

**ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE**  
**ENGINEERING AND TECHNOLOGY**

**POLYSULFONE BASED OLIGOMERS AS PRECURSORS FOR  
NETWORKS AND BLOCK COPOLYMERS**

**Ph.D. THESIS**

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**Chemistry Department**

**Chemistry Programme**

**FEBRUARY 2013**



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**İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ**

**AĞSI YAPILARDA VE BLOK KOPOLİMERLERDE ÖNCÜ POLİSÜLFON  
BAZLI OLİGOMERLER**

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## TABLE OF CONTENTS

	<u>Page</u>
<b>FOREWORD</b> .....	vii
<b>TABLE OF CONTENTS</b> .....	ix
<b>ABBREVIATIONS</b> .....	xi
<b>LIST OF TABLES</b> .....	xiii
<b>LIST OF FIGURES</b> .....	xv
<b>SUMMARY</b> .....	xvii
<b>ÖZET</b> .....	xix
<b>1. INTRODUCTION</b> .....	<b>1</b>
<b>2. THEORETICAL PART</b> .....	<b>5</b>
2.1 Introduction to Aromatic Polysulfones .....	5
2.1.1 Synthesis pathways of polysulfones.....	6
2.1.1.1 Polysulfonylation route .....	6
2.1.1.2 Polyetherification route .....	7
2.1.1.3 Strong base approach.....	8
2.1.1.4 Weak base approach .....	9
2.1.2 Chemical modification of polysulfones .....	9
2.1.2.1 Monomer modification.....	10
2.1.2.2 Post-modification .....	13
2.1.2.3 End chain approach .....	14
2.1.2.4 Side chain modification of polysulfones approach .....	15
2.1.2.5 Grafting of polysulfones with other polymers.....	22
2.1.3 Properties and applications of polysulfones.....	24
2.2 Telechelic Oligomers.....	25
2.3 Polymer Layered Nanocomposites .....	32
2.4 Block Copolymers by Macroazoinitiators .....	36
<b>3. EXPERIMENTAL WORK</b> .....	<b>41</b>
3.1 Materials and Chemicals .....	41
3.2 Characterization.....	43
3.2.1 Nuclear magnetic resonance spectroscopy (NMR) .....	43
3.2.2 Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectra .....	43
3.3.2 Differential scanning calorimetry (DSC) .....	43
3.2.4 Photo-differential scanning calorimetry (Photo-DSC).....	43
3.2.5 Gel permeation chromatography (GPC) .....	43
3.2.6 Thermal gravimetric analyzer (TGA) .....	44
3.2.7 X-ray diffraction (XRD).....	44
3.2.8 Transmission electron microscopy (TEM).....	44
3.3 Preparation Methods .....	44
3.3.1 Synthesis of polysulfone oligomers (PSU-2000 and PSU-4000) .....	44
3.3.2 Synthesis of polysulfone diacrylate (PSU-DA) .....	45
3.3.3 Synthesis of polysulfone dimethacrylate (PSU-DMA).....	45

3.3.4 Preparation of photo-curable formulations .....	46
3.3.5 Modification of MMT with methacryloyl chloride .....	46
3.3.6 Preparation of the PSU/MMT nanocomposites (NCs).....	46
3.3.7 Synthesis of 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS) ..	46
3.3.8 Synthesis of polysulfone macroazoinitiator (PSU-MAI) .....	47
3.3.9 Polysulfone- <i>b</i> -polystyrene block copolymers by conventional free radical polymerization technique .....	47
<b>4. RESULTS AND DISCUSSION .....</b>	<b>49</b>
4.1 Synthesis, Characterization and Photoinduced Curing of Polysulfones with (Meth)acrylate Functionalities .....	49
4.1.1 Synthesis of (meth)acrylate functional PSU telechelics .....	49
4.1.2 UV curing of (meth)acrylate functional PSU telechelics .....	52
4.2 Polysulfone/Clay Nanocomposites by in situ Photoinduced Crosslinking Polymerization.....	57
4.2.1 Modification of MMT with methacryloyl chloride .....	57
4.2.2 Preparation of the PSU/MMT nanocomposites and characterization .....	58
4.3 Novel Polysulfone Macroazoinitiator to Prepare Polysulfone- <i>b</i> -Polystyrene Block Copolymers .....	62
<b>5. CONCLUSIONS AND RECOMMENDATIONS .....</b>	<b>69</b>
<b>REFERENCES .....</b>	<b>73</b>
<b>CURRICULUM VITAE .....</b>	<b>99</b>

## ABBREVIATIONS

<b>ACPA</b>	: 4,4-Azobis(4-Cyanopentanoic acid)
<b>ATRP</b>	: Atom Transfer Radical Polymerization
<b>Bis-A</b>	: Bisphenol A
<b>CEC</b>	: Cation Exchange Capacity
<b>CHP</b>	: Cyclohexylpyrrolidone
<b>CMPSU</b>	: Chloromethylated Polysulfone
<b>DCDPS</b>	: 4,4'-Dichlorodiphenyl Sulfone
<b>DMEA</b>	: <i>N,N</i> -Dimethylethanolamine
<b>DMAC</b>	: Dimethylacetamide
<b>DMF</b>	: <i>N,N</i> -Dimethylformamide
<b>DMPA</b>	: 2,2-Dimethoxy-2-Phenyl-Acetophenone
<b>DMSO</b>	: Dimethylsulfoxide
<b>DP<sub>n</sub></b>	: Degree of Polymerization
<b>DPTS</b>	: 4-(Dimethylamino)Pyridinium 4-Toluene Sulfonate
<b>DSC</b>	: Differential Scanning Calorimetry
<b>FT-IR</b>	: Fourier Transform Infrared
<b>GPC</b>	: Gel Permeation Chromatography
<b>K<sub>2</sub>CO<sub>3</sub></b>	: Potassium Carbonate
<b>MAI</b>	: Macroazoinitiator
<b>MMT</b>	: Montmorillonite
<b>NaH</b>	: Sodium Hydride
<b>NC</b>	: Nanocomposite
<b>NMP</b>	: Nitroxide Mediated Polymerization
<b>NMP</b>	: <i>N</i> -methylpyrrolidone
<b>NMR</b>	: Nuclear Magnetic Resonance
<b>PSU-OH</b>	: Phenol-ended PSU Telechelic
<b>PSU</b>	: Polysulfone
<b>PSU-MAI</b>	: Polysulfone Macroazoinitiator
<b>PDMS</b>	: Polydimethylsiloxane
<b>PEO</b>	: Poly(ethylene oxide)
<b>PSU</b>	: Polysulfone
<b>PVDF</b>	: Poly(vinylidene fluoride)
<b>QPSU</b>	: Quaternized Polysulfone
<b>RAFT</b>	: Reversible Addition-Fragmentation Chain Transfer Polymerization
<b>SPSU</b>	: Sulfonated Polysulfone
<b>SIATRP</b>	: Surface-Initiated Atom Transfer Radical Polymerization
<b>TGA</b>	: Thermal Gravimetric Analysis
<b>T<sub>g</sub></b>	: Glass Transition Temperature
<b>TBAB</b>	: Tetra- <i>n</i> -Butyl Ammonium Bromide
<b>THF</b>	: Tetrahydrofuran



## LIST OF TABLES

	<u>Page</u>
<b>Table 2.1</b> : Commercial polysulfones.....	6
<b>Table 2.2</b> : Termination percentage by combination of different monomers at 25 °C. ....	27
<b>Table 2.3</b> : Differences between addition and step-growth polymerizations [239]. .	30
<b>Table 2.4</b> : Types of macroazoinitiators (MAIs). ....	39
<b>Table 2.5</b> : Types of block copolymers. ....	40
<b>Table 4.1</b> : Synthesis <sup>a</sup> and molecular weight characteristics of polysulfones. ....	52
<b>Table 4.2</b> : Photoinitiated crosslinking polymerization of PSU-DMA in the presence and absence of organomodified I-MMT, and thermal properties of neat PSU, I-MMT and resulting nanocomposites. ....	59
<b>Table 4.3</b> : Block copolymerization of styrene with PSU-MAI at 70 °C in 2 ml DMF under N <sub>2</sub> atmosphere. ....	67



