ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

POLY(VINYLIDENE FLUORIDE) BASED GRAFT COPOLYMER

M.Sc. THESIS

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Department of Polymer Science and Technology

Polymer Science and Technology Programme

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

POLİVİNİLİDEN FLORÜR TEMELLİ AŞI KOPOLİMERİ

YÜKSEK LİSANS TEZİ

Ahmet Yasir DEMİR
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Polimer Bilim ve Teknolojileri

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HAZİRAN 2015

Ahmet Yasir Demir, a **M.Sc.** student of **Institute of Science and Technology/ Graduate School of Istanbul Technical University** student ID **515131001**, successfully defended the thesis entitled **“POLY(VINYLIDENE FLUORIDE) BASED GRAFT COPOLYMER”**, which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To Demir Family,

FOREWORD

This master study has been carried out at Istanbul Technical University, Chemistry Department of Science & Letters Faculty.

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TABLE OF CONTENTS

Page

ABBREVIATIONS

ATRP	: Atom transfer radical polymerization
CRP	: Controlled radical polymerization
MMA	: Methyl methacrylate
PVDF	: Poly(vinylidene fluoride)
PCTFE	: Poly(chlorotrifluoro ethylene)
PTFE	: Poly(tetrafluoro ethylene)
PAA	: Poly(acrylic acid)
PSSA	: Poly(styrene sulfonic acid)
SPMAK	: 3-sulfo propyl methacrylate potassium salt
PMDETA	: N,N,N′,N″,N″-pentamethyldiethylenetriamine
PFSA	: Perfluorosulfonic acid
PEM	: Proton exchange membrane
CTFE	: Chlorotrifluoroethylene
RAFT	: Reversible Addition Fragmentation Chain Transfer Polymerization
SFRP/NMP	: Stable Free Radical Polymerization/Nitroxide Mediated Polymerization
DMSO	: Dimethyl sulfoxide
DMF	: Dimethyl formamide
THF	: Tetrahydrofuran
NMP	: *N*-Methylpyrrolidone
NMR	: Nuclear magnetic resonance
FT-IR	: Fourier transform infrared spectroscopy
TGA	: Thermo gravimetric analysis
DSC	: Differential scanning calorimeter
T_{g}	: Glass transition temperature
T_{m}	: Melting temperature

LIST OF TABLES

Page

LIST OF FIGURES

POLY(VINYLIDENE FLUORIDE) BASED GRAFT COPOLYMER

SUMMARY

During the last three decades, many special fluoropolymers have been developed, due to their chemical resistance, weathering elements and oxidants, low surface free energy properties and also oil/water repellence due to their hydrophobic properties. Fluoropolymers represent a rather specialized group of polymeric materials. Amphiphilic fluorinated graft copolymers are of considerable interest for proton exchange membrane applications. Poly(vinylidene fluoride) (PVDF) has commercial importance due to its excellent properties as well as for special properties such as resistance. Because of its commercial importance, various synthetic approaches for the preparation of graft copolymers from PVDF have been reported.

The limitations of the commercial fuel cell membranes are a susceptibility to chemical degradation at elevated temperature, including poor ionic conductivities at low humidity or elevated temperatures, finally, membrane expensiveness. Thus synthesizing alternative membranes for fuel cells is still a challenging goal.

Atom transfer radical polymerization (ATRP) is controlled free radical polymerization technique. The technique also permit advanced fluorinated polymers to be synthesized. They are one of the best route for the preparation of these well-defined amphiphilic graft copolymers with controlled molecular weight, polydispersity, terminal functionalities, and chain architecture composition due to the relavite ease of synthesis and their compability with a wide range of solvents.

Here are reported that PVDF backbone was grafted by methyl methacrylate (MMA) and 3-sulfopropyl methacrylate potassium salt (SPMAK) by using atom transfer radical polymerization (ATRP).

First, PVDF was functionalized to obtained ATRP macro-initiator by 2-bromo-2-methyl-propionyl bromide via lithiation reaction.

Second MMA and SPMAK was grafted to PVDF backbone using PVDF-Br as a macroinitiator by ATRP.

Then the graft copolymers were characterized by FT-IR, ^{1}H NMR and DSC methods.

Then the proton conductivity and thermal stability in grafted polymer have been investigated for PVDF based membranes.

POLİVİNİLİDEN FLORÜR TEMELLİ AŞI KOPOLİMERİ

ÖZET

Günümüzde enerji ihtiyacını karşılamak için kullanılan fosil yakıtların sınırlı olması ve bu tür yakıtların yanması ile oluşan ürünlerin çevreye verdiği ciddi zararlar sonucunda yeni ve temiz enerji kaynakların kullanımını zorunlu hale getirmiştir. Fosil yakıtlara alternatif olarak geliştirilecek bir enerji kaynağı özellikle çevreye zarar vermemeli, uygulanabilir ve düşük maliyetli olmalıdır. Bu yöndeki çalışmalar sonucunda ortaya çıkan temiz enerji kaynaklarından birisi de hidrojen enerjisidir. Hidrojenin doğrudan yakıt olarak kullanılmasının yanında hidrojenin ve oksijenin yakıt olarak kullanarak elektrokimyasal tepkime ile elektrik üreten yakıt pillerinin geliştirilmesi üzerine de yoğun bilimsel araştırmalar yapılmaktadır. Modüler olmaları nedeniyle yakıt pillerinin küçük taşınabilir elektronik cihazlardan ulaşım alanındaki uygulamalara kadar potansiyel kullanım sahaları çok geniştir. Elektrolit kullanım tiplerine göre yakıt pilleri birkaç çeşide ayrılabilir, bunlar başlıca bazik, erimiş karbonat, fosforik asit, katı oksit ve proton değişim membranlı (PEM) yakıt pilleridir.

PEM yakıt hücrelerinin temel bileşeni anot ve katot olmak üzere iki tane elektrot içerir. Bunlar birbirlerinden polimer membran elektrolit ile ayrılmışlardır. Her iki elektrot bir kenarlarından ince platin katalizör tabakası ile örtülmüştür. Yakıt olarak kullanılan hidrojen yakıt hücresinin anot kenarından beslenir. Anotta platin katalizör varlığında serbest elektronlar ve protonlara ayrışır. Serbest elektronlar dış çevrimde kullanılırlar ve elektrik akımını oluştururlar. Protonlar polimer membran elektroliti geçerek katota doğru hareket ederler, katotta havadan gelen oksijen dış çevrimden gelen elektronlar ve protonlar saf su ve ısı oluşturmak üzere birleşirler. PEM yakıt pili elektrotları üzerinde gerçekleşen reaksiyonlar aşağıdaki gibidir;

H_2 (g) → $2H^+ + 2e^-$ anot tepkimesi
$2H^+ + 2e^- + 1/2O_2 \rightarrow H_2O$ katot tepkimesi

PEM'lerin çalışma sıcaklığı 80-90 ºC gibi çok düşük sıcaklıklarda ve çalışma basınçları da 1-8 atm basınç arasındadır. Bu tip yakıt hücreleri belli bir nem oranında hidrojen ve oksijen ile çalışabilmektedir.

En yaygın ticari yakıt pillerinin membranlarının yüksek sıcaklıklarda kimyasal bozunmaya eğilimli olmaları, yüksek sıcaklık ve düşük nemde düşük proton iletkenliğine sahip olmaları ve pahalı olmaları mevcut ticari membranlara alternatif membranların araştırılmasına neden olmaktadır.

PEM yakıt hücreleri düşük sıcaklıkta çalışmaları, sessiz olmaları ve yüksek güç yoğunluğuna sahip olmalarından ötürü önemli bir alternatif enerji kaynağıdır. Yüksek güç yoğunluğu için önemli bir faktör olan konu; membran ve elektrot takımı arasındaki su dengesinin iyi yönetilmesidir. Ayrıca PEM yakıt hücrelerinin performansı

membranın iletkenliğine bağlıdır. PEM yakıt hücrelerinde su katotta üretilir. En ideal halde bu oluşan su, elektroliti gereken nemlilikte tutar. Katottan verilen hava, reaksiyon için gereken oksijeni karşılamaya ve oluşan fazla suyu uzaklaştırmaya yeterli olur. Katottan anoda suyun difüzyonu sonucu elektrolitin tüm yüzeyi istenilen nemlilikte olur. Bu nedenle katotta üretilen suyun yönetimi oldukça önem kazanır.

Yüksek güç yoğunluğu, hızlı ve çabuk marş yapabilme ve değişken güç çıkışına uygun olması PEM yakıt pillerinin ulaşım alanında kullanılabilmesini uygun kılmaktadır. Ayrıca PEM yakıt hücreleri, özellikle yüksek performanslı polimerlerin bulunmasından sonra, uzay çalışmalarında ve özel askeri sistemlerde uygulanmak üzere geliştirilmiştir.

Proton iletim özelliğine sahip polimerik membran bir PEM yakıt hücresinin en önemli elemanıdır. Günümüzde ticari olarak kullanılan membranların çeşitliliğinin az ve maliyetinin yüksek olmasından dolayı alternatif membranların geliştirilmesi üzerine yapılan çalışmalar ivme kazanmıştır. PEM yakıt hücrelerinde kullanılan membranlar;

- Proton geçirgen özellikte olması,
- Su, yakıt (hidrojen veya metanol), oksijen ve havadaki diğer gazları geçirmemesi,
- Mekanik dayanımının yüksek olması,
- Uzun süreli kullanımda ısıl ve kimyasal direnci yüksek,
- Teknolojik olarak yaygın bir şekilde kullanılabilmesi için emniyetli ve ucuz olması,

gerekmektedir. Tüm bu özellikleri ek olarak, membran yüksek iyon iletkenliğine ulaşabilmesi için su ile tamamen doyurulmalıdır.

Yakıt hücresindeki polimerik membranın iyon iletkenliğine sahip olmasına rağmen elektronları geçirmez bu nedenle görevi protonu anot bölgesinden katot bölgesine iletmektir. Membran bünyesindeki su molekülleri, proton ile zayıf bağlar oluşturarak hidrojen iyonunun anot bölgesinden katot bölgesine ilerlemesini sağlar. Plakadan geçemeyen elektronlar, harici bir devre yardımıyla hücrenin diğer tarafına (katot) alınır ve devrelerini tamamlarlar.

Son 30 yıl içerisinde flor içeren birçok özel kopolimerlerin sentezlenmesinin sebebi, flor içeren kopolimerlerin kimyasal dayanımı, çok düşük serbest yüzey enerjilerine sahip olmaları, oksidantlara ve aşınmaya karşı yüksek direnç gösteriyor olmaları ve hidrofob özelliklerinden dolayı su/yağı üzerlerinde tutmamalarıdır. Amfilik flor içeren aşı kopolimerlerinde pek çok uygulama alanları vardır. Proton değişim yakıt pillerinin membran sentezinde flor içeren kopolimerler önemli yer tutmaktadır. Polivinilidenflorid (PVDF) dayanıklılık gibi harika özelliklere sahip olmasından dolayı ticari öneme sahiptir. Onun ticari öneminden dolayı, PVDF ten çeşitli aşı kopolimerlerin hazırlanması için çeşitli sentetik yaklaşımlar bildirilmiştir.

Atom transfer radikal polimerizasyon (ATRP) kontrollü serbest radikal polimerizasyon yöntemidir. Bu yöntem iyi tanımlanmış, molekül ağırlığı kontrol edilebilen, düşük molekül ağırlığı dağılımına sahip, uç grup fonksiyonalitesi içeren ve farklı komposizyonlarda zincir yapısından oluşan polimerleri ve özellikle ampfifilik aşı kopolimerleri kolay sentez edebilmek için kullanılan ve bilinen çoğu cözücülerle uyumlu en iyi yoldur.

Bu çalışmanın ATRP basamağında, PVDF ilk önce butil lityum ile lityumlanarak aktif halde iken 2-metil-2-bromo propionil bromid ile fonksiyonlandırılmış ve elden edilen polimer makro başlatıcı olarak kullanılarak MMA monomeri ATRP koşulları altında PVDF ana zincirine aşı yöntemiyle bağlanmıştır.Sentezlenen aşı kopolimeri ^{1}H-NMR (d-DMSO d$_6$), FT-IR, DSC ve GPC ile karakterize edilmiştir.

1. INTRODUCTION

Fluorinated polymers have always attracted significant attention due to high thermal stability, good chemical resistance, excellent mechanical properties at extreme temperatures, superior weatherability, oil and water repellence and low flammability in addition to low refractive index [1]. The development of fluoropolymers began with the invention of polytetrafluoroethylene (PTFE) in 1938 by Dr. Roy Plunkett of DuPont Company, continuing in 1992 when a soluble perfluoropolymer (Teflon AF) was invented. Besides these commercially important examples many other routes toward fluorinated materials have been researched intensively by both academic and industrial teams. These efforts have led to the emergence of various functional materials with notable properties: biomaterials, surfactants, lubricants, insulators, ion conducting materials (e.g. for Li-ion batteries) and proton conducting materials (e.g. for membranes for fuel cells). A number of materials such as paints and coatings as well as materials for the optic and electronic industries have additionally been developed. The most investigated proton exchange membranes (PEM) are based on fluorinated polymers and, in particular, the DuPont Nafion®117.

