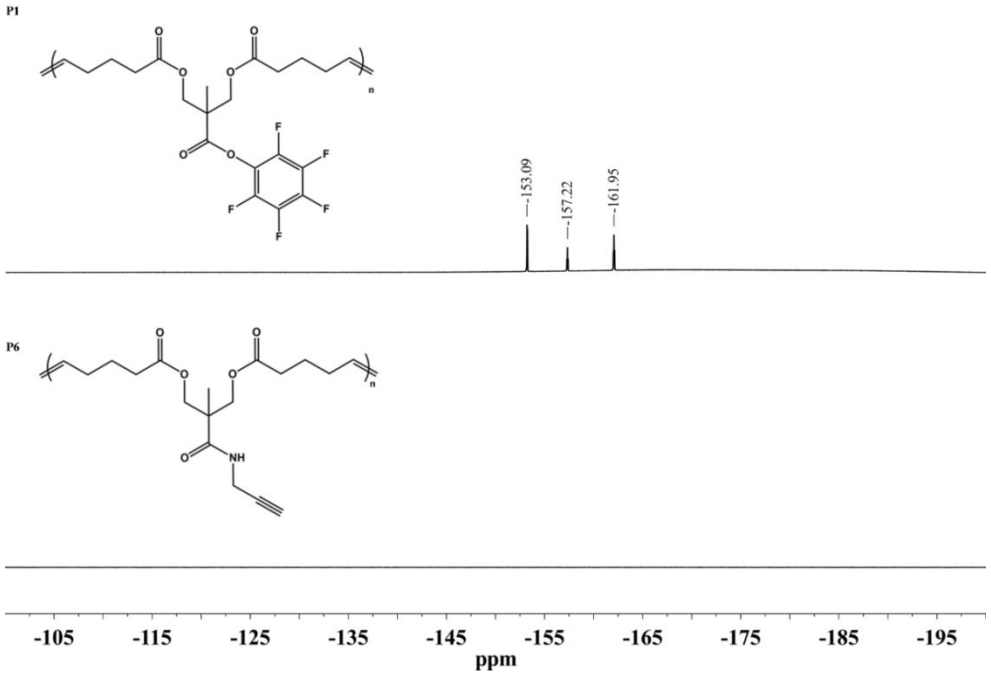


Figure 4.25 : ^{19}F NMR spectra of **P1** before (**up**) and after (**bottom**) the activate ester substitution reaction with propargylamine (**P6**) in $CDCl_3$.