## LIST OF FIGURES

	<u>Page</u>
<b>Figure 1.1</b> : Structure of commercially available UDEL polysulfone. ....	1
<b>Figure 2.1</b> : The simplest aromatic polysulfone. ....	5
<b>Figure 2.2</b> : Polysulfone synthesis by polysulfonylation route. ....	7
<b>Figure 2.3</b> : The mechanism of electrophilic aromatic substitution. ....	7
<b>Figure 2.4</b> : Polysulfone synthesis by polyetherification route. ....	8
<b>Figure 2.5</b> : Polysulfone synthesis by polyetherification route. ....	8
<b>Figure 2.6</b> : The synthetic pathways for the modifications of polysulfones. ....	10
<b>Figure 2.7</b> : Functional monomer approach. ....	10
<b>Figure 2.8</b> : Synthesis of poly(arylene ether phosphine oxide sulfone). ....	11
<b>Figure 2.9</b> : Post- modification of polysulfones-General approach. ....	14
<b>Figure 2.10</b> : End chain modification of polysulfones. ....	14
<b>Figure 2.11</b> : Halomethylation-General approach. ....	16
<b>Figure 2.12</b> : “Grafting onto” approach. ....	22
<b>Figure 2.13</b> : “Grafting from” approach. ....	24
<b>Figure 2.14</b> : Structures obtained by the reaction of telechelics. ....	26
<b>Figure 2.15</b> : Disproportionation and coupling reactions of propagating radicals. ....	27
<b>Figure 2.16</b> : Radical formation by cleavage of carbon-nitrogen bonds with heat. ..	27
<b>Figure 2.17</b> : Polysulfone telechelics obtained by one monomer excess case. ....	31
<b>Figure 2.18</b> : Size comparison of macro, micro and nano materials [283] .....	33
<b>Figure 2.19</b> : Representative scheme of montmorillonite (MMT)[332]. ....	34
<b>Figure 2.20</b> : Conventional, intercalated and exfoliated polymer/layered silicates. .	35
<b>Figure 2.21</b> : Formation of exfoliated polymer/layered silicates by polymerization of monomers in the layers. ....	35
<b>Figure 2.22</b> : Different types of block copolymers. ....	37
<b>Figure 2.23</b> : Synthetic ways for block copolymers. ....	38
<b>Figure 2.24</b> : Formation of AB or ABA block copolymers by disproportionation or combination. ....	39
<b>Figure 4.1</b> : Synthesis of (meth)acrylate functional PSU telechelics. ....	49
<b>Figure 4.2</b> : FT-IR spectra of PSU-2000, PSU-DA-2000 and PSU-DM-2000. ....	50
<b>Figure 4.3</b> : <sup>1</sup> H NMR spectra of PSU-2000 (a), PSU-DA-2000 (b) and PSU-DM-2000 (c) in CDCl <sub>3</sub> . ....	51
<b>Figure 4.4</b> : Rate (a) and conversion (b) of photo induced polymerization of PSU- DA-2000 and PSU-DM-2000 in precence of DMPA (2%) as initiator, cured at 30 °C by UV light with an intensity of 53 mW cm <sup>-2</sup> under nitrogen flow of 20 mL min <sup>-1</sup> .....	53
<b>Figure 4.5</b> : Rate (a) and conversion (b) of photo induced polymerization of PSU- DA-2000 and PSU-DA-4000 in precence of DMPA (2%) as initiator, cured at 30 °C by UV light with an intensity of 53 mW cm <sup>-2</sup> under nitrogen flow of 20 mL min <sup>-1</sup> .....	55
<b>Figure 4.6</b> : TGA thermograms of the precursor oligomers (PSU-2000) (a), and macromonomer, PSU-DA-2000 before (b), and after curing PSU-DA-2000 cross)(c).. ....	56

<b>Figure 4.7 :</b> DSC results of the precursor oligomer (PSU-2000) (a), and macromonomer, PSU-DA-2000 before (b), and after curing (PSU-DA-2000 cross) (c).....	57
<b>Figure 4.8 :</b> FT-IR spectra of Cloisite 30B and I-MMT.....	58
<b>Figure 4.9 :</b> Preparation of polysulfone/montmorillonite clay nanocomposites by <i>in situ</i> photoinitiated crosslinking polymerization. ....	58
<b>Figure 4.10 :</b> X-ray diffractions of organo-modified clay I-MMT, NC1, NC3 and NC5 nanocomposites.....	59
<b>Figure 4.11 :</b> TGA thermograms of neat PSU-DMA, organo-modified clay I-MMT, NC1, NC3 and NC5 nanocomposites. ....	60
<b>Figure 4.12 :</b> DSC traces of neat PSU-DMA, NC1, NC3 and NC5 nanocomposites. ....	61
<b>Figure 4.13 :</b> TEM micrographs of PSU/MMT nanocomposites (A, NC1), (B, NC3) and (C, NC5) in high (scale bar: 20 nm, upper images) and low magnification (scale bar: 50 nm).....	62
<b>Figure 4.14 :</b> Synthesis of PSU, PSU-MAI and PSU- <i>block</i> -PS copolymer.....	63
<b>Figure 4.15 :</b> FT-IR spectra of ACPA, PSU and PSU-MAI. ....	64
<b>Figure 4.16 :</b> FT-IR spectra of PSU- <i>block</i> -PS copolymers, (1) and (2).....	65
<b>Figure 4.17 :</b> <sup>1</sup> H NMR spectra of ACPA, PSU-MAI and PSU- <i>block</i> -PS copolymer.....	66
<b>Figure 4.18 :</b> TGA thermograms of the precursor oligomer (PSU), polystyrene (PS), macro-azoinitiator (PSU-MAI), and block copolymer (PSU- <i>b</i> -PS)...	68
<b>Figure 4.19 :</b> DSC results of ACPA, the precursor oligomer (PSU), macroazoinitiator (PSU-MAI), and copolymer (PSU- <i>b</i> -PS).....	69

## POLYSULFONE BASED OLIGOMERS AS PRECURSORS FOR NETWORKS AND BLOCK COPOLYMERS

### SUMMARY

Polysulfone (PSU) is a highly engineered thermoplastic with chemical resistance to hydrolysis, acids and bases and favorable high temperature properties. Due to these excellent properties, PSU can be used in medical devices, food processing, feeding systems, automotive and electronic industry. Depending on the area of application, PSU polymers are often modified to give materials with additional physical properties.

In the first part of the thesis, telechelic strategy has been applied for modification of polysulfones. Firstly, functional phenol-ended polysulfone telechelics with low and high molecular weights have been prepared simultaneously by condensation reaction of bisphenol-A and bis (p-chlorophenyl) sulfone with different ratios in the presence of potassium carbonate. After that the obtained telechelics have been modified with acrylate or (meth) acrylate groups in order to be used as polymeric precursors for preparation of cross linkable networks.

The structure of the telechelics before and after functionalization was confirmed by proton nuclear magnetic resonance spectroscopy ( $^1\text{H}$  NMR) and fourier transform infrared spectroscopy (FT-IR). The molecular weights have been determined by gel permeation chromatography (GPC). Photo induced curing behaviour of the acrylate or (meth) acrylate functional telechelics has been carried out by photo differential scanning calorimetry (photo-DSC) using 2,2-dimethoxy-2-phenyl-acetophenone (DMPA) as the photoinitiator. Thermal properties of the crosslinked networks were studied by thermal gravimetric analysis (TGA) and dynamic scanning calorimetry (DSC).