Currently, Nafion® is the most widely proton exchange membrane used for both PEMFC and DMFC systems. Nafion® is based on sulfonated fluorocarbon polymer and shows good thermal stability and high proton conductivity as advantages, while high methanol permeability (methanol crossover), high cost (about 900-1000 US $\$/m^2$) and proton conductivity loss above 100 °C represent the disadvantages. Therefore, several studies have been carried out to identify different types of non-fluorinated polymers as alternative to the Nafion® and and in some case, comparable performances to the Nafion® in terms of proton conductivity and thermo-chemical properties, as well as lower crossover and costs [2].

The fluorinated backbone of fluorinated polymers possesses the chemical, mechanical and thermal resistivity to the molecule, the ionizable end groups at the side chain has high proton permeability and cation transfer capacity properties. The limitations to large-scale commercial use include poor ionic conductivities at low humidities and/or elevated temperatures, a susceptibility to chemical degradation at elevated temperatures and finally, cost.

In order to overcome the limitations, mayn other alternative polymers have been tested during these years. The partially fluorinated polymer poly(vinylidene fluoride) (PVDF) based proton exchange membranes seem to offer the most promising performances. Because of PVDFs advantages many methods for preparing PVDF based graft copolymers received attention.

PVDF has a commercial importance due to its excellent resistance to chemicals, weathering elements and oxidants. Because of its commercial importance, various synthetic approaches for the preparation of graft copolymers from partially fluorinated poly(vinylidene fluoride) (PVDF) have been reported [3].

Methods for preparing PVDF based graft copolymers are generally classified: (1) the grafting through; (2) the grafting from; (3) the grafting onto methods. The most used method is “grafting from” method. Grafting from method has main techniques: (i) by the irradiation ii) by transfer to the polymer; (iii) by ozonization of PVDF (iv) by the direct terpolymerization of two fluoroalkenes [4]. To avoid the drawbacks of the grafting from method techniques, the controlled radical polymerization methods was used and has become one of the most useful techniques for the synthesis of graft polymers [5]. Atom transfer radical polymerization (ATRP) is one of the controlled free radical polymerization techniques. ATRP is one of the most versatile methods for synthesizing homopolymers and copolymers with predetermined molecular weights and narrow molecular weight distributions. It is based on the combination of an organic halide initiator (RX) with a metal/ligand catalytic system, which is able to promote fast initiation compared to propagation and then reversibly activate halogenated chain, ends (P_nX) during polymerization.

In this study, PVDF based graft copolymers were synthesized by using ATRP, beside MMA also acidic group containing ionic monomers was used.

First, the graft copolymers of PVDF backbone with poly(methyl methacrylate) (PVDF-*g*-PMMA) and poly(sulfopropyl methacrylate, potassium salt) (PVDF-*g*-PSPMAK) were synthesized using PVDF-Br as a macroinitiator for atom transfer radical polymerization (ATRP). The choice of PVDF instead of PTFE backbones is mainly due to cost, moderate hydrofibility and processability considerations.

The proton conductivity, thermal stability and acid content in copolymer have been investigated for PVDF based membranes.

Second, we have also studied for the first time, the use of Lithiation for the functionalization of PVDF for the ATRP macroinitiator. To the best of our knowledge, no reports have been published on application of Lithiation in functionalization of PVDF so far.

2. THEORETICAL PART

2.1 Graft Copolymers

Graft copolymers have received much attention as “novel polymeric materials” with multi-components, since they are made of different polymeric sequences linked together. It is well known that heterogeneous graft copolymers tend to show the properties of both (or more) polymeric backbone and the oligomeric or polymeric grafts rather than averaging the properties of both homopolymers.

Basically, three different methods enable one to synthesize fluorinated graft copolymers, recently summarized: (1) the grafting through; (2) the grafting from; (3) the grafting onto routes. The different pathways are schematically depicted in Figure 2.1.

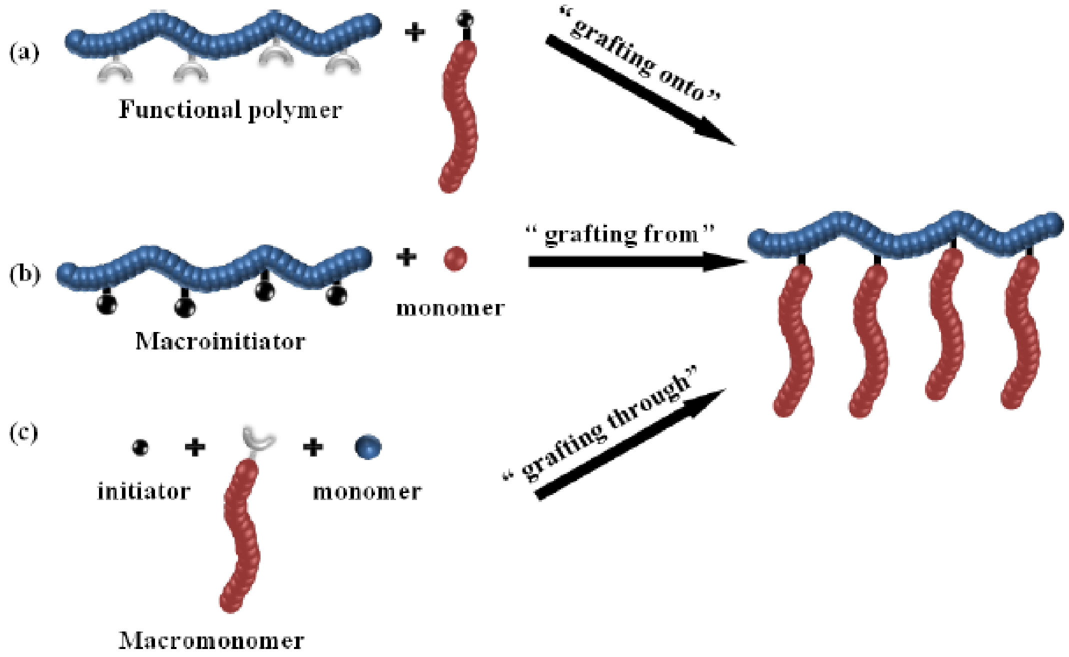


Figure 2.1 : Strategies for the synthesis of graft copolymer.

The ‘‘*grafting onto*’’ strategy involves the attachment of preformed polymer chains via chemical reaction with reactive side chains of a polymer backbone. Secondly, the ‘‘*grafting from*’’ strategy, consists in a polymerization of the grafts from a polymer backbone bearing initiating sites. The last approach is the ''grafting through'' strategy which relies on polymerization of appropriate macromonomers. There are different ways to obtain graft copolymers by grafting from" method: (i) by the irradiation (plasma, swift heavy ions, X-rays, or electron beam, mainly under γ rays or ^{60}Co source) of fluoropolymers followed by a grafting (that strategy was extensively used by Holmberg et al. who synthesized PVDF-*g*-poly(styrene sulphonic acid) graft copolymers for fuel cell membranes); (ii) by transfer to the polymer; (iii) by ozonization of PVDF [4]. By ozone activation of PVDF, Boutevin's team prepared PVDF-*g*-poly(M) where M represents styrene, acrylic acid, dimethylaminoethyl methacrylate, or phosphonated monomers. [6] (iv) by the direct of terpolymerization of two fluoroalkenes such as VDF and chlorotrifluoroethylene (CTFE) with *tert*-butylallyl peroxycarbonate at low temperature leading to terpolymers bearing peroxycarbonate dangling groups. Hence, these original macroinitiators were able to initiate the radical polymerization of VDF to yield poly(VDF-*co*-CTFE)-*g*-PVDF graft copolymers as original thermoplastic elastomers. However, not all these above methods allow assessing the molecular weights of the graft segments. To avoid this drawback, the controlled radical polymerization was used and has become one of the most useful strategies for the synthesis of graft polymers while this technique was also successful in achieving fluorinated block copolymers from initiators containing C-I, C-Br, and C-Cl bonds. It was reported the synthesis of graft copolymer by reversible addition-fragmentation chain transfer polymerization (RAFT) to obtain original PVDF-*g*-PMMA and PVDF-*g*-poly (acrylic acid) (PVDF- *g*-PAA) graft copolymers. It was prepared PVDF-*g*-PAA and PVDF-*g*-PAA-*b*-PNIPAAM copolymers by RAFT polymerization of AA with an ozone-pretreated PVDF [11].

A significant disadvantage of these free radical techniques is that homopolymerization of the comonomer always occurs to some extent, resulting in a product which is a mixture of graft copolymer and homopolymer. Moreover, backbone degradation and gel formation can occur as a resulf of uncontrolled free radical production, often limiting the attainable grafting density [3].

Indeed, ATRP is regarded as one of the most efficient controlled polymerization methods to prepare polymers and copolymers endowed with different architectures and low polydispersities [11].

2.1.1 Grafting through

The "grafting through" method (or macromonomer method) is one of the simplest ways to synthesize graft copolymers with well defined side chains.

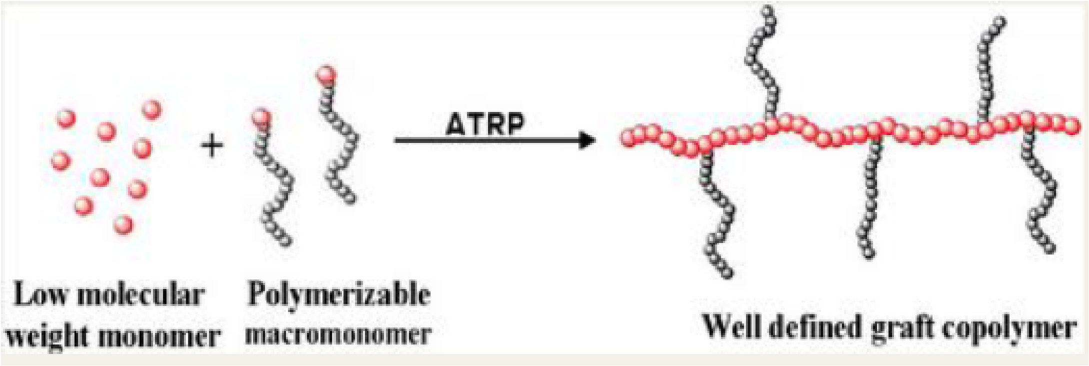


Figure 2.2 : Grafting through via ATRP.

Typically a low molecular weight monomer is radically copolymerized with a (meth)acrylate functionalized macromonomer. This method permits incorporation of macromonomers that have prepared by other controlled polymerization processes into a backbone prepared by a CRP.

Moreover, it is possible to design well-defined graft copolymers by combining the CRP "grafting through" macromonomers procedure where the macromonomers had been prepared by any controlled polymerization process. This combination of controlled polymerization processes allows control of polydispersity, functionality, copolymer composition, backbone length, branch length and branch spacing by consideration of mole-ratio of the MM in the feed and reactivity ratio of both the monomer and macromonomer. Branches can be distributed homogeneously or heterogeneously based on the reactivity ratio of the terminal functional group on the macromonomer and the low molecular weight monomer; and, as shown in the properties section, this has a significant effect on the physical properties of the materials.

Figure 2.3 : Homogeneous (a) and heterogeneous (b) distribution of grafts.

The first was a single-step approach in which a methacrylate monomer (methyl methacrylate or butyl methacrylate) was copolymerized with a mixture of a PLA macromonomer and a PDMS macromonomer. The second strategy was a two-step approach in which a graft copolymer containing one macromonomer was chain-extended by a copolymerization of the second macromonomer and the low-molecular weight methacrylate monomer. The molecular structure of the terpolymers was investigated by 2D GPC which indicated that well-defined terpolymers with controlled branch distribution were prepared via both pathways. The topologies of the graft terpolymers prepared by different combinations of the two step approach. While properties have yet to be fully explored, it is likely that phase separation is modified by polymer topology and hence the properties of the material will differ even though compositions were held constant.

2.1.2 Grafting from

In the "*grafting from*" (b) method, a polymer backbone (macroinitiator) with a predetermined number of initiation sites is generated, followed by grafting the side chains from the macroinitiator. The number of grafted chains can be controlled by the number of initiation sites generated along the backbone assuming that each one participates in the formation of one branch.

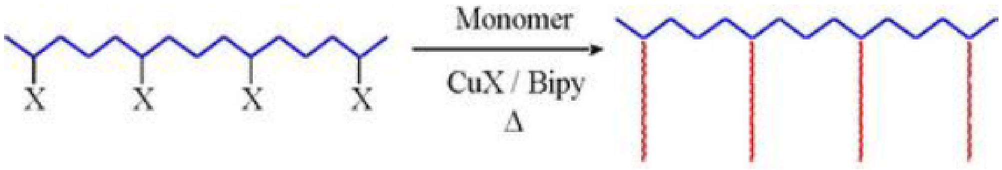


Figure 2.4 : Grafting from method.

The "*grafting from*" approach has been extensively used in the synthesis of well-defined macromolecular grafts and brushes.C/LRP techniques are suitable for polymer brush synthesis via grafting from method since low concentration of instantaneous propagating species limit the coupling and termination reactions and the gradual growth of side chains can effectively decrease the steric effect which is inevitable for either ''*grafting-onto*'' or ''*grafting-through*'' strategies.

ATRP is a particularly attractive and has been proved to be a highly versatile method to synthesize the graft polymers with well-defined structure including the controllable molecular weight and narrow molecular weight distribution. Matyjaszewski and co-workers have previously described the controlled synthesis of molecular brush copolymers by “*grafting from*” a macroinitiator using ATRP [12].