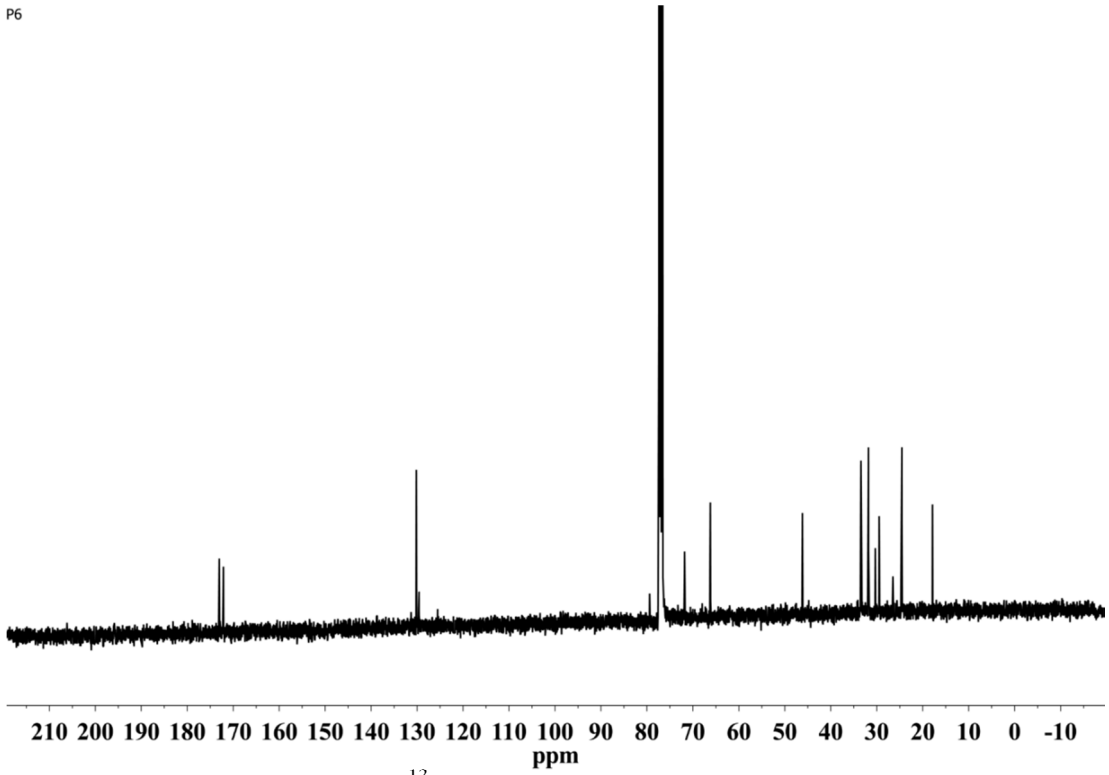


Figure 4.26 : ^{13}C NMR spectrum of **P6** in $CDCl_3$.

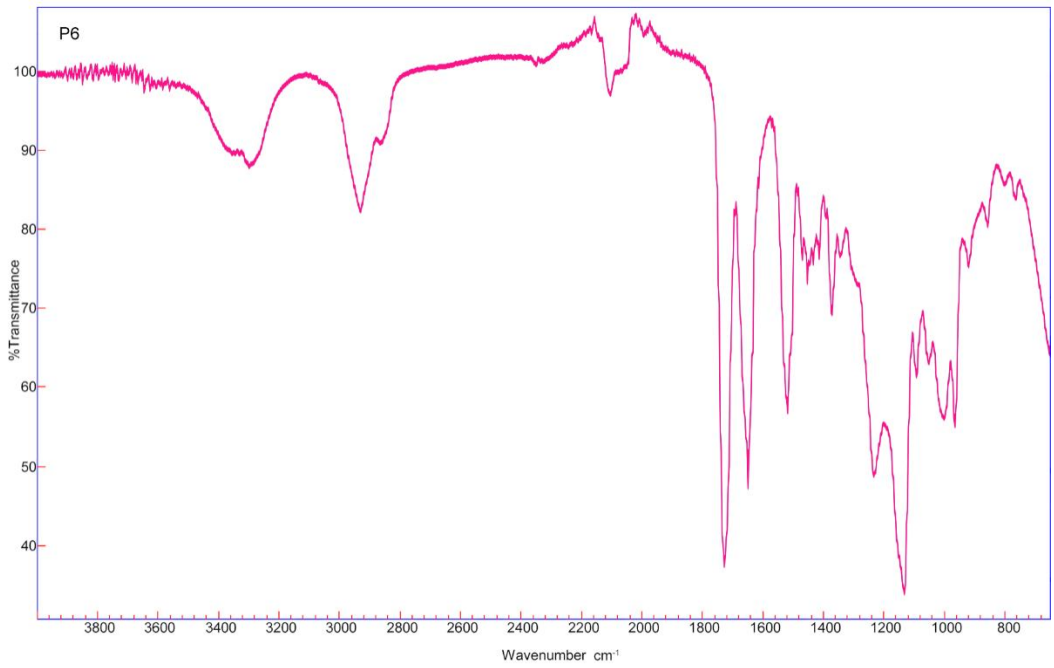
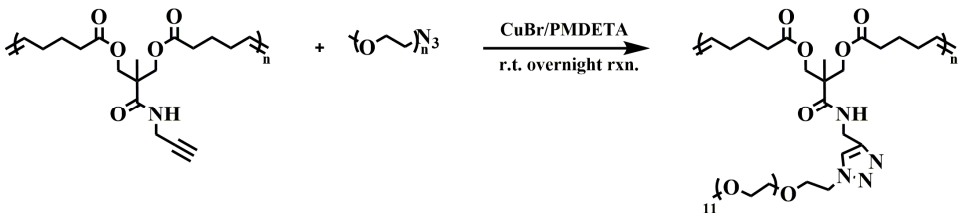


Figure 4.27 :FTIR spectrum of **P6**.