The effects of the molecular weight of the PSU precursor and type of functionality on the rate of polymerization and conversion were evaluated. The thermal stability of the photochemically cross-linked polymers indicates that these oligomers may be important ingredients of photo curable formulations for obtaining networks that could have useful application in coatings and membranes. Thus we thought the use of these telechelics for the formation of polysulfone based nano composites with improved properties.

In the second part of the study, a new class of photo cross linkable oligomers consisting of polysulfone structure as backbone with methacrylate functional groups connected to both ends has been successfully applied for the preparation of polysulfone/clay nanocomposites. Polysulfone/montmorillonite (PSU/MMT) nanocomposites are prepared successfully dispersing the inorganic nanolayers of MMT clay in an organic PSU matrix via *in situ* photoinduced crosslinking polymerization. The morphology of the nanocomposites is investigated by X- ray

diffraction (XRD) and transmission electron microscopy (TEM) techniques, which suggests the random dispersion of silicate layers in the PSU matrix. Thermogravimetric analysis results confirms that the thermal stability and char yield of PSU/MMT nanocomposites increases with the increase of clay loading.

In the third part, macroazoinitiator (MAI) having polysulfone (PSU) units was synthesized from 4,4'-azobis(4-cyanopentanoic acid) (ACPA) and PSU oligomer by direct esterification process at ambient conditions. It was used for the preparation of block copolymers by conventional free radical polymerization method. The block copolymers were achieved by free-radicals generated from the cleavage of the azo group from macroazoinitiator in the presence of styrene monomer in dimethylformamide (DMF) solution by heating. The effect of the polymerization time and the macroazoinitiator concentration has been studied. The polysulfone macroazoinitiator (PSU-MAI) and polysulfone-*b*-polystyrene block copolymers were characterized by spectral analysis using FT-IR, <sup>1</sup>H-NMR, GPC, TGA and DSC.

## AĞSI YAPILARDA VE BLOK KOPOLİMERLERDE ÖNCÜ POLİSÜLFON BAZLI OLİGOMERLER

### ÖZET

Polisülfon (PSU) asitlere, bazlara ve hidrolize karşı kimyasal dayanıma sahip ve yüksek sıcaklıklarda kullanıma uygun olma özelliği olan yüksek performans polimerlerinden biridir. Bu üstün özelliklerinden dolayı polisülfonlar tıp cihazlarında, besleme sistemlerinde, otomotiv ve elektronik endüstrisinde kullanılırlar. Uygulama alanına bağlı olarak PSU polimerleri genellikle modifiye edilerek artı fiziksel özelliklere sahip malzemeler elde edilir. Bu kapsamda polisülfonların fonksiyonlandırılmasında iki yöntem kullanılır: (i) Monomerlerin fonksiyonlandırılması ve daha sonra başka monomerlerle polimerleştirilmesi ve (ii) PSU polimer elde edildikten sonra fonksiyonel gruplarla veya başka polimerlerle modifiye edilmesi.

Son zamanlarda, araştırmacılar genellikle polisülfonların film olabilme özelliklerinden yararlanmışlardır. Gözenek boyutlarının kontrol edilmesi ve kolayca imal edilmelerinde dolayı PSU polimerlerinin membran uygulamaları çok fazladır. Endüstriyel olarak hemodiyaliz, su temizleme, gaz ayırma ve yakıt hücrelerinde membran uygulamaları çok yaygındır. Ayrıca fonksiyonel polisülfonlar veya oligomerler epoksi reçinelerle birlikte kullanılarak oluşan ürünlerin kırılgenliklerini azaltırlar.

Fonksiyonel gruplara sahip öncü polimerler telekelik oligomerler olarak adlandırılırlar. Bu fonksiyonel gruplar kullanılarak başka reaksiyonların gerçekleşmesi sağlanır. Telekelik oligomerlerin sentezi ve kullanılmaları halen güncel bir konudur. Telekelik oligomerler kendilerine has özelliklere sahiptirler ve blok kopolimerlerin elde edilmesinde öncü ara madde olarak kullanılırlar. Telekelik oligomerler ayrıca dallanmış dentritik polimerleri, aşı polimerleri veya çapraz bağlı sistemlerin elde edilmesinde öncü yapılar olarak kullanılmaktadırlar. Endüstriyel olarak termoplastik elastomerlerin elde edilmesinde telekelik oligomerler ve polimerlerinin kullanımı çok önemlidir. Ayrıca telekelik oligomerler boya, mürekkep, yapıştırıcı, kauçuk ve kompozit malzemeler gibi bir çok endüstri alanında çok yaygın kullanıma sahiptirler.

Polimer-kil nanokompozitler, 1 ila 100 nm boyut aralığına sahiptirler. Polimer-kil nanokompozitler ısı, alev ve çözücü dayanımı, düşük gaz geçirgenliği ve mekanik özellikler gibi sade bir polimerle kıyaslandığında bir çok üstün özelliğe sahip malzemelerdir. Mikro kompozitlerle kıyaslandığında nanoyapıların polimerlere çok az miktarlarda eklenmesi bile polimerlerde çok fazla özelliği değiştirip daha dayanıklı ve ısı, mekanik ve fiziksel gibi bir çok üstün özelliklere sahip polimer-nanokompozitlerin elde edilmesini sağlar. Çok az eklenmeleri ile yüksek performanslı ürünlerin elde edilmesini sağladığından ekonomik olarak da çok cazip materyallerdir. Endüstriyel termoplastik ve termoset polimerlerin nanokompozitlerinin geliştirilmesi için çalışmalar devam etmektedir. Polimer-kil

nanokompozitlerin hazırlanmasında kilin polimere uygunluğu, fiziksel ve kimyasal yapısı ve yüzey alanı gibi özellikleri çok önemlidir.

Montmorillonit polimer-kil nanokompozitlerin hazırlanmasında çokça kullanılan bir kil çeşitidir. 2:1 tabaka yapısına sahip olan bu kilin tabakaları arasına polimer veya monomerlerin eklenip açılması ile polimer-kil nanokompozit oluşumu sağlanır. Üç çeşit yol ile polimer-kil nanokompozitleri elde edilebilir. Bunlar, (i) erime interkalasyonu, (ii) solüsyon eksfoliasyonu ve (iii) *in situ* polimerizasyonu. En fazla kullanılan yöntem üçüncü yöntem olup tezde de bu yöntemle polimer-kil nanokompozitlerinin elde edilmiştir.

Makroazobaşlatıcılar blok kopolimerlerin elde edilmesinde sıklıkla kullanılırlar. Makroazobaşlatıcıların önceden karakterize edilmeleri radikal polimerizasyon öncesi büyük avantaj sağlar. Bütün polimerizasyon çeşitleri ile makroazobaşlatıcıların sentezi gerçekleştirilebilir. İkinci bloğun eklenmesinde azo grupları makroazobaşlatıcıdan ayrılarak radikalik merkezlerin oluşmasını sağlarlar. Azo grupları ısı ile veya ışık kullanılarak kırılırlar. Kondenzasyon veya ekleme mekanizmaları ile makroazobaşlatıcılar elde edilebilirler. İkinci bloğun eklenmesi sonrasında zincir sonlanması blok kopolimerin hangi çeşit olacağını belirler. Bu nedenle disproporsiyasyon veya kombinasyon sonlanması sonucu ABA veya AB çeşidi kopolimerlerin elde edilebilir. Kombinasyon ile sonlanan stiren veya akrilat gibi monomerlerin ikinci blokta kullanılması ile ABA kopolimerleri oluşurken metakrilat monomerleri disproporsiyasyon ile sonlanarak genelde AB tipi blok kopolimerlerin elde edilmesine neden olurlar. Azo grupları merkezde bir tane veya birden çok olabilecekleri gibi uç gruplarda bir veya iki tane olarak da elde edilebilirler. Azo grupların yerine göre elde edilecek blok kopolimerinde çeşidi değişir.