2.1.2.1 Lithiation

Functionalized polymers are of general interest in many technology applications [13]. Catalysts, reagents, controlled release formulations, chromatographic medium, conductive substances, photoresist and liquid crystals can be given as examples for special made polymers. In this project, aromatic polysulfone is functionalized to obtain adapted properties in membrane functions. Thermal and chemical stability of polysulfone is got together with membrane making conditions and positive mechanical properties [14].

Polysulfones which include bisphenol A (PSUs) related to the poly(arylene ether sulfone)s are aromatic main-chain polymers with high mechanical, thermal and chemical stabilities. Although functionalized PSUs have not only valuable properties when used as high-performance thermoplastics but also have attractive quality in different applications, natural chemical stability of PSUs involve that only a few methods are possible for profitable modification. This functionalization methods can be nitration, chloromethylation, halogenation, sulfonation or by use of lithiation which occurred as a result of electrophilic substitution reaction of PSUs [15].

Lithiation of PSUs is an useful modification since it can give rapid and near quantitative conversions, site specificity, absence of chain degradation or crosslinking and also changeable with a wide variety of functional groups. The strong electron-attraction effect of the sulfone units gives a slight acidic character to the ortho-to sulfone aromatic hydrogens (Figure 2.5). So, the carbons at these positions can be metalized by use of a strong base such as n-BuLi [14].

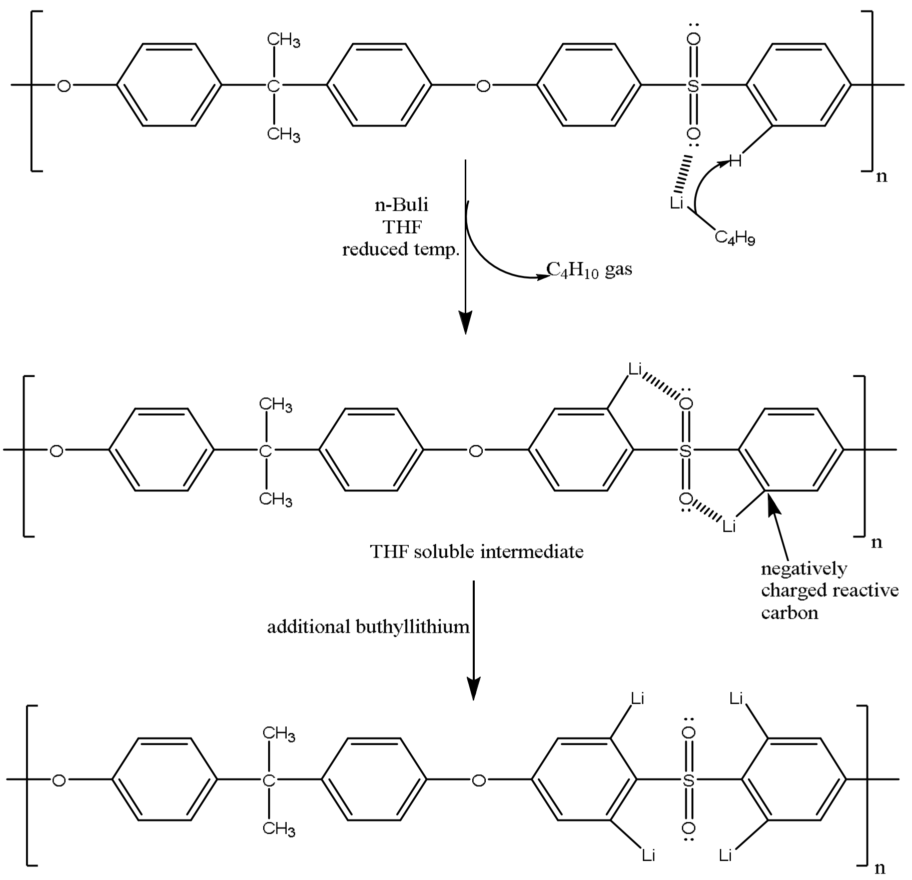


Figure 2.5 : Lithiation of Polysulfone.

2.1.3 Grafting onto

The ''*grafting onto*'' method (a) relying on grafting of preformed side chains onto a backbone is carried out via a coupling reaction between the pendant functional groups distributed randomly on the backbone and the complementary end-functional groups of side chains. The primary advantage of this method is that both backbone and side chains are prepared separately via different living polymerization techniques allowing the more accurate characterization of the resulting polymer with respect to their backbone and side chains. On the other hand, the number of grafted polymer chains is limited due to the steric hindrance and low reactivity of functional groups of the polymer chains resulting in insufficient grafting efficiency. Usually, ''*grafting onto*'' reactions involve the preparation of well-defined side chains by living anionic polymerization and their subsequent reaction with a backbone of monomer units that are susceptible to nucleophilic attack. Examples of such functional groups include esters, anhydrides, benzylic halides, nitriles, chlorosilanes, and epoxides.

2.2 Controlled/Living Radical Polymerizations

Free radical polymerization (FRP) has many advantages over other polymerization processes. Free radical polymerizations are of significant importance in the industrial sector for a variety of reasons. First, many monomers capable of undergoing chain reactions are available in large quantities from the petrochemical sector [6]. In addition, free radical mechanisms are well understood and extension of the concepts to new monomers is generally straightforward. A third advantage of free radical routes is that the polymerization proceeds in a relatively facile manner: rigorous removal of moisture is generally unnecessary while polymerization can be carried out in either the bulk phase or in solution. However, the major limitation of FRP is poor control over some of the key elements of the process that would allow the preparation of well-defined polymers with controlled molecular weight, polydispersity, composition, chain architecture, and site-specific functionality.

Mechanistically, FRP with a thermal initiator can be broken down into three basic steps – initiator decomposition and initiation, propagation, and termination by combination or disproportionation as shown in Figure 2.6.

Initiator dissociation	$I \overset{k_d}{\rightarrow} 2R\cdot$
Initiation	$R\cdot + M \overset{k_i}{\rightarrow} P_1\cdot$
Propagation	$P_n\cdot + M \overset{k_p}{\rightarrow} P_{n+1}\cdot$
Termination by combination	$P_n\cdot + P_m\cdot \overset{k_{tc}}{\longrightarrow} D_{n+m}$
Termination by disproportionation	$P_n\cdot + P_m\cdot \overset{k_{td}}{\longrightarrow} D_n + D_m$

Figure 2.6 : FRP mechanism.

Due to the high reactivity of transient radical species, polymer chain lifetimes are short with unavoidable termination and transfer reactions that yield a broad molecular weight distribution with statistical polymer architecture. This makes it difficult to generate more complex and defined structures, which are required for advanced applications [16].

Living polymerizations such as anionic, cationic, coordination, ring opening polymerizations are almost free from side reactions such as termination and chain transfer reactions, and thus, can generate polymers with well-defined architectures, controlled molecular weights and living end groups [17]. In addition, living polymerizations provide synthesis of polymers with low polydispersities. However, monomers, polymerization conditions may be limited for the type of the living polymerization technique chosen. In some cases, functional groups on the monomers may result in side reactions, and thus, for some processes control over the polymerization can be difficult.

The main limitations of radical polymerization are the lack of control over the molar mass, the molar mass distribution, the end-functionalities and the macromolecular architecture. Mainly for that reason, the recent emergence of many so-called 'living' or controlled radical polymerization (CRP) processes has opened a new area in this old polymerization method that had witnessed relatively small progress in the previous year's [18].

To overcome the limitations, CRP has been developed and there is a sharp increase in the number of the publications on the controlled radical processes from 1990s up to now. In CRP, synthesized polymers have narrow molecular weight distributions ($1.1<M_w/M_n<1.5$). The polymers obtained have living end groups. Different polymer architectures (linear, star, comb and branched) as well as polymer compositions (random, block, graft and gradient copolymers) can be achieved [19].

In the last 20 years, several methods of CRP have been introduced that allow for much greater control over polymer microstructure. The most studied methods of CRP are stable free radical polymerization/nitroxide mediated polymerization (SFRP/NMP) [8], reversible addition fragmentation chain transfer polymerization (RAFT) [6,7] and atom transfer radical polymerization (ATRP) [9,10]. The central principle between all forms of CRP is to suppress bimolecular termination by maintaining a low radical concentration throughout the polymerization. This is accomplished through an equilibrium between dormant polymer chains which are capped by a mediating species, and active polymer chains which are free to undergo propagation and other FRP mechanisms. In order to successfully suppress termination, the equilibrium must favor the formation of dormant chains, and the formation of a dormant chain should be fast.

2.3 Atom Transfer Radical Polymerization (ATRP)

The pioneering work on ATRP was conducted independently by two groups in 1995. Kato et al. demonstrated the polymerization of methyl methacrylate (MMA) using a ruthenium based complex [10], while at the same time Wang and Matyjaszewski showed the polymerization of styrene using a copper based mediator [20]. Since then, an immense amount of literature has been published on ATRP in bulk and solution, mostly using copper bound to a nitrogen based ligand as the mediating species due to its low cost and versatility compared to other transition metals [17,18].

In ATRP, growing radicals can be reversibly activated or deactivated via a dynamic equilibrium with a transition metal complex (Mt^n-X/Ligand) with an exchange of halide species (X) between the chain end and metal complex, as shown in Figure 2.7. As the rate coefficient for deactivation (k_{deact}) is much higher than the activation rate coefficient (k_{act}), the majority of chains exist in a dormant (halogen capped) state (R-X), thereby suppressing bimolecular radical termination and enabling control over polymer microstructure. In addition, unavoidable termination between radicals will lead to a build-up of deactivating species. This shifts the equilibrium towards the dormant state and further lowers the active radical concentration to suppress termination. This is also known as the persistent radical effect (PRE) [23].

In addition, k_{deact} is of a similar order of magnitude as that for k_t; as deactivator concentration is much higher than radical concentration, deactivation becomes the dominant chain ending reaction.

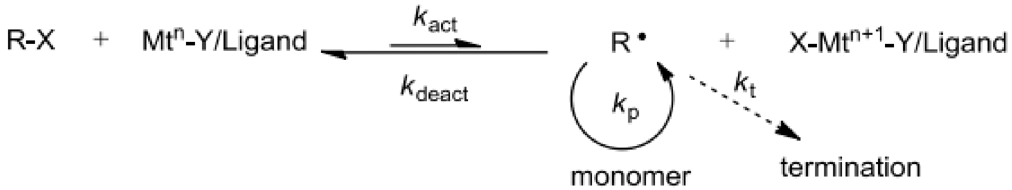


Figure 2.7 : General mechanism for ATRP.

Traditionally, the transition metal complex which governs the ATRP equilibrium is used in stoichiometric or slightly sub-stoichiometric ratio to the initiating alkyl halide species. The ratio of monomer to initiator provides the target molecular weight (M_w), and for the desired M_w in most applications this results in a high level of residual metal in the final polymer. The catalyst residue can be toxic and adds undesired color to the polymer. Therefore, the catalyst residue must be reduced to a low level for most applications. The usual method of removing the catalyst is that polymerization solution is passed through a column containing aluminum oxide. Another method is that polymers are purified by precipitation from acidified methanol solution instead of simply passing through aluminum oxide columns. The third method is the liquid–liquid extraction. The catalyst can be extracted from the organic phase to the water phase. Then the purified polymers can collected after evaporating solvent. This additional level of post-process purification can add significantly to production costs, and is a considerable hurdle towards commercial scale applications of ATRP [24-26].

2.3.1 Components of ATRP

ATRP consists of the monomer, an initiator with a transferable (pseudo)halogen, and a catalyst (composed of a transition metal species with any suitable ligand), so ATRP is a multicomponent system. Sometimes an additive is used and to generate a successful ATRP solvent and temperature must be taken into consideration [21].

2.3.1.1 Monomers

Monomers: In ATRP, a variety of monomers, such as styrenes, (meth)-acrylates, acrylonitrile, acrylamides, methacrylamides, N-vinylpyridine and diens can be used to obtained well-defined polymers. However, even under the same conditions using the same catalyst, each monomer has its own unique atom transfer equilibrium constant for its active and dormant species [27].

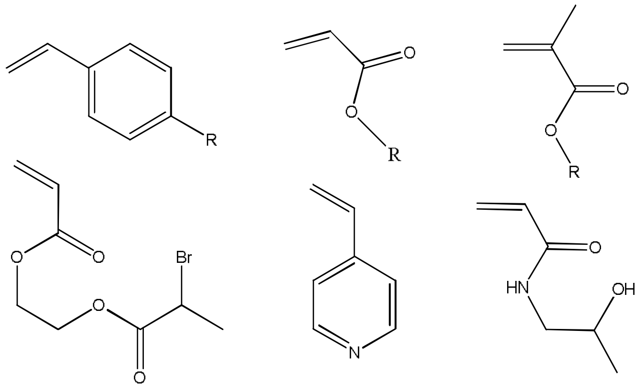
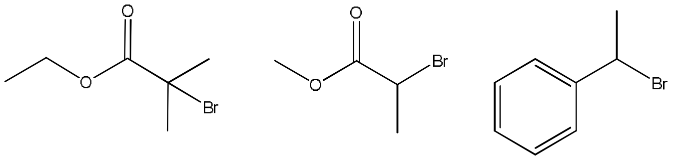


Figure 2.8 : Some of the monomers used in ATRP.

2.3.1.2 Initiators

An initiator is used to determine the number of growing polymer chain. In ATRP, R-X are typically used as the initiator and the rate of the polymerization is first order with respect to the concentration of R-X [28]. The alkyl halides used as initiators can contain one or more halogen atoms. Depending on the exact initiator structure and the number of halogen atoms, the architecture of the prepared polymers can be varied from linear (using alkyl halides with a single halogen atom), to star-like or brush-like (multiple halogen atoms in the initiator) [29]. To obtain well-defined polymers with narrow molecular weight distributions, the halide groups, X, must rapidly and selectively migrate between the growing chain and the transition-metal complex [17,18].