At the final step, successfully synthesized **P6** was reacted with azide end-functional PEG in DMF in the presence of CuBr/PMDETA at room temperature for 24 h (Equation 4.11).



(4.11)

According to the ^{1}H NMR and FT-IR results, click reaction succeeded with high yield. In addition to the characteristic proton peaks of the **P1**, new peaks of the PEG appeared at 3.39, 3.70, 3.87, 4.60 and 7.74 ppm (Figure 4.28). Figure 4.30 shows the FT-IR results as a comparison and the stretching band of the C-O-C belonging to the click product around 1100 cm^{-1} .The ^{13}C NMR spectrum of the final product is shown below (Figure 4.29).

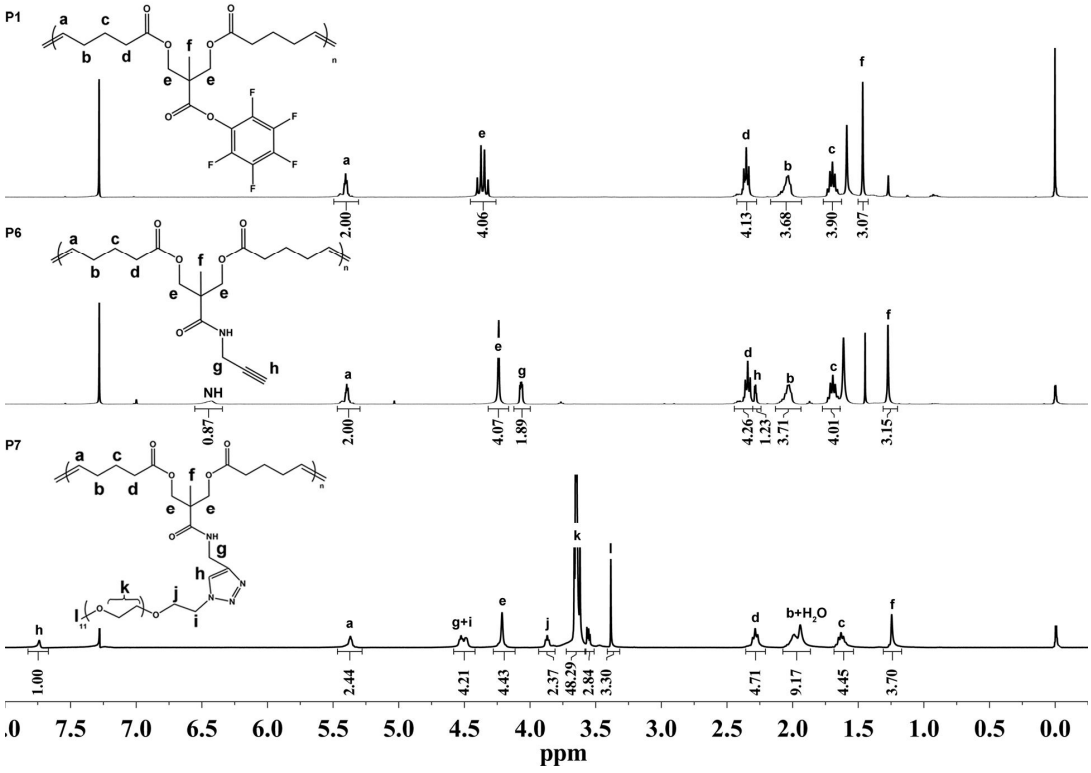


Figure 4.28 :^{1}H NMR spectra of **P1**, **P6** and **P7**in $CDCl_3$.