Bu tezin ilk kısmında telekelik stratejisi polisülfonların modifikasyonu için kullanıldı. İlk olarak düşük ve yüksek molekül ağırlıklarına sahip fonksiyonel fenol uçlu polisülfon telekelikler potasyum karbonat varlığında bisfenol-A ve bisklorofenilsülfonun farklı oranlarda kondanzasyon polimerizasyonu ile elde edildi. Daha sonra elde edilen telekelikler çapraz bağlı yapıların hazırlanmasında öncül olmaları için akrilat ve metakrilat grupları ile modifiye edildiler. Fonksiyonlanma öncesi ve sonrası telekeliklerin yapılarının belirlenmesi proton nükleer magnetik rezonans spektroskopisi ile ( $^1\text{H}$  NMR) ve fourier transform infrared spektrofotometresiyle (FT-IR) gerçekleştirilmiştir. Molekül ağırlıklarının belirlenmesi için jel geçirgenlik kromatografisi (GPC) kullanılmıştır. Ayrıca GPC ile belirlenen molekül ağırlıkları proton NMR ile de kıyaslanmıştır. Elde edilen sonuçlar benzer özellik göstermiştir. Akrilat ve metakrilat fonksiyonlu telekeliklerin ışık uyarılma kürlenme davranışı foto başlatıcı olarak 2,2-dimetoksi-2-fenil-asetofenon (DMPA) kullanılması ile foto-diferansiyel tarama kalorimetresi (foto-DSC) ile gerçekleştirilmiştir. Çapraz bağlı ağsı yapıların termal özellikleri ısı ağırlıksal analiz (TGA) ve diferansiyel tarama kalorimetresi (DSC) kullanılarak çalışılmıştır. Bu sonuçlara göre polisülfon oligomerinin molekül ağırlığı arttıkça uç grupların daha serbest hareket etmesi nedeniyle çapraz bağlanma derecesi artmıştır. Çapraz bağlanma ile ısı kararlılığında arttığı gözlenmiştir.

Polimerizasyon hızına ve dönüşüme fonksiyonel grup ve molekül ağırlığının etkileri değerlendirildi. Foto kimya ile çapraz bağlanan polimerlerin ısı kararlılığı bu oligomerlerin kaplama ve membran uygulamalarına uygun ağsı yapıların eldesi için foto-kürlenabilir formülasyonlarda önemli katkı malzemeleri olabileceğini gösterdi.

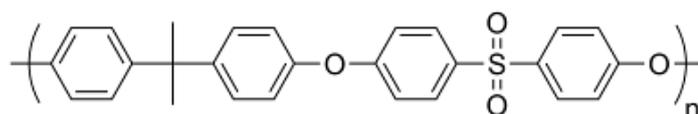
Bu sonuçla bu telekeliklerin polisülfon bazlı üstün özellikli nanokompozitlerde de etkili olabilecekleri düşünüldü. Tezin ikinci kısmında iskeleti iki ucu metakrilat gruplu polisülfon olan yeni bir sınıf çapraz bağlanabilen oligomerler polisülfon/kil nanokompozitlerin hazırlanması için uygulandı. *In situ* ışıkla uyarılmış çapraz bağlama polimerizasyonu kullanılarak inorganik montmorilonit nanotabakaların organik polisülfon matrisinde dağıtılmasıyla polisülfon/montmorilonit (PSU/MMT) nanokompozitler başarılı bir şekilde hazırlandı. PSU matrisinde silika tabakalarının rastgele dağıldıklarını gösteren X-ışını kırınım yöntemi (XRD) ve geçirimli elektron mikroskopu (TEM) teknikleri ile nanokompozitlerin morfolojisi tanımlandı. XRD sonuçlarına göre nano tabakaların tamamen eksfoliyeye oldukları gözlenmesine rağmen TEM analizlerinde bazı kil tabakalarının birbirinden ayrılmadıkları fakat interkale oldukları gözlemlendi. Termo ağırlıksal analiz ısı kararlılığın ve kül veriminin kil miktarı arttıkça PSU/MMT nanokompozitlerde arttığını gösterdi.

Üçüncü bölümde, polisülfon (PSU) birimlerine sahip makroazobaşlatıcı (MAI) 4,4-azobis(4-siyanopentenoik asit) (ACPA) ve PSU oligomerinden esterifikasyon işlemi ile oda sıcaklığında elde edildi. Bu başlatıcı konvansiyonel serbest radikal polimerizasyon metodu kullanılarak blok kopolimerlerin hazırlanmasında kullanıldı. Blok kopolimerler stiren varlığında dimetilformamit (DMF) solüsyonunda ısıtma ile azo gruplarının azo başlatıcıdan kopmasıyla oluşan serbest radikallerden elde edildi. Stiren monomeri kombinasyon ile sonlandığından genellikle ABA tipi blok kopolimerlerinin elde edilmesi sağlandı. Polimerizasyon zamanının ve makroazobaşlatıcının konsantrasyonunun etkisi çalışıldı. Elde edilen sonuçlara göre polimerizasyon zamanı arttıkça verim ve molekül ağırlığı artarken makroazobaşlatıcı konsantrasyonu arttıkça verimin arttığı fakat molekül ağırlığının düştüğü gözlenmiştir. Polisülfon makrobaşlatıcı ve polisülfon-*b*-polistiren blok kopolimerleri FT-IR, <sup>1</sup>H-NMR, GPC, TGA and DSC kullanılarak karakterize edildi. Polisülfon oranının artması ile camsı geçiş sıcaklığı ve ısı kararlılığında beklendiği gibi arttığı gözlenmiştir.



## 1. INTRODUCTION

Polysulfone (PSU)(Figure 1.1) is a high performance thermoplastic with significant properties such as, thermally and oxidatively stable at higher temperatures, good mechanical properties, high glass transition temperatures, high strength and stiffness at high temperatures, continuously use, perfect resistance to acids and bases [1]. PSU offers good film forming properties as well [2]. Due to these superior features, PSU have been applied in many different applications such as, automotive parts, food processing systems, medical equipments, feeding technology and electronic industry [3]. Depends upon the area of application, materials with additional physical and chemical properties can be obtained by the modification of PSU polymers [4]. Functionalization of PSU polymers may be achieved by two general ways: (i) Firstly monomers are functionalized and then copolymerized and (ii) postpolymerization technique in which PSU polymer is modified with other functional groups or polymers after PSU polymers are obtained [5, 6].



**Figure 1.1 :** Structure of commercially available UDEL polysulfone.

Recently researchers are benefitted from the film forming properties of polysulfones. Due to ease of manufacturing of reproducible membranes having controlled pore sizes PSU polymers finds places in membrane technology such as hemodialysis, water purification, gas separation and fuel cells. Also PSU polymers have been used in preparation of block copolymers after postmodification of their side chains or terminal groups with functional groups that may be used in polymerization of monomers or in chemical bonding with other polymers [7, 8]. End functionalized PSU polymers or oligomers are also used in combination with thermosets based on epoxy resins for dissolving the problem related to brittleness [9].