EBiB MBrP PEBr

Figure 2.9 : Some of the most used initiator in ATRP.

2.3.1.3 Catalyts

The catalyst is the most important component of ATRP because it determines the equilibrium constant between the active and dormant species. This equilibrium determines the polymerization rate and an equilibrium constant too small may inhibit or slow the polymerization while an equilibrium constant too large leads to a high distribution of chain lengths [22]. There are several prerequisites for an efficient transition metal catalyst. First, the metal center must have at least two readily accessible oxidation states separated by one electron. Second, the metal center should have reasonable affinity toward a halogen. Third, the coordination sphere around the metal should be expandable upon oxidation to selectively accommodate a (pseudo)-halogen. Fourth, the ligand should complex the metal relatively strongly [21]. To differentiate ATRP from the conventional redox-initiated polymerization and induce a controlled process, the oxidized transition metal should rapidly deactivate the propagating polymer chains to form the dormant species [17]. As the catalyst, a variety of transition metal such as Cu, Fe, Ni, Ru have been used to compose complexes with various ligands have been studied in ATRP.

2.3.1.4 Ligands

The main roles of the ligand in ATRP is to solubilize the transition metal salt in the organic media and to adjust the redox potential and halogenophilicity of the metal center forming a complex with an appropriate reactivity and dynamics for the atom transfer. The ligand should complex strongly with the transition metal. It should also allow expansion of the coordination sphere and should allow selective atom transfer without promoting other reactions.

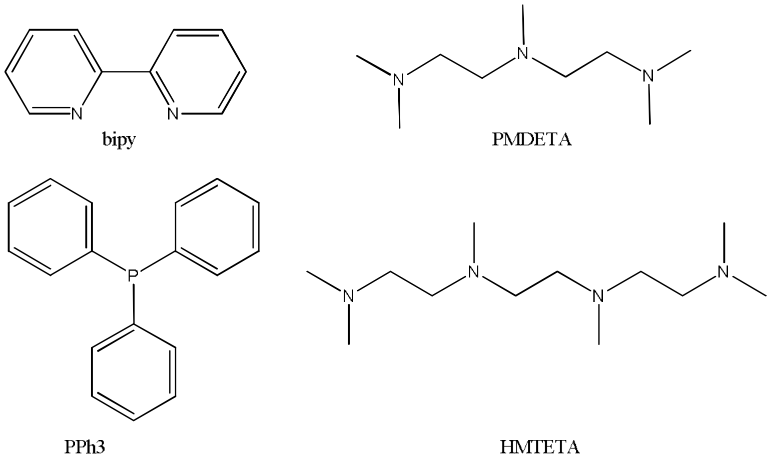


Figure 2.10 : Some of the most used ligands in ATRP.

2.3.1.5 Solvents

ATRP can be performed in all polymerization techniques: bulk, solution, emulsion, suspension. For different monomers, several solvents such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide (DMF), ethylene carbonate, alcohol, water, carbon dioxide have been used. Several factors affect the solvent choice. Chain transfer to solvent should be minimal. In addition, interactions between solvent and the catalytic system should be considered. Catalyst poisoning by the solvent and solvent-assisted side reaction should be minimized [30,31].

2.3.1.6 Temperature and reaction time

The rate of polymerization in ATRP increases with increasing temperature due to the increase of both the radical propagation rate constant and the atom transfer equilibrium constant. As a result of the higher activation energy for the radical propagation than for the radical termination, higher k_p/k_t ratios and better control ("livingness") may be observed at higher temperatures. However, chain transfer and other side reactions become more pronounced at elevated temperatures. The optimal temperature depends mostly on the monomer, the catalyst, and the targeted molecular weight. Therefore, for successful ATRP, optimum temperature should be found depending on the monomer, catalyst and the other components of ATRP [17].

2.4 Fluoropolymers

Fluoro polymers represent a rather specialized group of polymeric materials. Their chemistry is derived from the compounds used in the refrigeration industry, which has been in existence for more than 60 years. In the 1930s, efforts were made to develop nontoxic, inert, low boiling liquid refrigerants mainly for reasons of safety. The development of fluoropoylmers began with the invention of polytetrafluoroethylene (PTFE) in 1938 by Du Pont Company, continuing in 1992 when a soluble perfluoropolymer (Teflon® AF) was invented. Besides these commercially important examples, a large number of new types of fluoropolymers have been developed and a relatively high proportion of those in the last three decades.

Monomers for commercially important large-volume fluoropolymers are shown in Table 2.1. These can be combined to yield homopolymers, copolymers, and terpolymers .

Table 2.1 : Monomers Used in Commercial Fluoropolymers.

Ethylene	$CH_2=CH_2$
Tetrafluoroethylene	$CF_2=CF_2$
Chlorotrifluoroethylene	$CF_2=CClF$
Vinylidene fluoride	$CH_2=CF_2$
Vinyl fluoride	$CFH=CH_2$
Propene	$CH_3CH=CH_2$
Hexafluoropropene	$CF_3CF=CF_2$
Perfluoromethylvinyl ether	$CF_3OCF=CF_2$
Perfluoropropylvinyl ether	$CF_3CF_2CF_2OCF=CF_2$

The three principal strategies developed for the synthesis of functional fluoropolymers. The first concerns the direct radical copolymerization of fluoroalkenes with fluorinated functional monomers. The latter are either fluorinated vinyl ethers, a,b,b-trifluorostyrenes or trifluorovinyl oxy aromatic monomers bearing sulfonic or phosphonic acids. The second route deals with the chemical modification of hydrogenated polymers (e.g polyparaphenylenes) with fluorinated sulphonic acid synthons. The third alternative concers the synthesis of FP-*g*-poly(M) graft copolymers where FP and M stand for fluoropolymers and monomer, respectively, obtained by activation (e.g. irradiation arising from electrons, g-rays, or ozone) of FP polymers followed by grafting of M monomers. The most used M monomer is styrene, and a further step of sulfonation on FP-*g*-PS leads to FP-*g*-PS sulfonic acid graft copolymers. Synthesized fluoropolymers are generally characterized by using atomic-force microscopy (AFM), transmission electron microscopy (TEM), light scattering, fluorescence spectroscopy, small-angle neutron scattering (SANS), small-angle X-ray scattering (SAXS), potentiometric titration, microcalorimetry, electrokinetic analyzer, TGA, DSC.

Fluoropolymers are widely used in chemical, automotive, electrical, and electronic industries; in aircraft and aerospace; in communications, construction, medical devices, special packaging, protective garments, and a variety of other industrial and consumer products. They represent a group of macromolecules offering a variety of unique properties, in particular, a good-to-outstanding chemical resistance and stability at elevated temperatures.

The worldwide annual production capacity for fluoropolymers is estimated to be 203,300 metric tons, with the market demand being about 180,000 metric tons in 2006. Because of their special properties and relatively low production volumes when compared with typical engineering resins, their prices are relatively high, ranging typically from \$7 to \$25 per pound (\$15 to \$55 per kg) for the more common types and may be \$50 or more per pound (\$110 per kg) for the specialty products [1].

In contras to hydrogenated polymers, fluoropoylemrs are potential candidates due to their outstanding properties that open various applications. The small size and the high electronegativity of the fluorine atom confers a strong C-F bond and a low polarizability. Such polymers show low intermolecular interactions, which leads to low cohesive energy, and therefore, to low surface energy. They also exhibit high thermostability and chemical inertness, low refractive index and friction coefficient, good hydrophobicity and lipophobicity, valuable electrical properties, and low relative permivity. In addition, they are non-sticky and resistant to UV, to ageing and to concentrated mineral acids and alkalies [1]. On the other hand, they exhibit some deficiencies when comparedth most engineering polymers. They typically have poorer mechanical properties, higher permeability, and often considerably higher cost.

In order to overcome the deficiencies of fluoro polymers, many other alternative polymers have been tested during these years. Today, the poly (vinylidene fluoride) (PVDF) and PVDF-based graft copolymers seem to offer the most promising performances,combining high room temperature proton conductivity, chemical stability, low permeability, and resistance to nuclear radiations, and good mechanical properties.

There are two process to produce its monomer, vinylidene fluoride. One process to produce VDF starts with acetylene, which reacts with 2 mol of hydrogen fluoride using a Lewis acid (BF_3) as catalyst giving 1,1-difluoroethane.

$$CH \equiv CH + 2HF \xrightarrow{BF_3} CH_3CHF_2$$

1,1-difluoroethane is then chlorinated to 1-chloro-1,1-difluoroethane:

$$CH_3CHF_2 + Cl_2 \rightarrow CH_3CClF_2 + HCl$$

Subsequently, 1-chloro-1,1-difluoroethane is dehydrochlorinated, yielding vinylidene fluoride:

$$CH_3CClF_2 \rightarrow CH_2{=}CF_2 + HCl$$

Another, somewhat different process, starts from 1,1,1-trichloroethane, which after dehydrochlorination gives 1-chloro-1,1-difluoroethane. The second step, dehydrochlorination of 1-chloro-1,1-difluoroethane, is the same.

Vinylidene fluoride is a colorless gas at ambient temperature and pressure. It is flammable and can form explosive mixtures with air. VDF is used either for the production of homopolymer or as a comonomer for a number of fluorinated monomers (HFP, TFE, CTFE) for the production of fluoroplastics and fluoroelastomers. The most common methods of producing homopolymers and copolymers of vinylidene fluoride are emulsion and suspension polymerizations, although other methods are also used.

Emulsion polymerization requires the use of free radical initiators, fluorinated surfactants, and often chain transfer agents. Aqueous suspension polymerization requires the usual additives, such as free radical initiators, colloidal dispersants (not always), and chain transfer agents to control molecular weight. Commercial products based on PVDF contain various amounts of comonomers such as HFP, CTFE, and TFE that are added at the start of the polymerization to obtain products with different degrees of crystallinity. Products based on such copolymers exhibit higher flexibility, chemical resistance, elongation, solubility, impact resistance, optical clarity, and thermal stability during processing.

2.4.1 PVDF

Poly(vinylidene fluoride) (PVDF) has been known since the 1960's for its excellent mechanical and physicochemical properties. It has found widespread industrial applications and research interests [32]. PVDF conprises alternating $–CH_2$ and $–CF_2$ groups.These alternating units can crystallize with larger $–CF_2$ groups adjacent to smaller $–CH_2$ units on an adjacent chain. This interpenetration gives rise to high modulus. In fact. PVDF has the highest flexural modulus of all fluoropolymers. The above alternating groups create a dipole that renders the polymer soluble in highly polar solvents, such as dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), trifluorotoluene and dimethylacetamide. Other consequences of this structure are a high dielectric constant and high dieletric loss factor and piezoelectric behavior under certain conditions. The shielding effect of the fluorine atoms adjacent to the $–CH_2$ groups provides the polymer with a good chemical resistance and thermal stability [32].

In addition, PVDF is not toxic and less expensice than other fluoropolymers such as poly(chlorotrifluoroethylene), poly(trifluoroethylene) or poly(tetrafluoroethylene). Thus, graft copolymers containing a PVDF backbone would be particularly interesting, and potentially useful, because the incorporation of PVDF would raise the chemical resistance and thermal stability of the polymer and should lower the surface energy. On the other hand, PVDF is hydrophobic in nature; therefore, in order to confer hydrophilic properties and, consequently, proton conductivity, a chemical modification by means of grafting is needed.

2.4.2 PVDF based graft copolymers

2.4.2.1 Synthesis of PVDF-based graft copolymers by ozone activated PVDF

Ozone, commonly written O_3, is an inexpensive gas (quite soluble in fluorinated solvents), but it is well known for environmental concerns. The ozonization allows the activation of a wide range of polymers, mainly polyolefin (polyethylene, polypropylene, PVC) but also PS, poly (dienes), PDMS, polyurethanes, PVDF and finally copolymers.

The direct oxidation of polymer chains by ozone is a well-known method for introducing peroxides and hydroperoxides for the subsequent graft polymerization. Generally, the amount of peroxides introduced into a polymer sample by ozone treatment can be regulated by the treatment temperature, ozone concentration, and treatment time [33] .PVDF graft copolymers were synthesized in a two-step procedure; first step is the ozone treatment of PVDF, final step is monomer grafting or grafting the ozone activated PVDF to a polymer.

Molecular modification of ozone-pretreated PVDF via thermally induced graft copolymerization with acrylic acid (AA) in N-methyl-2-pyrrolidone (NMP) solution was carried out (the PVDF-*g*-PAA copolymer). The microstructure and composition of the PVDF-*g*-PAA copolymers were characterized by FT-IR, X-ray photoelectron spectroscopy (XPS), elemental analysis, and thermo gravimetric (TG) analysis. In general, the graft concentration increased with the AA monomer concentration used for graft copolymerization. PVDF powders in solution activated by fixed O_3/O_2 mixture concentration at room temperature 15 min. This pretreatment time gives rise to a peroxide content of about 10^{-4} mol/g of the polymer. The peroxides on the activated PVDF chains are used as initiators for the subsequent radical-induced graft polymerization. Based on these data, the half-life for the decomposition of peroxides on the ozone-treated PVDF was estimated to be about 45 min at 60^{o}C. Thus, a polymerization time of 3 h at 60^{o}C should be sufficient for the complete decomposition of the peroxides.