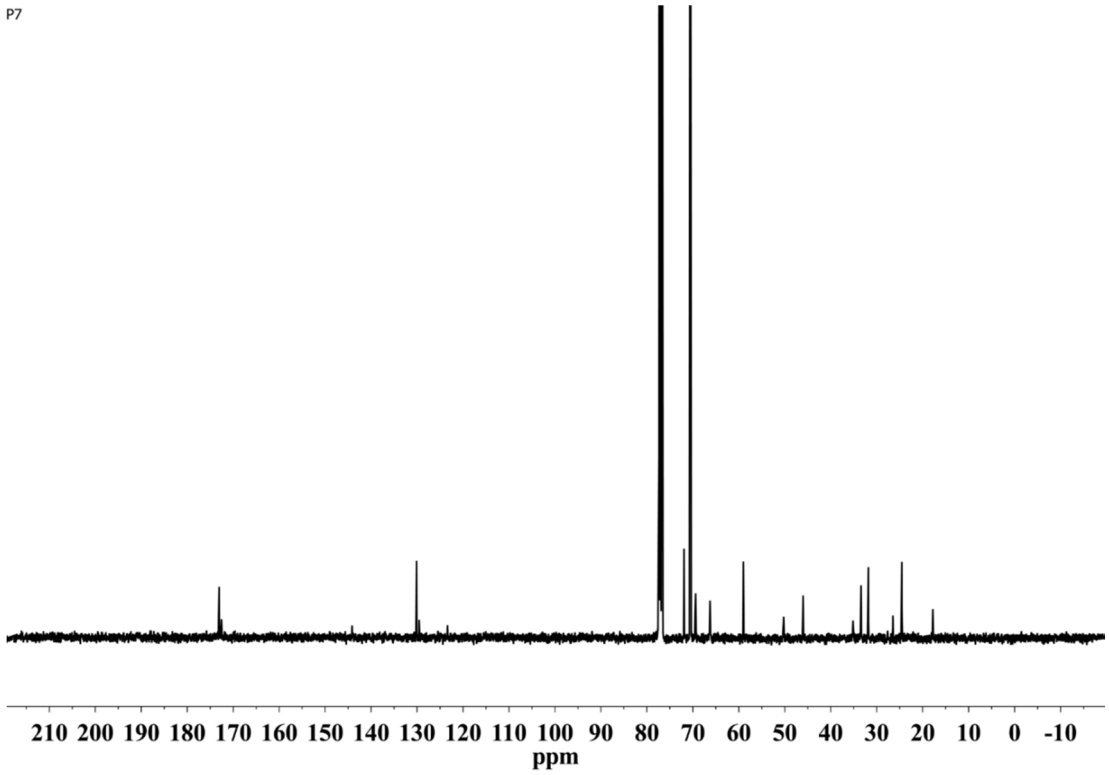


Figure 4.29 : ^{13}C NMR spectrum of **P7** in $CDCl_3$.

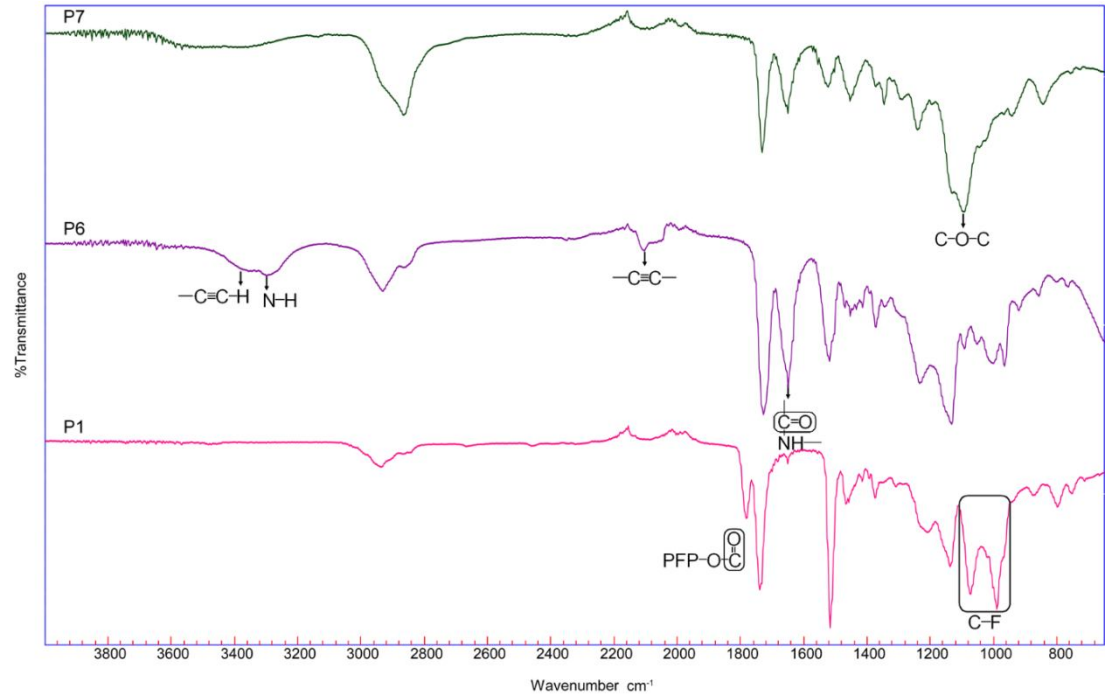


Figure 4.30 :FTIR spectra of **P1, P6** and **P7**.