Prepolymers having functional end groups can be defined as the telechelic oligomers. These end groups may function in further reactions [10]. Development of methods in

the synthesis of telechelic oligomers and their use are still an active area of research. These materials have unique properties and may serve as preintermediates for block polymers. They can also be used in many different fields as crosslinking agents, curatives, star and precursors for hyper branched dendritic polymers, graft polymers or networks [11]. Industrial interest in telechelic polymers have increased by their use as thermoplastic elastomers. Their positive effects on the process and producing materials with improved properties are important factors that increase their usage [12, 13]. Different industrial sectors dealing with paints, inks, adhesives, rubbers and composites make use of telechelics. The type of functionality, structure and length of the backbone are important issues for telechelics and ultimately the polymeric material being produced there from. The functional groups can be diols, diamines, diacids, and olefins that can result in the production of gels and networks. Many review articles related to syntheses and modifications of them have been written in detail [14, 15]. Reportedly, there are a wide range of methods to prepare the telechelic oligomers including conventional and controlled radical, ionic and condensation polymerization. The most used technique is the radical polymerization due to its simplicity, tolerance to many functional groups, and applicability to wide range of monomers [16]. The major problem of synthesizing telechelics arises from the incompleteness of reactions and difficulties in the determination of end-groups.

Polymer-layered clay nanocomposites have received much attention in industry and in academia because they show significant enhancements in materials features such as, thermal, flame and solvent resistancy, lower gas permeabilities and mechanical properties in comparison with neat polymer or micro and macro-composites [17]. Nano-sized clay layers having a large surface area interact with the polymer matrix. Therefore, the use of suitable clay types and modification of the clays are very important. Montmorillonite (MMT) is the mostly applied clay with hydrophilic nature, because it can be converted to hydrophobic nature by ion exchange process to enhance the compatibility of polymer with the clay layers. Generally, three methods are used to prepare polymer/clay nanocomposites: melt intercalation, solution exfoliation, and *in situ* polymerization [17]. Latter is the best and mostly applied technique for the preparation of nanocomposites by the reason that various nanofillers and polymer subunits can be used to get improved features [18]. In this approach, initiator, monomer and catalyst are put altogether between the clay layers

and the *in situ* polymerization is started via an external stimulation such as, UV light or heat [19, 20] resulting the separate the layers from each other in the host matrix to form polymer/clay nanocomposites. Several polymer/clay nanocomposites have been widely prepared by using *in situ* polymerization techniques such as, cationic polymerization [21], anionic polymerization [22], controlled radical polymerization [23-25], conventional free radical polymerization [26-28], ring-opening polymerization [29-32], and ring-opening metathesis polymerization [33]. Free radical polymerization is the mostly applied method by its simplicity and suitability to form nanocomposites with several monomers. In comparison to thermal polymerization, photopolymerization offers various advantages such as, room temperature curing conditions, higher polymerization rate and solvent-free formulations [34, 35]. Several types of polymers, such as polyacrylamide [36], polymeth(acrylate)s [37, 38], poly(vinyl)ether and epoxides [39], have been applied to prepare polymer/clay nanocomposites. Some papers about PSU/clay nanocomposites are reported in the literature [40-44].

Macroinitiator technique is the mostly applied technique to synthesize block copolymers. This technique is advantageous due to the characterization of the macroinitiators before starting the radical polymerization and all polymerization techniques can be used to achieve macroinitiators. Azo or peroxy groups incorporated into the polymers may serve as the radical initiating sites for the preparation of second block [45, 46].

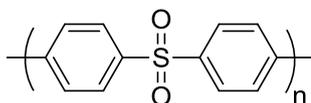
Macroazoinitators (MAIs) containing azo functional groups exhibit a most versatile way of preparing block copolymers by conventional radical polymerization [47-50]. Block copolymerization is initiated from the radical existed by the cleavage of the azo group from the polymer backbone thermally or photochemically. According to type of MAI, whether contains one or more azo group, and termination reaction, whether it is terminated with combination or disproportionation, di (AB), tri (ABA or BAB) or multi (AB)<sub>n</sub> block copolymers can be synthesized. MAIs can be synthesized from the materials having polycondensation or polyaddition functions [51-53]. Several block copolymers containing condensation segments (e.g, polyamide, polyether, polyester, polysiloxane and polyurethane) have been reported [54-58].



## 2. THEORETICAL PART

### 2.1 Introduction to Aromatic Polysulfones

Aromatic polysulfones are an important group of commercially available amorphous or semi-crystalline high performance engineering thermoplastics with several desirable properties such as, thermally and oxidatively stable at higher temperatures, good mechanical properties, high stiffness and strength at high temperatures, high glass transition temperatures, continuously use, perfect resistance to acids and bases. Poly (p-phenylene sulfone) is the simplest aromatic polysulfone (Figure 2.1). It melts above 500 °C with decomposition so it can not show any thermoplastic behaviour. Therefore, incorporation of ether linkages into the backbone is suitable to obtain more flexible thermoplastics capable of injection molding in conventional machines [59]. For this reason, from the chemical point of view these polymers are characterized by phenylene, sulfone (-SO<sub>2</sub>-), ether (-O-), and in some cases, other groups in the chain. Due to the diarylsulfone group in the main chain backbone, polysulfones offer good film-forming properties as well [60-62].



**Figure 2.1 :** The simplest aromatic polysulfone.

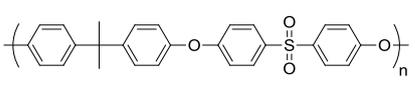
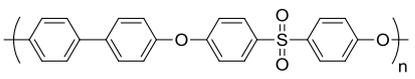
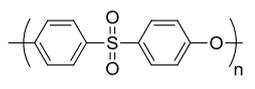
Because of their superior thermal, chemical and mechanical properties polysulfones have been benefitted in many applications such as filtration membranes [63-65] coatings [66, 67], composites [68, 69], microelectronic devices [70, 71], thin-film technology [72], biomaterial [73], and fuel cells etc [74-76].

However, they have several disadvantages such as higher solvent sensitivities, creeping under load at higher temperatures above their Tg's, susceptible to stress cracking with certain solvents, the non-resistance to ultra violet (UV) radiations, poor tracking resistance and poor weathering properties, which may limit their uses such as in blood filtration its hydrophobicity causes fouling of the proteins [77-79]. Without losing the polymer properties, chemical modifications of the end-groups or

polymer backbone of polysulfones gave good results as compared to the blended systems, in which two or more different polymers combine to get new polymeric systems for specific purposes [80-82]. After chemical modifications these polymers can be used in many different industrial areas such as automobiles, electronics, aerospace, membrane etc [83-85].

The synthesis of condensation polymers from p, p'- dihalodiphenyl sulfones and p-phenylenedithiols by Kreuchunas in 1958 was the first study on the polysulfones [86, 87]. High molecular weight polysulfones was discovered successfully by Johnson and his coworkers. Since 1965 several types of polysulfones with the other poly aryl ethers have become commercially available such as UDEL® (polysulfone), Radel® PPSF and Victrex® PES (Table 2.1.) [87].

**Table 2.1 :** Commercial polysulfones.

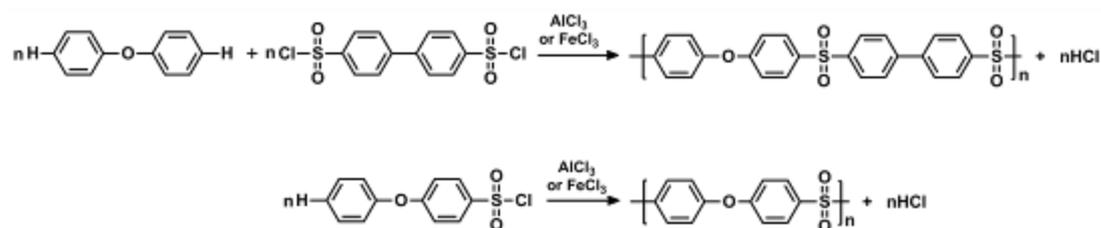
Structure	Trade Name	Chemical Company	Year
	UDEL (PSU or PSF)	Union Carbide	1965
	RADEL(PPSF)	Union Carbide	1976
	VICTREX(PES)	ICI America Inc.	1972

### 2.1.1 Synthesis pathways of polysulfones

The synthesis of polysulfones can be achieved by several routes. The major ones are (i) polysulfonylation (a classical electrophilic aromatic substitution) and (ii) polyetherification (a nucleophilic substitution of activated aromatic dihalides) [88, 89].