Amphiphilic graft copolymers prepared using ozone penetrated PVDF incorporating poly(oxyethylene methacrylate) (PEOMA), a hydrophilic macro-monomer. Under the grafting conditions a limiting grafting density of 23-wt % co-monomer was obtained [3]. The polymerization carried out at 100 ^{o}C in NMP from [PEOMA]:[PVDF] with weigh ratio ranging from 1:1 to 6:1. The structures of the resulting PVDF-*g*-PPEOMA graft copolymers were investigated by FT-IR and XPS, showing, as expected, that the graft concentration increased with increasing PEOMA macro-monomer concentration [1].

2-(2-Bromoisobutryloxy) ethyl acrylate (BIEA) was polymerized on the surface of ozone-penetrated PVDF and further used as macro-initiator for functional monomers sodium 4-styrene sulfonate (NaSS) and PEGMA (M_n~360 g/mol) to yield branched graft copolymers (Fig. 2.11). Copolymers of PVDF-*g*-PBIEA-*g*-NaPSS cast in 1 M aq. NaCl solution were enriched in poly(sodium 4-styrene sulfonate, NaPSS) side chains on the surface. PVDF-*g*-PBIEA copolymers were used to run ATRP of EGMA and the resulting PVDF-*g*-PBIEA-*g*-PEGMA copolymers. 2-Dimethylaminoethyl methacrylate (DMAEMA) was also polymerized by ATRP from a PVDF-*g*-PBIEA copolymer and the resulting PVDF-*g*-PBIEA-*g*-PDMAEMA copolymer [1].

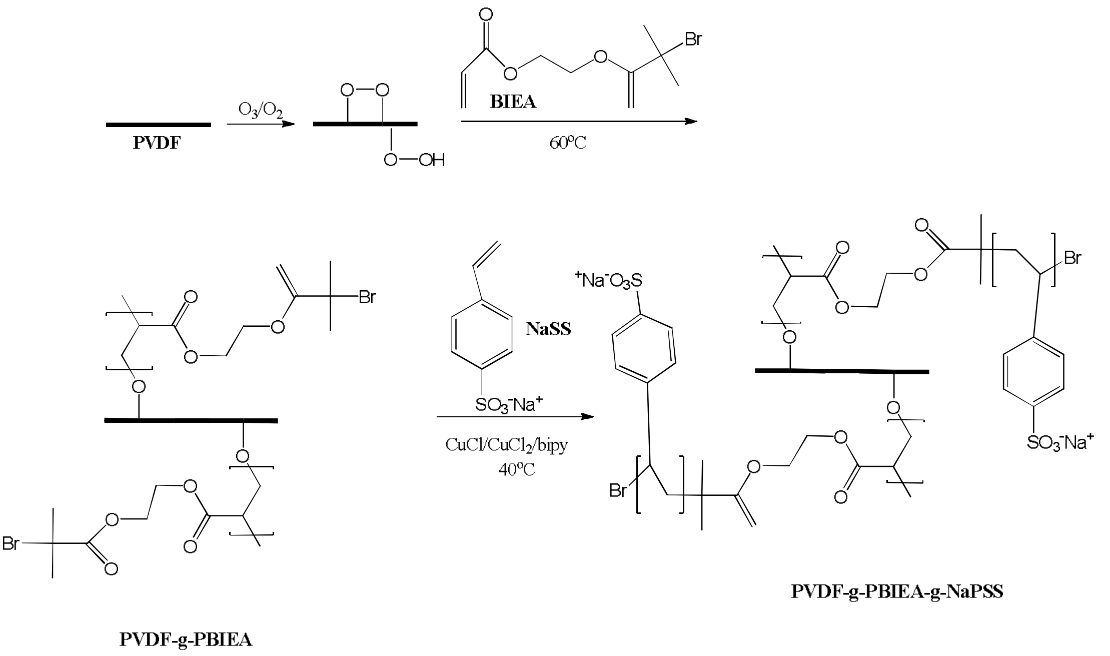


Figure 2.11 : Synthesis of Branched Copolymer PVDF-*g*-PBIEA-*g*-NaPSS.

PVDF with "living" PEGMA (M_n~300 g/mol) side chains (PVDF-*g*-PEGMA) were prepared through molecular graft copolymerization of the PEGMA macromonomer with ozone-preactivated PVDF backbone in a RAFT-mediated process.

PVDF-*g*-PAA copolymers with well-defined PAA side chains were synthesized by RAFT-mediated graft copolymerization of acrylic acid with ozone-pretreated PVDF. The PVDF-*g*-PAA copolymers were further functionalized in a subsequent surface-initiated block copolymerization with *N*-isopropylacrylamide (NIPAAM) resulting PVDF-*g*-PAA-*b*-PNIPAAM copolymer [1].

2.4.2.2 Synthesis of graft copolymer by irradiated PVDF

Radiation induced grafting can also be used fort he synthesis of original graft copolymers. Fort his method, a polymer endowed with the required mechanical, chemical or thermal properties is irradiated with electron beams or γ-rays (usually emitted from various radioactive isotopes: ^{60}Co obtained by beaming ^{59}Co with neutrons in a nuclear reactor, and ^{137}Cs which is a product of fission of ^{235}U). Generally, the use of an electron beam enables activation on the surface. Hence, the polymer to be activated can first be processed into thin films. By contrast, irradiation is efficient in the bulk of the substrate and thicker films can hence be treated. The irradiation causes free radical centers formed in the polymeric matrix.

Different types of high-energy radiation are available for use in the grafting process, although crosslinking may ocur, the radiation-chemical effects in PVDF showed that crosslinking may ocur, the radiation-chemical effects in PVDF showed that crosslinking proceeds mainly through an alkyl nacroradical. This radiation may be either electromagnetic, such as X-rays and γ-rays, or charged particles, such as β particles or electrons.

Radical generation throughout the film thickness is necessary. Fortunately, all of the radiation discussed above has sufficient energy to penetrate into the bulk of fluorinated films, which are usually 25-200 mm thick.

The irradiation and grafting can be carried out in one step, in two, or in more steps.This remainder of this sub-section is divided into two parts: (i) investigations on the activation of fluorinated homopolymers followed by the grafting, and (ii) methods starting from the irradiation of fluorinated copolymers, with a subsequent grafting. PVDF-*g*-PM graft copolymer syntheses, properties, starting from the activation of PVDF. Styrene, vinyl benzyl chloride are grafted to synthesis PVDF-*g*-PM graft copolymers [1].

PVDF-*g*-PSSA fully characterized novel sulfonated PVDF-*g*-PS (or PVDF-*g*-PSSA) copolymers was synthesized in a three step-procedure: first, the irradiation of porous films of PVDF by electron beam at various doses, followed by the grafting of styrene, and in a final step, the sulfonation of the aromatic ring in the presence of chlorosulfonic acid. Activation of PVDF was carried out under nitrogen atmosphere. As expected, it was observed that the higher the döşe-rate and the longer the grafting time, the higher degree of grafting. Then, the PVDF-g-PS copolymers was immersed in chlorosulfonic acid in methylene chloride for 2-12 min, leading to a degree of sulfonation of 11-71 % [1]. Reaction for 2h with a doubled $ClSO_3H$ concentration was required to achieve 95-100 % of sulphonation. This procedure is summarized in Figure 2.12.

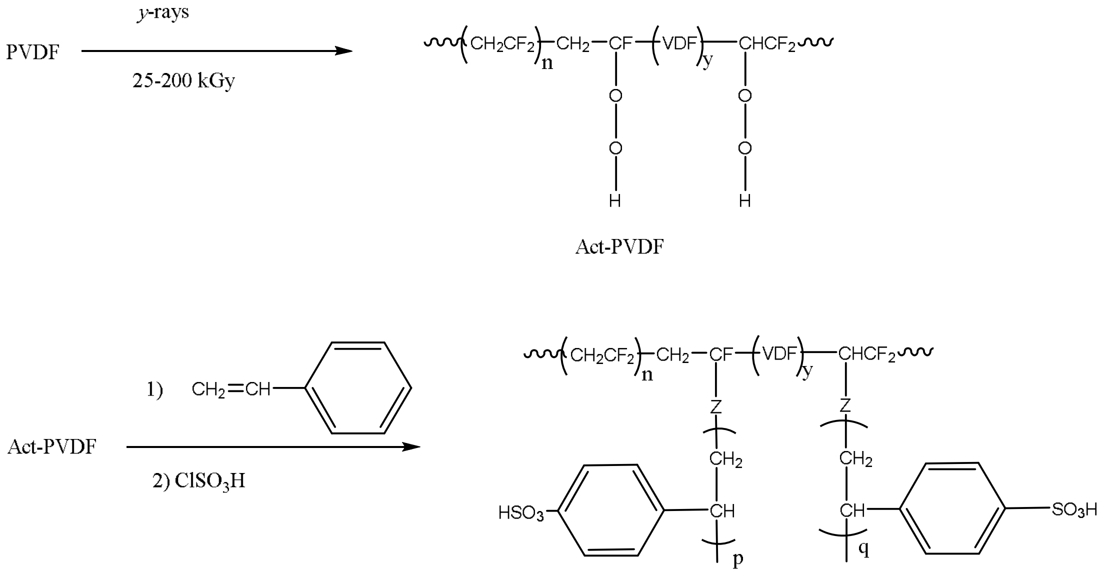


Figure 2.12 : Synthesis of PVDF-*g*-PSSA Graf Copolymer.

The grafting reaction of styrene, initiated in the amorphous regions, and at the surfaces of the crystallites in the semi-crystalline PVDF matrix, was quite efficient, with a high degree of grafting (50-86%), and with grafts formed both from C-H and C-F branch sites of PVDF. Grafting was assumed to take place in the amorphous regions of PVDF. The sulfonation step was realized in high yields (up to 100%), occuring mainly in the para position of the phenyl ring. These novel films were characterized by Raman and NMR spectroscopy, wide angle X-ray scattering (WAXS), and small angle X-ray scattering (SAXS) [1].

PVDF-*g*-PVBC copolymers was synthesized in a two step-procedure: first, PVDF was activated under nitrogen atmosphere by γ ray from a ^{60}Co source at a dose of 6.3 Mrad, at 70 ^{o}C for 1 week, the final step is the grafting of VBC monomer [1].

PVDF-*g*-PVBC copolymers, where VBC stands for vinyl benzyl chloride, acted as suitable macroinitiators via their chloromethyl side groups in ATRP of styrene, with a copper bromide/bipyridine catalytic system, leading to control PVDF-*g*-[PVBC-*g*-PS] graft copolymers. The high degree of grafting achieved would not be possible with conventional uncontrolled radiation induced grafting methods owing to termination reactions. The polystyrene grafts were sulfonated, leading to well-defined PVDF-*g*-[PVBC-*g*-PSSA] copolymers.

The chlorometyhl end groups of PVDF-*g*-PVBC copolymers underwent and amination reaction into benzyl trimethylammonium (BTMA) hydroxide or BTMA chloride (BTMAC) for PVDF-*g*-PBTMAC graft copolymers.

Poly(methyl methacrylate) (PMMA) was anchored to PVDF film surface via electron beam pre-irradiation grafting technique to prepare PVDF/PMMA brushes. The conformation of the PVDF/PMMA brushes was verified through Attenuated Total Reflection-Fourier transform infrared spectroscopy (ATR-FTIR), energy dispersive X-ray spectroscopy (EDX), and scanning electron microscopy (SEM). Thermal stability of PVDF/PMMA brushes was characterized by thermo gravimetric analysis (TGA) [35].

PVDF-*g*-PCMS copolymers have been prepared by pre-irradition grafting of *p*-chloromethyl styrene (CMS) solutions in toluene onto 80 μm PVDF films. These copolymers were employed for ATRP of styrene CuCl or CuBr and bipy at 120^{o}C. The polymerization increased linearly with time up to at least 400% PS grafting. This implicated first-order kinetics and a controlled radical polymerization. Finally, the PS grafts are sulfonated. SEM/EDX-ray results implied that the copolymers had to be grafted throughout the matrix with both PCMS and PS to become proton conducting after sulfonation [1].

2.4.2.3 Synthesis of PVDF-based graft copolymers by direct initiation of PVDF

The direct initiation method using PVDF macroinitiator allows synthesizing graft copolymers with minimized homopolymer formation [4]. Direct initiation of the secondary fluorinated site of high molecular weight PVDF has been exploited in the preparation of amphiphilic graft copolymers [1].

Amphiphilic copolymer derivatives of PVDF with poly (oxyethylene methacrylate) (PVDF-*g*-POEM) side chains and having poly (methyl methacrylate) side chains (PVDF-*g*-PMMA) are prepared using this "grafting from" method (Figure 2.13) [3].

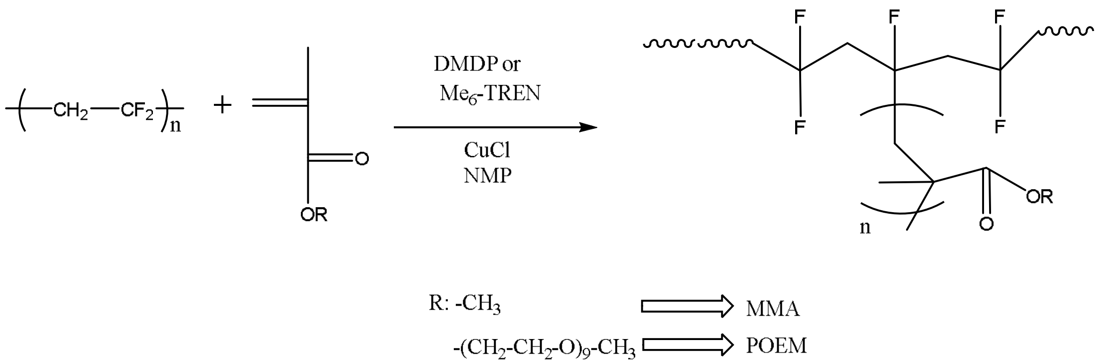


Figure 2.13 : Synthesis of PVDF-*g*-PMMA and PVDF-*g*-POEM.