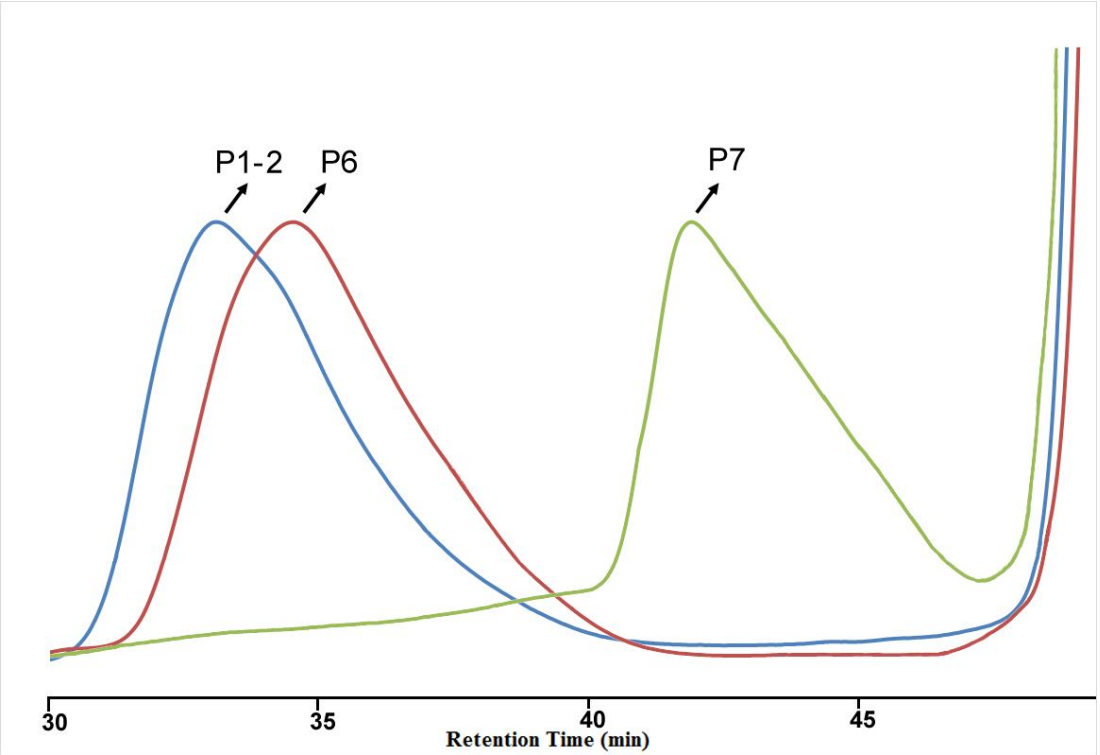


Figure 4.31 : Overlay GPC traces of **P1-2**, **P6** and **P7** in THF at 30°C.