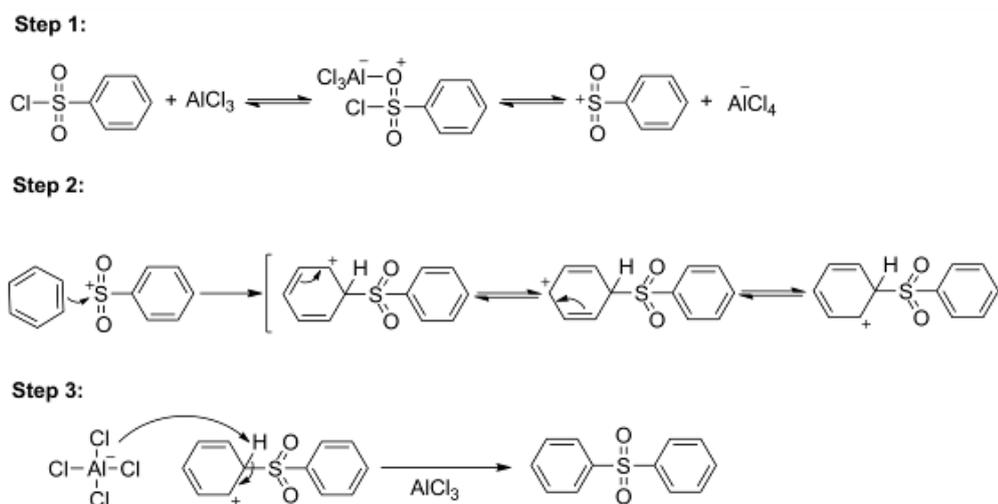
#### 2.1.1.1 Polysulfonylation route

Polysulfonylation is an electrophilic pathway in which the synthesis of polysulfones is achieved via Friedel-Crafts electrophilic substitution. Two types of polysulfonylation reactions are shown in Figure 2.2 and explained below.



**Figure 2.2 :** Polysulfone synthesis by polysulfonylation route.

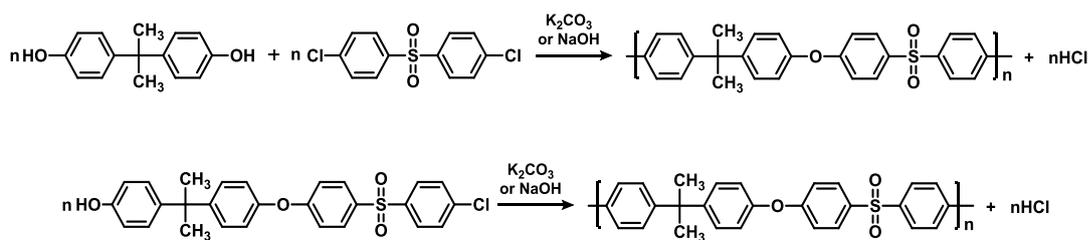
Firstly, electrophilic sulfonylium cation is formed by attacking of the Lewis catalyst to the sulfonyl group. Then, a positively charged intermediate arenium complex is obtained by attacking of  $\pi$  electrons to the formed cation. This is the rate-limiting step of this reaction. After that a proton acts as the leaving group and the aromatic benzene rings with sulfone linkages are formed. Because of the arenium ion reactivity, the third step is always faster than the second step. For these type of reactions, in order to activate the electrophile Lewis acid catalysts such as  $\text{AlCl}_3$ ,  $\text{AlBr}_3$ ,  $\text{FeCl}_3$ ,  $\text{SbCl}_5$ ,  $\text{BF}_3$  are used since the benzene ring suffers from electron deficiency. The detailed reaction mechanism is drawn in Figure 2.3.



**Figure 2.3 :** The mechanism of electrophilic aromatic substitution.

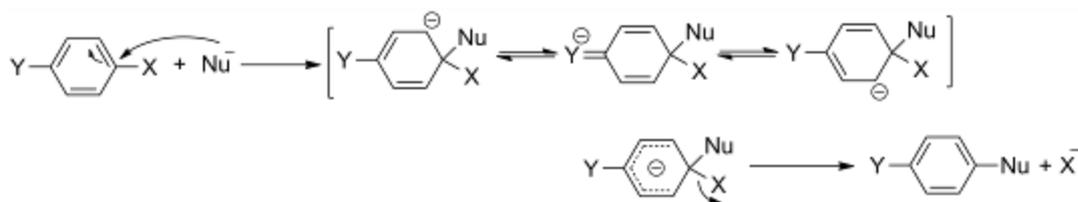
### 2.1.1.2 Polyetherification route

Polyetherification route is the most preferred way of polysulfone synthesis in which a nucleophilic substitution of activated dihalides with phenols is achieved by condensation reaction proceeding by reactions of types.



**Figure 2.4 :** Polysulfone synthesis by polyetherification route.

Diphenols are activated by metal salts and condensation reaction occurs with the dihalides at elevated temperatures in a reaction medium in which aprotic dipolar solvents, cyclohexylpyrrolidone (CHP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO) and *N*-methylpyrrolidone (NMP), are used. As shown in Figure 2.5., addition and elimination reactions occur. Firstly, Meisenheimer complex is formed by attacking of a nucleophile to the aromatic carbon in which halide is bonded. Then the electron withdrawing group (sulfone group) exhibits  $-I$  effects that accelerate the aromatic substitution.



**Figure 2.5 :** Polysulfone synthesis by polyetherification route.

The leaving groups are released and Meisenheimer complex decomposes. As compared to the other leaving groups, F is the strongest electron withdrawing group that can easily activate the aromatic dihalides.

According to the basicity, the nucleophile powers can be ordered as  $\text{ArS}^- > \text{RO}^- > \text{R}_2\text{NH} > \text{ArO}^- > \text{OH}^- > \text{ArNH}_2 > \text{NH}_3 > \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{H}_2\text{O} > \text{ROH}$ .

Nucleophilic substitution of diaryl halides can be achieved mainly by using strong bases or weak bases that have some advantages and disadvantages towards each other.

### 2.1.1.3 Strong base approach

In strong base path, DMSO is generally used solvent in which calcium, lithium and magnesium salts of bisphenol A are not soluble so that they can not be used. Sodium or potassium hydroxide are suitable in many syntheses. The time needed for the high molecular weight condensates is short about 6 hours. Despite its time shortness, this