PVDF-*g*-POEM and PVDF-*g*-PMMA with high grafting density was prepared under moderate conditions, i.e., 30 °C and 30 min polymerization time, using 4,4-dimethyl-2,2-dipyridyl (DMDP) and tris(2-aminoethyl)amine (Me_6-TREN) as ligands; 1-methyl-2-pyyrolidinone (NMP) as solvent and CuCl as a coinitiator.

Copolymers were characterized by gel-permeation chromatography (GPC), ^{1}H-NMR, DSC and AFM. Linear $\ln([M]_o/[M])$ vs. time and molecular weight vs. conversion plots confirm the living nature of the graft copolymerization. AFM on PVDF-*g*-POEM revealed a microphase-separated morphology characteristic of graft copolymers [34].

The preparation of PVDF-*g*-PMAA was a two-step synthesis. In the first step, poly(*tert*-butyl methacrylate) (P*t*BMA) side chains were graft copolymerized onto PVDF using ATRP. In the second step, the P*t*BMA side chains were hydrolyzed to yield poly(methyl methacrylate) (PMAA). It is well known that P*t*BMA can be selectively and quantitatively hydrolyzed to PMAA in the presence of *p*-toluenesulfonic acid monohydrate (TSA). The combined GPC, TEM, NMR, and elemental analysis results indicate unambiguously that P*t*BMA are grafted to the PVDF base polymer, hydrolized to PMAA, apparently by ATRP initiation at the secondary fluorinated site [3].

A PVDF membrane filled with nano-sized Al_2O_3 and a polymeric acid, poly(2-acrylamido-2-methyl propylene sulfonic acid), exhibiting high conductivity, water uptake and stability has been also reported for fuel cell applications [37]. PEMs ofPVDF grafted with PSSA and doped with Al_2O_3 (10%), showed low methanol permeability (6.6×10^{-8} cm^2 s^{-1}) and moderate proton conductivity (4.5×10^{-2} S.cm^{-1}) and better DMFC performance with high OCV and power density [37]. Turner and Herring and co-workers [38] studied the polarization curves for HPA ($H_3PW_{12}O_{40}$, $H_3P_2W_{18}O_{62}$, $H_6P_2W_{21}O_{71}$, and $H_6As_2W_{21}O_{69}$) doped in PVDF-HFP composite PEMs, demonstrating that they were promising candidates for fuel cells above 200 ^{o}C. They showed high proton conductivities at RT and 1.6 mA.cm^{-2} limiting current densities with dry O_2 and H_2 but comparatively low OCV because of porous nature. Recently, PSSA was grafted on silica particles by atom transfer radical polymerization and their composite membranes with a PVDF-HFP polymer matrix (30–60 wt% loading) exhibited 15–95 mS.cm^{-1} proton conductivity at RT and 1.0 mW.cm^{-2} power density at 70 ^{o}C in single-cell fuel cell test with non-hydrated gas feeds [39].

For the preparation of PVDF-*g*-PNIPAAM membrane, one piece of the PVDF flat membrane (0.084 g), NIPAAM (0.672g), CuCl (15 mg), and Me_6TREN (69 mg) were added to 20 mL ethanol [36]. The reaction flask was sealed under a nitrogen atmosphere and kept in at 60 ^{o}C oil bath for 12, 24, or 36 h. After the reaction, the PVDF membrane with surface-grafted PNIPAAM was removed from the reaction mixture and washed thoroughly with distilled water, to remove any residual monomer and PNIPAAm homopolymer [40].

PVDF-*g*-PNIPAAm membrane was successfully prepared by the modification of PVDF membrane with thermo-responsive monomer NIPAAM through the method of surface-initiated ATRP. The pore sizes of the PVDF-*g*-PNIPAAM membrane were reduced for the grafting of PNIPAAM, and the hydrophilicity of the modified membranes was improved. The PVDF-*g*-PNIPAAM membranes have good thermal stability, thermo-responsive permeability, and antifouling property, and with the increase of the reaction time, the hydrophilicity, thermo-response, and antifouling property were all improved [40].

2.4.2.4 Synthesis of PVDF-based graft copolymers by functionalised PVDF

Films of PVDF were treated by Liu et al. with LiOH to generate oxygen-containing functionalities on the polymer chains by elimination of HF followed by reduction, ultimately forming a OH-groups functionalized on the PVDF surface. This was in turn reacted with 2-bromo-isobutyryl bromide (BIBB) yielding a macroinitiator for ATRP equipped for fashioning polymer brushes on the film surface. Brushes of MMA and PEGMA (M_n~300 g/mol) were synthesized succesfully using CuBr/HMTETA and CuCl/$CuCl_2$/bpy, respectively. 2-dimethylaminoethyl methacrylate (DMAEMA) was further copolymers onto the PMMA and PEGMA brushes (CuBr/HMTETA) forming block copolymer grafts on the PVDF surface [1].

3. EXPERIMENTAL PART

3.1 Chemicals

N,N,N',N'',N''-Pentamethyldiethylenetriamine (PMDETA, 99 %), 2-bromo-2-methyl-propionyl bromide (BrIBBr, 98% in Figure 3.1) were purchased from Across Organics Co., tetrahydrofuran (THF), methanol (MeOH), were purchased from J.T. Baker Co., Copper (I) bromide (CuBr, 99.99 %), was purchased from Merck, methyl methacrylate (MMA), 3-sulfopropyl methacrylate, potassium salt (SPMAK, 98 % in Figure 3.2), poly(vinylidene fluoride) (Apollo), dimethylformamide (DMF, Labscan, 99.8 %), n-Butyl lithium solution (1.6 M in hexane), *N*-Methyl-2-pyrrolidone (NMP, 99.5 %), were purchased from Aldrich. All reagents were used without further purification.

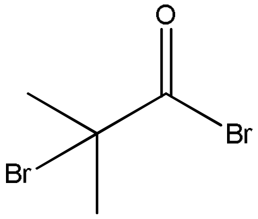


Figure 3.1 : 2-bromo-2-methylpropionyl bromide (BrIBBr).

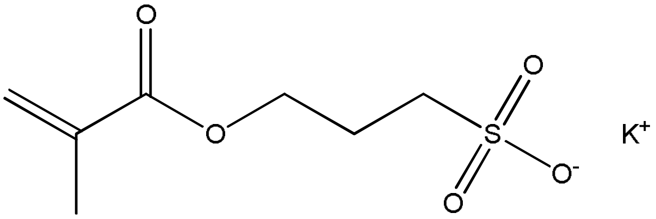


Figure 3.2 : 3-Sulfopropyl methacrylate potassium salt (SPMAK).

3.2 Modificatin of PVDF

3.2.1 Synthesis of ATRP macroinitiator via lithiation

15 eqivalent mmol of PVDF (1 g) was dissolved in 60 ml of THF in round bottom reactor and the mixture was stirred. After de-oxigenated, the reactor was placed in a cooled bath (-5 ^{o}C) and after 30 minutes, 15 mmol of n-BuLi (9.37 ml) was added to the reactor under inert atmosphere. After 45 minutes, 0.03 mol 2-bromo-2-methyl-

propionyl bromide (3.71 ml) was added to the mixture. After 45 minutes, the reaction mixture was precipitated in methanol and polymers were isolated by filtration. Then filtered and dried under vacuum overnight at 35 °C. The brown product (PVDF-Br) was obtained.

3.3 Synthesis of Graft Copolymer

3.3.1 Synthesis of PVDF-*g*-PMMA

CuBr as catalyst, PVDF-Br as macroinitiator were added into a 48 mL Schlenk flask and de-oxygenated by three vacuum-nitrogen cycles, then mixture were dissolved addition of NMP (5 ml) followed by nitrogen bubbled 20 minutes. MMA as a monomer, PMDETA as ligand were added to the flask, respectively. After 15 minutes nitrogen purging, the flask was replaced in thermostatically controlled oil bath at 90 °C. All liquids, ligand and solvent, were purged with nitrogen prior to use. Different conditions of ATRP reactions at different ratios of the chemicals were carrried out. To follow the kinetic of the reaction, alequot was taken via syringe from the reaction solution and were precipitated in methanol and filtered. After filtration, polymer samples were dried for 24 hours in a vacuum oven at 35 °C.

3.4 Characterization Methods

3.4.1 Infrared spectrometer (FT-IR)

FT-IR spectra were recorded on a Thermo Nicolet 6700 FT-IR spectrometer.

3.4.2 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC, Figure 3.3) measurements were done to find out glass transition temperature (T_g) values using TA instruments Q1000 series. All tests were carried out under 50 ml.min^{-1} rate of nitrogen purge. All T_g measurements were investigated on TA Universal Analysis software by the inflection of change in the endothermic direction of the heating ramp.

Figure 3.3 : Differential scanning calorimetry (DSC, TA Q1000).

3.4.3 Nuclear magnetic resonance spectroscopy (NMR)

^{1}H-NMR measurements were recorded in DMSO-d_6, using an Agilent VNMRS500 (500 MHz) instrument.

3.4.4 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopic (Figure 3.4) measurements were conducted at room temperature (25 ^{o}C) using the conventional three electrode cell configuration. The electrochemical cell was connected to a potentiostat (Parstat 37 2263-1), which interfaced to a computer. An electrochemical impedance software (Powersine) was used to carry out impedance measurements by scanning in the 10 -100 kHz frequency range with applied AC signal amplitude of 10 mV. The impedance spectra were analyzed using AC impedance data analysis software (ZSimpWin V3.10).

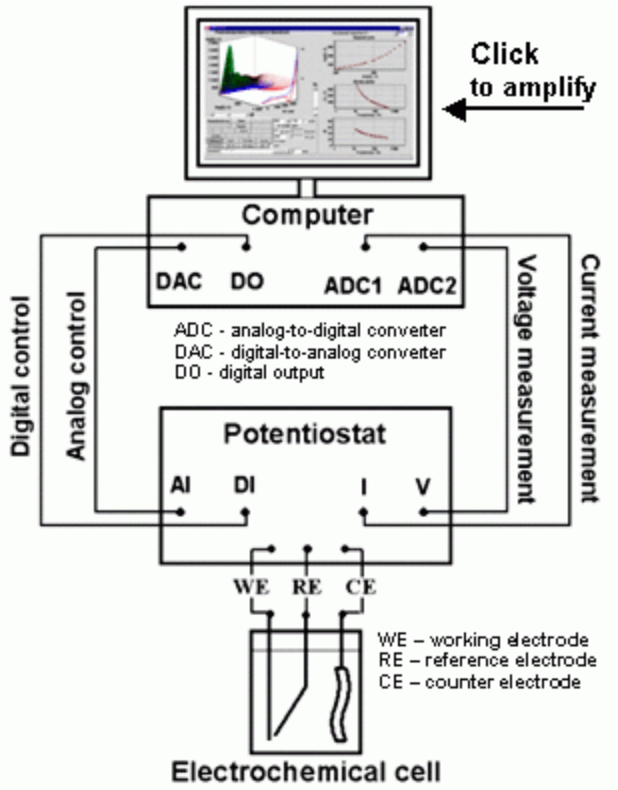


Figure 3.4 : General diagram of electrochemical impedance spectroscopy.

4. RESULTS AND DISCUSSION

4.1 Modification of PVDF

4.1.1 Synthesis of ATRP macroinitiator via lithiation

To obtain PVDF based graft copolymer by ATRP, macroinitiator (PVDF-Br) was synthesized by lithiation and BrIBBr reaction according to Figure 4.1.

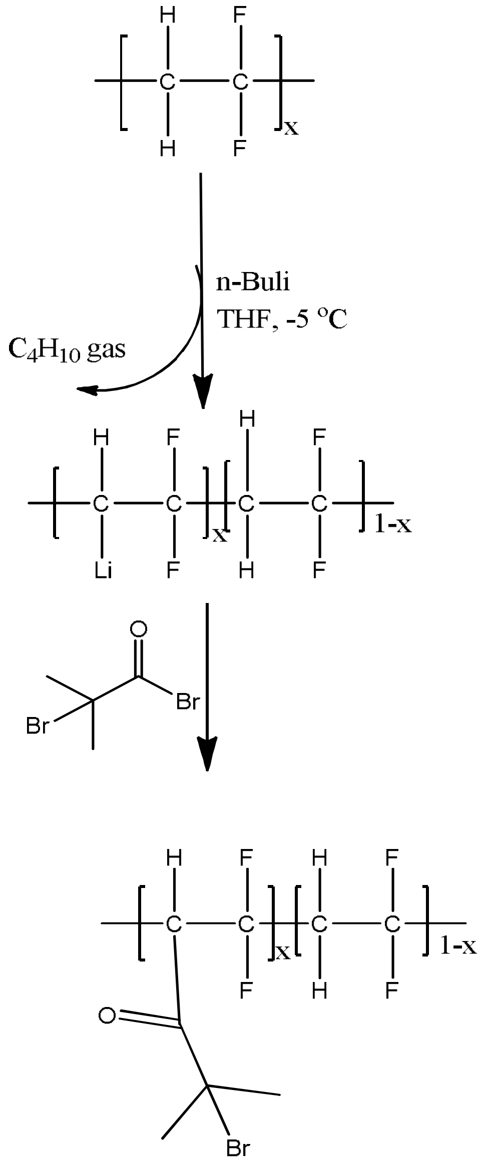


Figure 4.1 : Functionalization of PVDF.