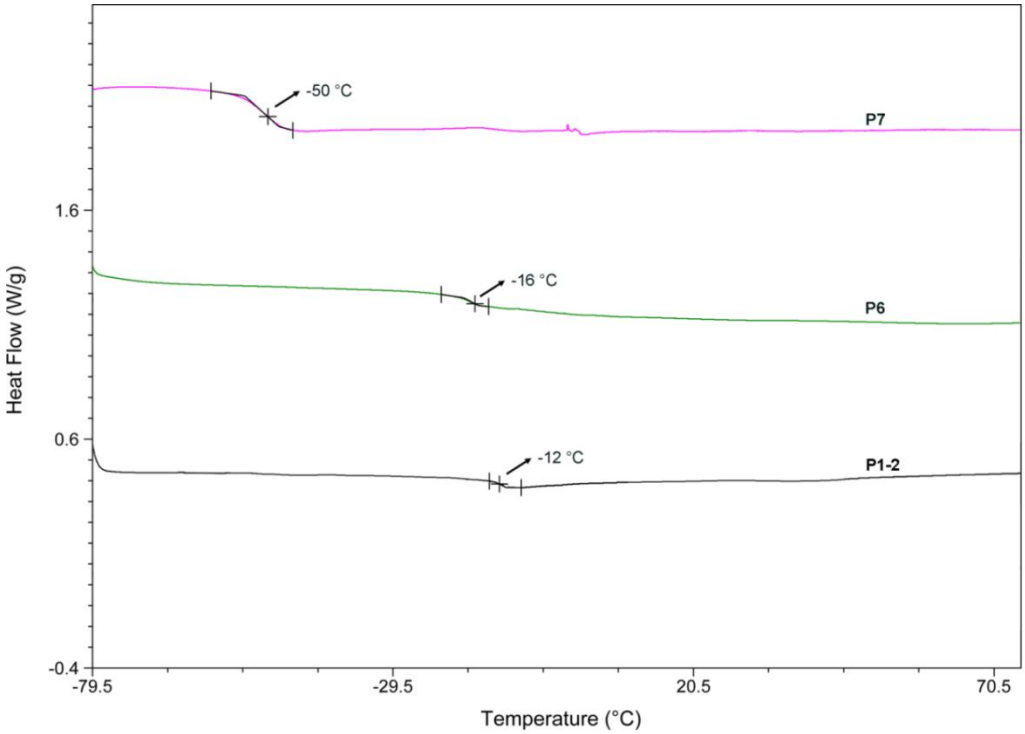


Figure 4.32 :DSC overlay of **P1-2**, **P6** and **P7**.

Gpc overlay traces (Figure 4.31) and DSC overlay (Figure 4.32) showed that, every modification process changed the structure and the properties of the synthesized polymers. Acquired results (Table 4.3) showed that, after the click reaction of **P6** with PEG, the molecular weight and Tg was decreased drasticly. Since the column of the used GPC system is not a suitable column for a PEG polymer, the results were not shown correctly. However, the characteristic GPC results of the PEG structures for this system proves that, the click reaction with PEG compound was successfully made

Table 4.3: The results of **P1-2** modifications.

	M_n	M_w	M_w/M_n	T_g
P1-2	30800	58500	1,9	-12 ^oC
P6	20000	33600	1,68	-16 ^oC
P7	2250	2510	1,12	-50 ^oC

5. CONCLUSION

The objective of this thesis was the synthesis of ADMET polymer with pendant functional groups that can be modified easily and post-modifications of synthesized polymer with desired properties.

In the first study, active ester containing monomers were synthesized. The monomer which is suitable for the ADMET polymerization was tried to polymerize in different reaction conditions. These conditions were; using G1 catalyst with bulk polymerization, GHII catalyst with bulk polymerization, G1 catalyst with solution polymerization and lastly GHII catalyst with solution polymerization. The obtained results showed that, for both polymerization techniques, G1 is a better catalyst than GHII in this system. But the other result was, that solution polymerization is not suitable for this monomer. For ADMET polymerization, diluted reaction mixture causes side reactions like ring closing metathesis reactions. In other words, making reaction environment diluted in ADMET polymerization causes only oligomers to be obtained. After the reaction was made in optimum conditions, characterizations were made with ^{1}H NMR ^{19}F NMR GPC DSC and IR. With the successful synthesis of the main polymer, modifications with amines were started. Active ester substitution reactions with amines required additional bases for substitution reactions. After the characterization of the compounds, it was observed that all conversions of the reactions were almost 100%. In addition, behaviour of solubility of these products have changed drastically.

In the second study, active ester containing polymer was reacted with propargylamine to be suitable for the click reactions. After the synthesis, the polymer was reacted with pre-existing azide end-functional PEG. After the click reaction with PEG, the ADMET polymer has become water soluble.

In the light of these results, we can say that, an ADMET polymer with proper functional groups, can be easily modified and characteristics can be changed drastically. With the solubility changes, these types of polymers can be used in areas

like drug delivery systems or having unsaturated double bonds in its backbone can offer further modifications.

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