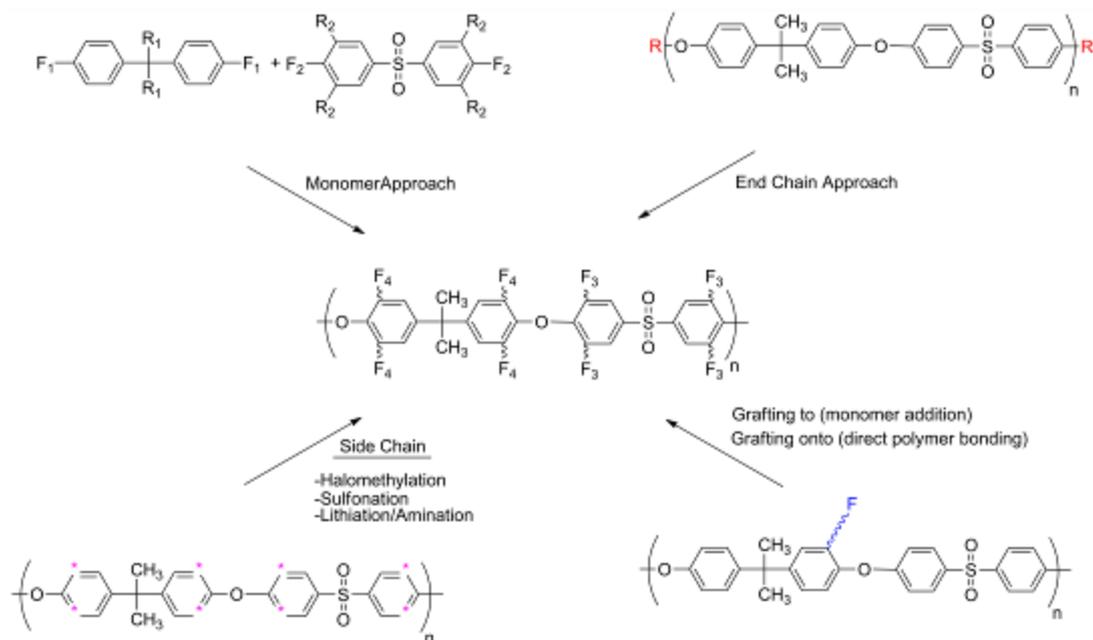
route suffers from the requirement of the stoichiometric control of the base ratio. The addition of too much base results in two negative consequences: (i) hydrolysis of activated aromatic dihalides resulting non-reactive phenolates that decreases the yield and polymerization degree, and (ii) ether linkages can be broken down that leads to the formation of low molecular weight polysulfones. The addition of too low base results the formation of hydrogen bonding between the formed phenolates with free phenols and because of that no phenolates attack to the aromatic halides resulting again low molecular weight polysulfones. Water can behave as the nucleophile like the phenols giving the same negative results. Since it is difficult to get rid of the water from the reaction media, an azeotropic agent, toluene, xylene, or o-dichlorobenzene, is used.

#### **2.1.1.4 Weak base approach**

Weak base approach is generally used because of the independency of base amount. If used excess amount it does not affect the reaction without giving any side reactions. But less usage may give the same result as in the strong base approach resulting low molecular weight polysulfones. Mostly potassium carborane is used because of the strong solubility and basicity parameters. Potassium carbonate decomposed to water and carbon dioxide is preferred as compared to sodium carbonate because it is more basic and more soluble in the reaction media. Potassium carbonate results in formation of water and carbon dioxide that can easily be removed from the reaction media with an azeotropic agent.

#### **2.1.2 Chemical modification of polysulfones**

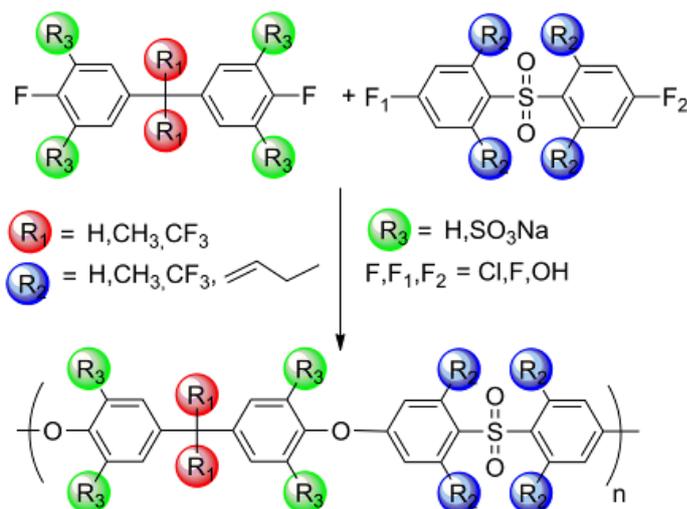
Currently, two strategies have been developed for the modification of polysulfones (i) functional monomer approach and (ii) post-polymerization approach. Both routes have been successfully used to incorporate functional groups into the polysulfone backbones to enhance their properties and act as access points to further modification. Although, there are many articles for modification of polysulfones since 1960 [90-99], the recent studies are related to the easy preparation of novel functionalized polysulfones and their use in the preparation of block, graft or networks with novel properties.



**Figure 2.6 :** The synthetic pathways for the modifications of polysulfones.

### 2.1.2.1 Monomer modification

In order to make more control over the chemical structure of polysulfones, monomers are modified before condensation. This approach involves multi-step synthetic procedures and each time modification is desired.

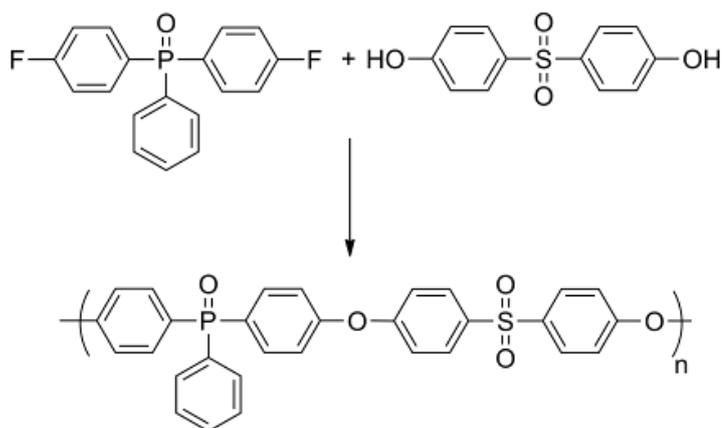


**Figure 2.7 :** Functional monomer approach.

The functional groups should not react with the monomers, and should also be stable enough to survive until the end of polymerization. A number of monomers with a variety of functional groups such as, halide, trifluoromethyl, allyl and sulfone groups have been directly prepared by condensation reactions. For example, highly

sulfonated polysulfones with high molecular weights were prepared by copolymerization of sulfonated aromatic dihalides with various diphenolic monomers. Highly sulfonated aromatic dihalide comonomers, namely 3,3'-disulfonated-4,4'-dichlorodiphenyl sulfone or 3,3'-disulfonated-4,4'-difluorodiphenyl sulfone, were prepared by the sulfonation of 4,4'-dichlorodiphenyl sulfone or 4,4'-difluorodiphenyl sulfone with fuming sulfuric acid at 110 °C for 6 h under a nitrogen atmosphere [100]. One of the major drawbacks of the use of disulfonated monomers in the preparation of polysulfones is higher degrees of sulfonation (above 50%), which become mechanically unstable and exhibit excessive swelling. To arrange the degree of sulfonation, different type of bisphenols (4,4-bisphenol A, 2,2-bis-(4-hydroxyphenyl) hexafluoropropane, 4,4-biphenol, and hydroquinone) have been benefitted as a comonomer for the synthesis of new copolymers [101].

In another study, McGrath and co-workers found that aryl phosphine oxide groups in the polymer structure notably enhanced their flame retardancy. These phosphorus-containing monomers are hydrolytically stable and easily incorporated into polysulfones by a nucleophilic aromatic-substitution polycondensation route. This polymer had improved thermal stability in air and increased char yield when compared to the virgin polysulfone [102].



**Figure 2.8 :** Synthesis of poly(arylene ether phosphine oxide sulfone).

Poly(ethylene oxide) (PEO) was used as a functional comonomer for the formation of segmented polysulfone-poly(ethylene oxide) copolymers. The resulting copolymers were well soluble in common organic solvents and showed high tensile strength and good elasticity. The gas transport properties of these copolymers was changed according to the PEO content and was determined by using light gases e.g., He, H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub>. However, the gas permeation properties of these

copolymers were reduced by increasing PEO amounts. This may be explained by less phase-separated microstructures resulting that the copolymers exhibited single  $T_g$ . Compatibility of polymer segments may lead to no formation of PEO domains separated from polysulfone domains in the membrane and reduce the gas permeabilities. Their drug release properties were also investigated using two major drugs, sirolimus and paclitaxel for the treatment of coronary arterial disease. Increasing PEO content in the polymer resulted drug release occurred rapidly because of higher liquid uptakes and swelling rates [103].