FT-IR spectrum of PVDF, PVDF-Br were represented in Figure 4.2. A strong absorption at 500 and 1733 cm^{-1} belong to -C-Br stretching and C=O stretching of ketonic group of PVDF-Br (PVDF-43, PVDF-45, PVDF-46), respectively.

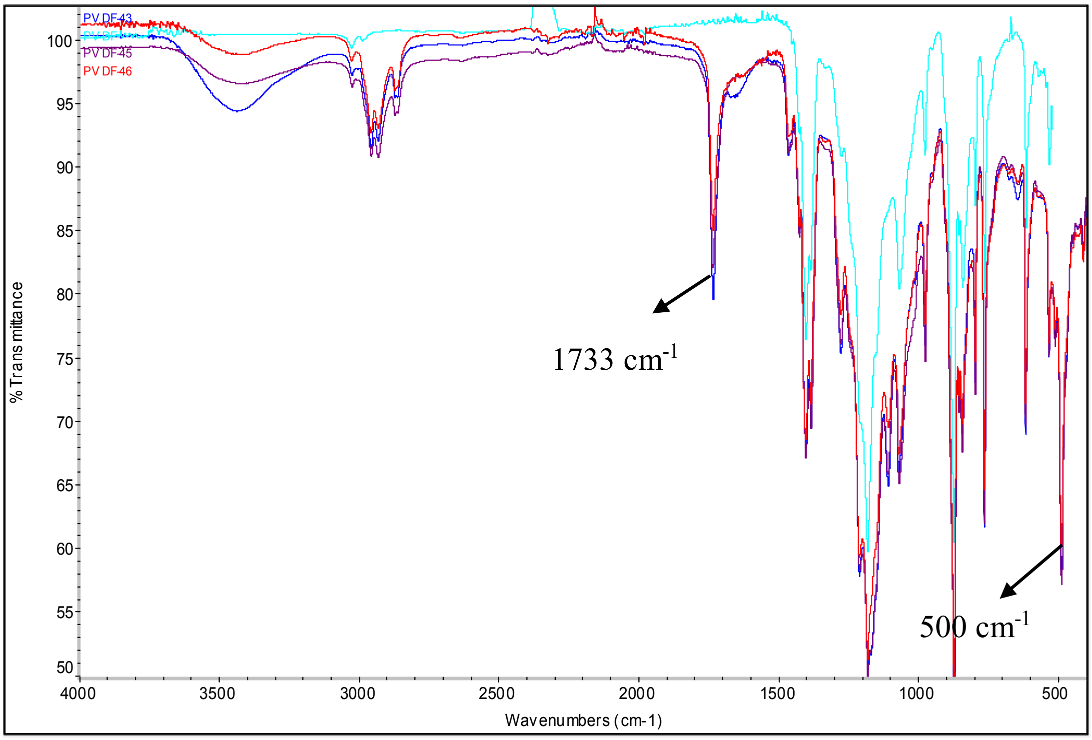


Figure 4.2 : FT-IR spectrum of PVDF and PVDF-Br.

^{1}H-NMR measurement was applied in order to determine degree of substitution of 2-methyl-2-bromo-propionyl group in PVDF. A representative ^{1}H-NMR spectrum of brominated PVDF was shown in Figure 4.3.

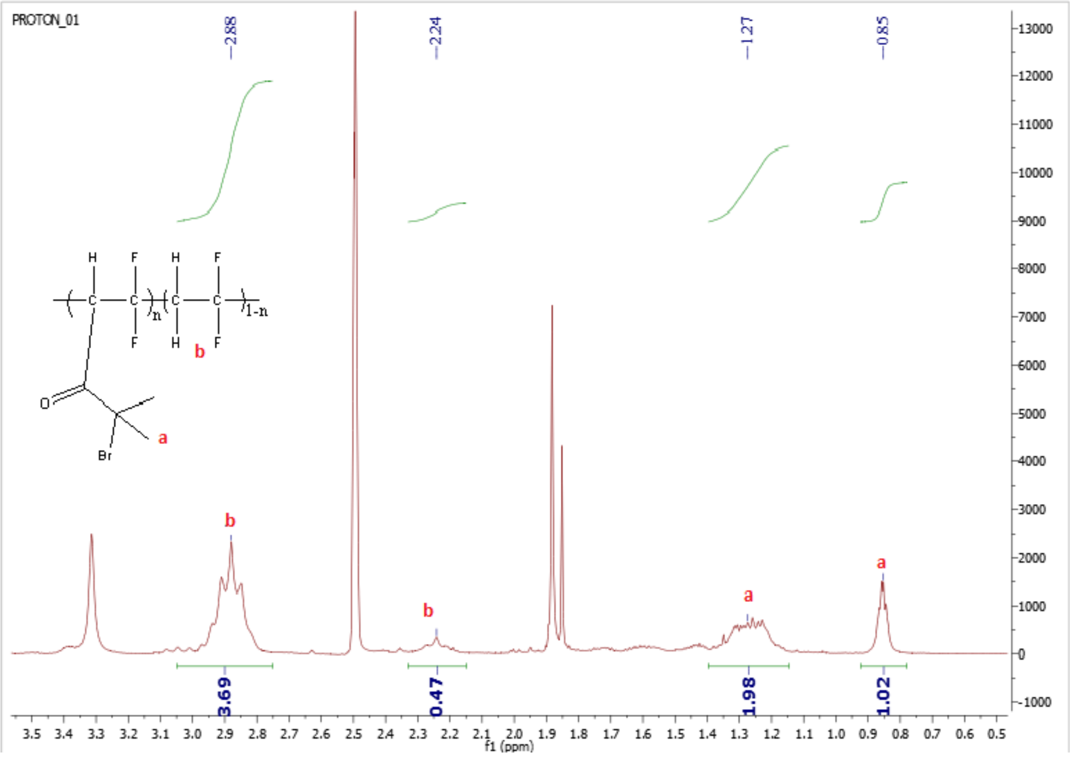


Figure 4.3 : ^{1}H-NMR spectrum of PVDF-Br in DMSO-d$_6$.

As can be seen from Figure 4.3, six hydrogens of -CH$_3$ group (a) are appeared at 1.27 and 0.85 ppm and hydrogens of –CH$_2$CF$_2$ group (b) are appeared at 2.28 ppm and 2.24 ppm. Degree of substitution of brom functionalized group into PVDF (n) was calculated relative integral ratio for corresponding groups as mentioned above. Table 4.1 shows brominated groups content % per PVDF repeat unit in PVDF backbone. Linear feed ([BrIBBr]) and found (DS) relation was obtained in functionization process (Fig. 4.4).

Table 4.1 : Brom functionalization of PVDF^a.

Run	x (BrIBBr)	Degree of substition
PVDF-45	1.1	0.215
PVDF-43	2.0	0.336
PVDF-46	3.0	0.508

^{a}[PVDF]: 1 g in 60 ml of THF at -5 °C. [PVDF]:[n-BuLi]:[BrIBBr]=1:1:x.

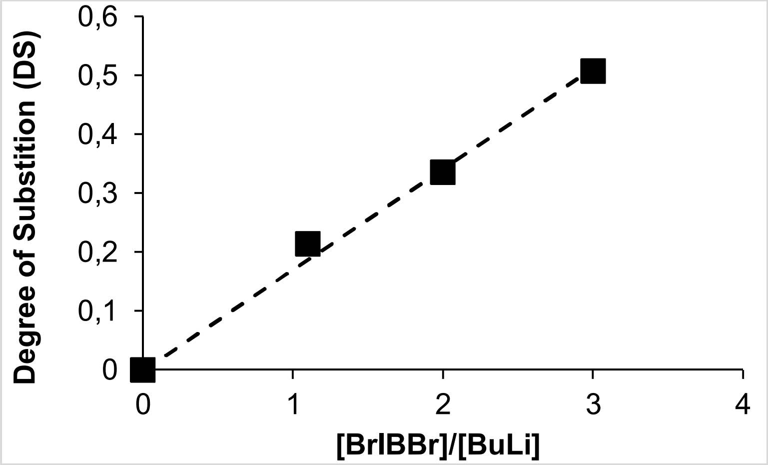


Figure 4.4 : Feed vs found of 2-bromo-2-methyl-propionyl group in PVDF.

4.2 Synthesis of Graft Copolymer

4.2.1 Synthesis of PVDF-*g*-PMMA

PVDF-Br as macroinitiator and MMA as monomer was used in ATRP method for 145 min at 90 °C to obtain MMA grafted PVDF (PVDF-*g*-PMMA). Synthesis reaction of PVDF-*g*-PMMA via ATRP method is shown in Figure 4.5.

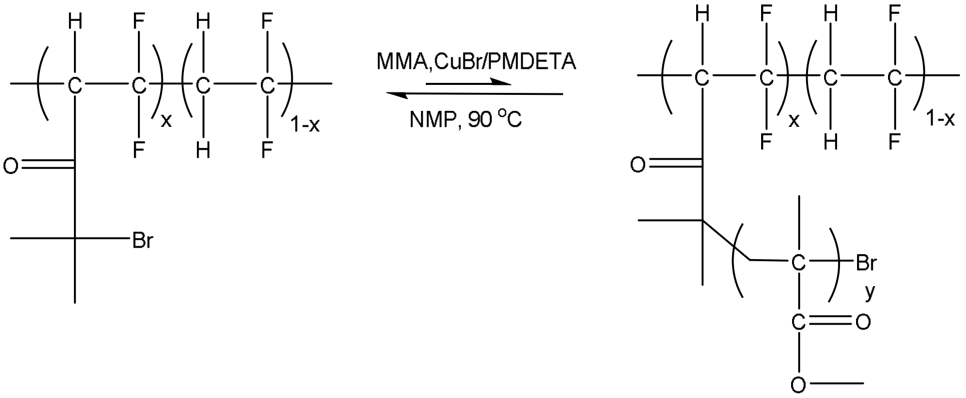


Figure 4.5 : Synthesis of PVDF-*g*-PMMA by ATRP.

The monomer addition to PVDF backbone was prufied according to FT-IR, NMR, GPC and DSC mesurements. FT-IR results are shown in Figure 4.6.

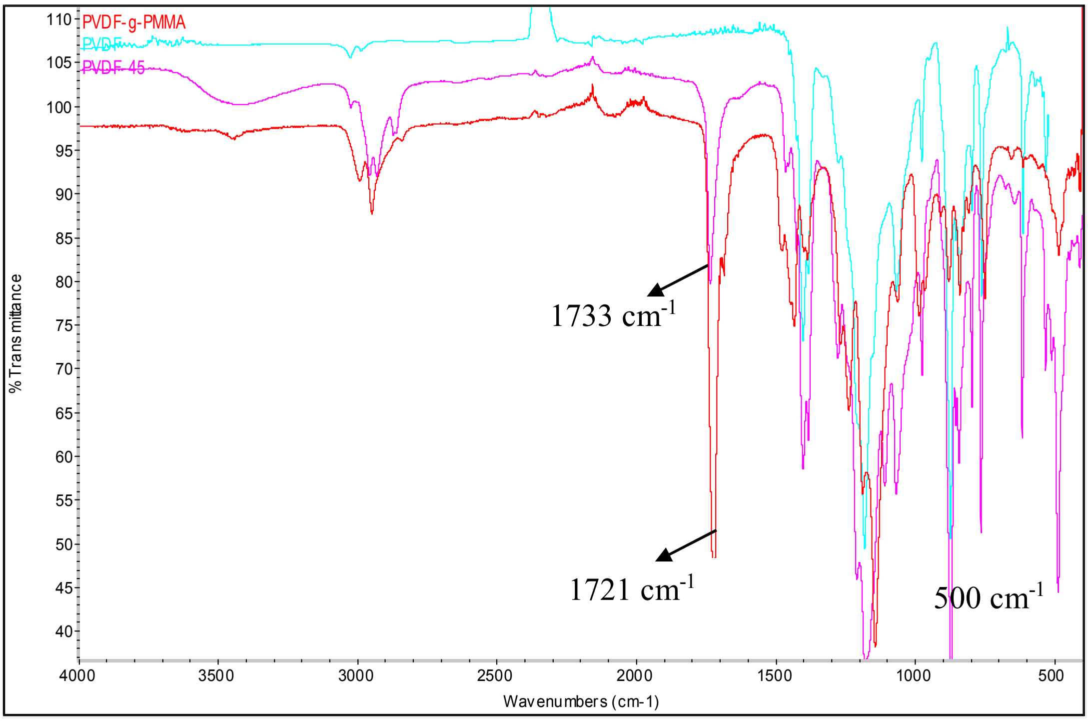


Figure 4.6 : FT-IR results of PVDF-*g*-PMMA.

A strong absorption at 1733 cm^{-1} belongs to C=O stretching of ketonic group of PVDF-Br is shifted to the 1721 cm^{-1}. It is C=O stretching of ester group of PVDF-*g*-PMMA. Carbon-bromine stretching absorption intensity was decreased due to MMA addition.

A representetive ^{1}H-NMR spectra of PVDF-*g*-PMMA was shown in Figure 4.7. PVDF-Br spectrum exhibits a well-known peaks in the regions 2.88 ppm for hydrogens of PVDF (a), 3.56 ppm for three methoxy hydrogens of PMMA (b), and 0.74 ppm and 0.93 ppm for methyl of PMMA (c) (as can be seen in Figure 4.7). Grafting of MMA to PVDF resulted in the appearance of peaks in the region 3.56 ppm due to protons of methoxy group and another new peaks in the region 0.74 ppm and 0.93 ppm due the protons of methyl groups which are connect to double bond in methyl methacrylate. Methoxy groups and methyl groups protons have the same integral. And also decreasing of peaks in the region 1.2 ppm and 0.8 ppm which are coming from PVDF-Br methyl groups.

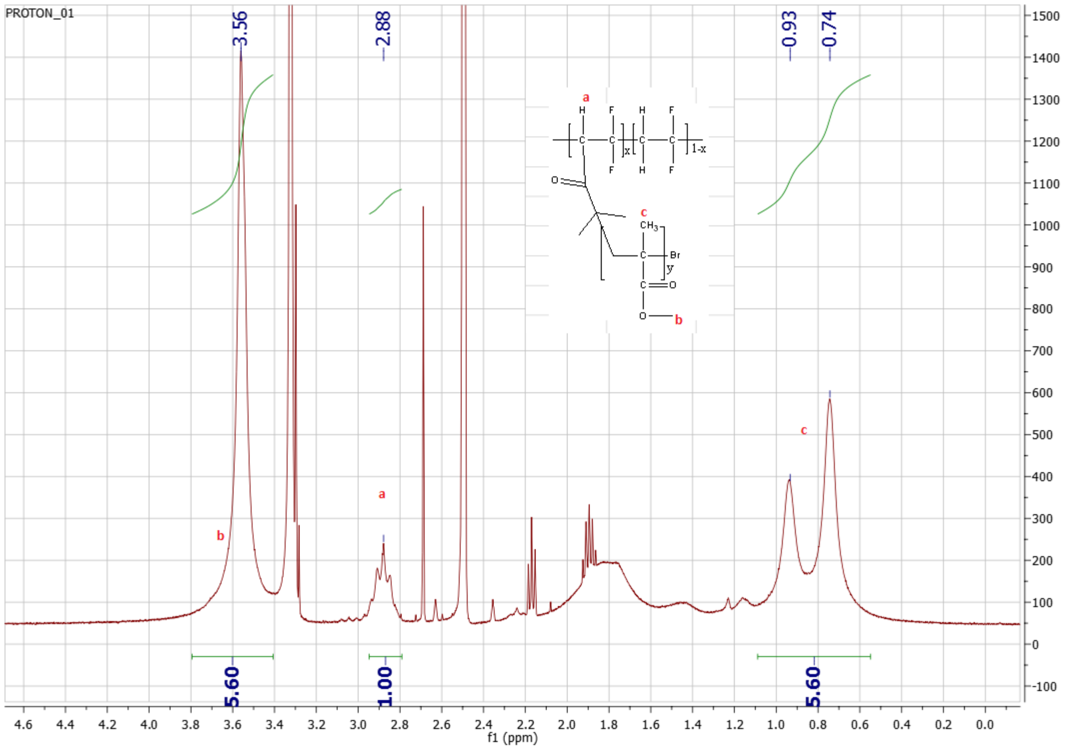


Figure 4.7 : ^{1}H-NMR spectrum of PVDF-*g*-PMMA.

After ^{1}H-NMR and FT-IR, the thermal behavior of PVDF-*g*-PMMA was investigated by using differantial scanning calorimetry in order to see T_g and T_m values of the pure PVDF and also graft materials. The samples were heated from -80 to 250 ºC for PVDF, PVDF-Br (PVDF-45), PVDF-*g*-PMMA. After first heating cycle, materials were cooled to -80 ºC. For second heating cycle, samples were also heated again from -80 to 250 ºC. All thermogram were recorded for second heating scan and shown in Figure 4.8. As can be seen from DSC curve of PVDF, T_m and T_g values were seen at 168.83 and -39.59 ºC, respectively. T_m and T_g values for macro-inititiator PVDF-Br (PVDF-45) were seen at 163.05 and -39.27 ºC, respectively. Whereas, only glass transition temperature (T_g), can be found at 114.71 ºC for PVDF-*g*-PMMA. Results are also shown in Table 4.2.

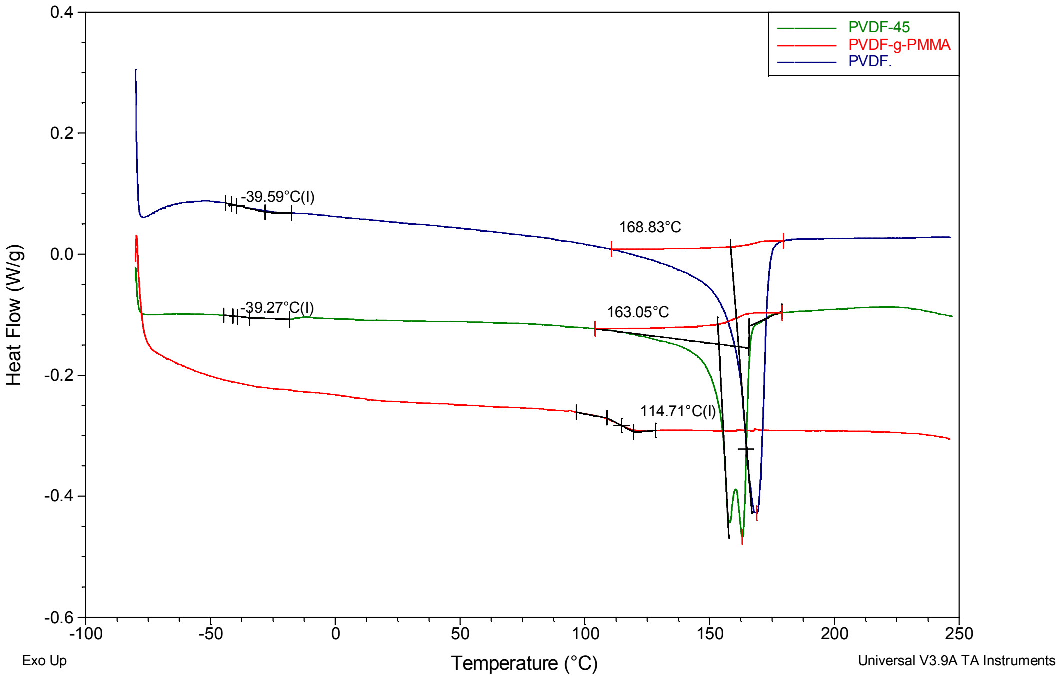


Figure 4.8 : DSC curves of PVDF, PVDF-Br and PVDF-g-PMMA.

Table 4.2 : T_g and T_m values of PVDF and obtained polymers.

Run	T_g (°C)	T_m (°C)
PVDF	-39.59	168.83
PVDF-45	-39.27	163.05
PVDF-*g*-PMMA	114.71	-

PVDF chromatogram has special effect in DMF GPC. Because it gives a negative peak, so if the graft copolymer shows a positive signal this is also evidence of grafting process. After FT-IR, ^{1}H-NMR and DSC characterization we investigated GPC measurement and the results were shown in figure 4.9.

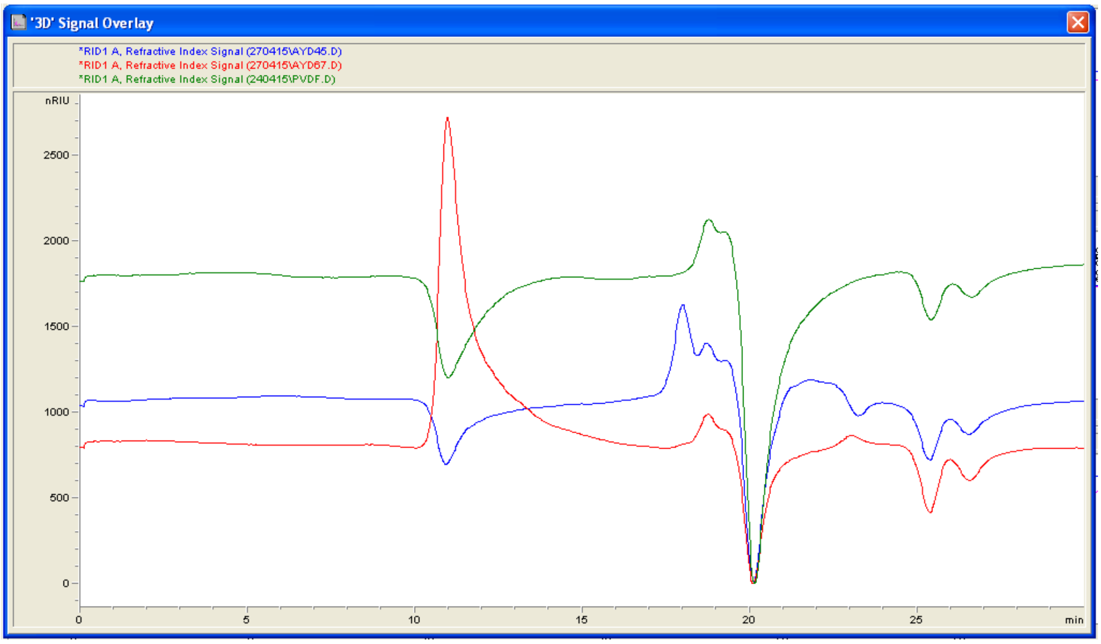


Figure 4.9 : GPC Results of PVDF^{a}, PVDF-Br^{b} and PVDF-*g*-PMMA^{c} (a: green, b: blue, c: red).

After characterization of PVDF-*g*-PMMA, the kinetic of MMA graft copolymerization were carried out in two times. Conversions were calculated both gravimetric and ^{1}H-NMR calculations. The obtained repeatable results were depicted in Figure 4.10. In both calculations, the linear relationship show that the controlled polymerizations were achieved in graft copolymerization processes.

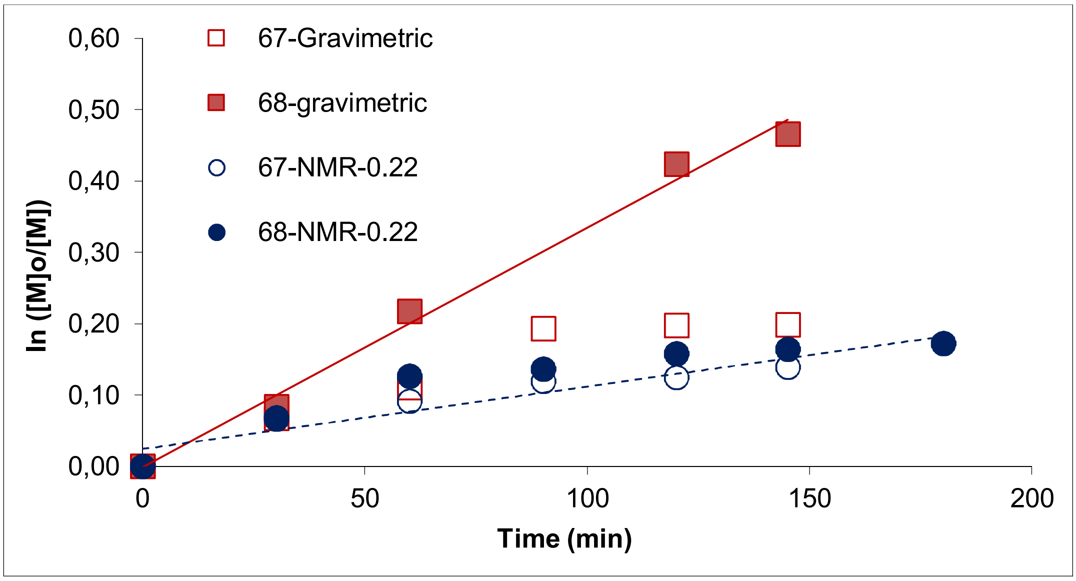


Figure 4.10 : Kinetics of PVDF-*g*-PMMA polymerization. [PVDF-Br]: 1.4×10^{-3} equivalent mol. [MMA]/[PVDF-Br]/[PMDETA]/[CuBr]: 21.9 /1/1/1 for 145 minutes at 90 °C in 5 mL of NMP.

5. CONCLUSION

In this study, PVDF based macro-initiator (PVDF-Br) was synthesized by lithiation and BrIBBr reaction of PVDF. Macro-initiator was characterized by ^{1}H-NMR (d-DMSO d_6), FT-IR ATR spectroscopy for structure.

Then, graft copolymer of polyvinylidene fluoride (PVDF) was synthesized by copper-mediated atom transfer radical polymerization (ATRP). In the graft copolymerization, methyl methacrylate (MMA) was used as monomers and PVDF-Br as a macro-initiator in the presence of different catalyst complex and reaction conditions. The PVDF-based graft copolymer was characterized gel permeation chromatography (GPC) for molecular weight, ^{1}H-NMR (d-DMSO-d_6), FT-IR ATR spectroscopy for structure, differential scanning calorimerty (DSC).

Some problems were encountered during the ^{1}H-NMR and GPC characterizations of PVDF, PVDF-Br, PVDF-*g*-PMMA due to the insolubility in commercial solvents such as tetrahydrofuran, chloroform and dimethylformamid.

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