The structure of polysulfone is directly affected the transport properties of the membrane such as selectivity and permeability. For example, the substitution of the elastic bisphenol A units with rigid naphthalene bisphenol [104], or substituted bisphenol A derivatives [105], have also resulted in higher selectivity, but less permeability or the opposite in membrane application. The combination of rigid and bulky moieties in the polysulfone backbones leads to higher glass transition and thermal decomposition temperatures. Good gas transport behaviours for the separation of the gas pairs  $O_2/N_2$ , and  $CO_2/CH_4$  is achieved. Although, the obtained polysulfones have the same permeability, their selectivity is much higher than commercial UDEL-type polysulfones [106].

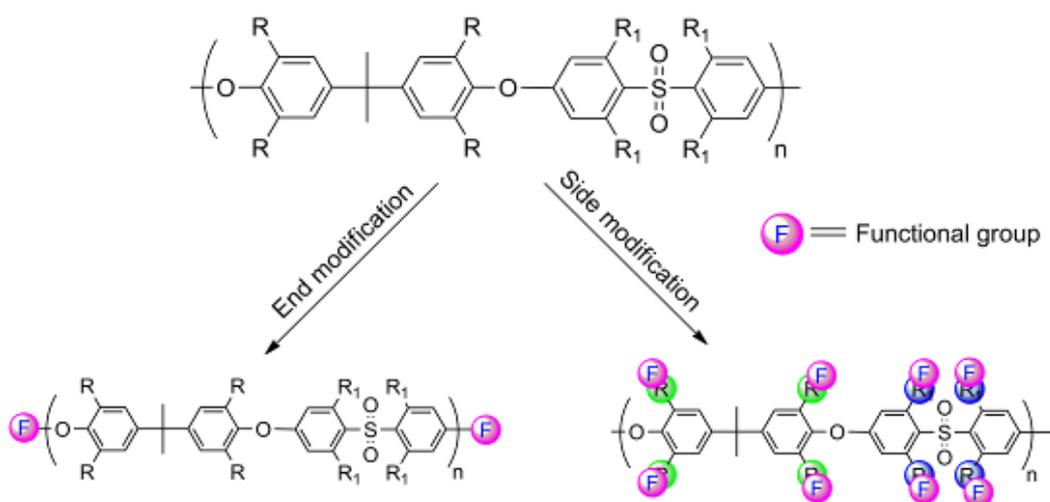
Recently, using functional bisphenols, 2,2'-dimethylaminemethylene-4,4'-biphenol, 2,7-di(4'-phenol)-9,9-bis(6'-(1,2-dimethylimidazole)) fluorene bromine or 3,3-bis(4-hydroxyphenyl)-2-(3-(methylamino)propyl)isoindolin-1-one, it is possible to obtain directly quaternary ammonium-functionalized polysulfones for anion exchange membranes [107]. This approach is suitable to manage the amount and place of the quaternary ammonium groups in along the polymer backbone, but also it is more environmentally friendly due to avoiding the use of chloromethyl methyl ether.

Photoreactive polysulfones were successfully prepared by polycondensation reactions of polysulfones bearing pendant aldehyde groups with *p*-aminoazobenzene. The precursor polysulfones were formed by polycondensation reaction of bis (4-chlorophenyl) sulfone with 5,5'-methylene bis-salicylaldehyde and bisphenol A in the presence of dimethyl sulfoxide, chlorobenzene and anhydrous potassium carbonate. The azobenzene modified polysulfones exhibited good thermal stabilities up to about 350-380°C and high glass-transition temperatures [108]. Polycondensation of 4,4-bis(4-hydroxyphenyl) pentanoic acid with bis(4-

chlorophenyl) sulfone yielded to polysulfones with pendant carboxylic acid group. This functionality readily condensed with alkylamines or alkoxy-phenols to modify the solubility and glass transition of the polysulfones in a wide range [109]. Hyperbranched polysulfone ionomers have been reported by polycondensation of a hydroxyl functional polysulfone oligomer ( $A_2$ ) and triphenyl phosphine ( $B_3$ ) monomer [110]. A monomer with crosslinkable units was used to obtain a polysulfone having pendant groups that can be used as self-crosslinker. Recently, self-crosslinkable polysulfones bearing allyl pendant groups can be synthesized by two routes; (i) using functional diallyl bisphenol A [111] and (ii) deprotection of methoxyphenyl functionalized polysulfones and subsequent etherification reaction with allyl bromide [112]. The self-crosslinked polysulfones membranes exhibit high dimensional stability, excellent alkaline stability, admirable fuel resistance and high thermal stability. While, the post-polymerization approach is another option to introduce additional sulfone groups onto the polymer backbones, the use of sulfuric and chlorosulfuric acids results in unacceptable side reactions such as cross-linking, heterogeneous reaction, and cleavage of the chains, that leads to not control of sulfonation resulting no maintaining the same properties of the final polymer in every reaction. The functional monomer approach not only overcomes aforementioned difficulties but also it affords to control distribution of proton conducting sulfonic acid groups by varying of the monomer feed.

#### **2.1.2.2 Post-modification**

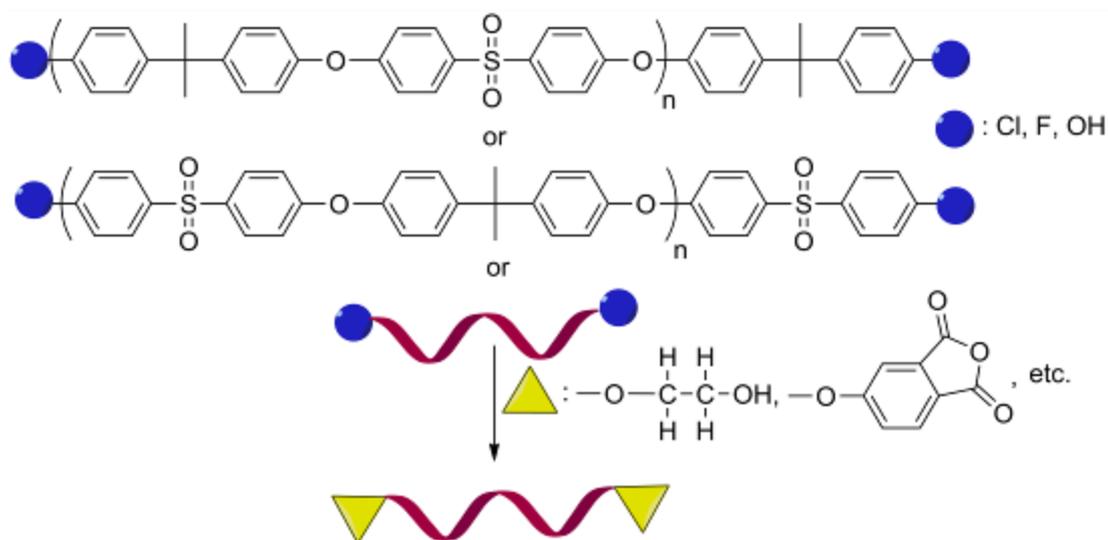
Post-modification of polysulfone polymers can be achieved after polymer synthesis. Chemical modification can be done by electrophilic and nucleophilic reactions. On the electron rich bisphenol part of polysulfone polymer, electrophilic reactions such as sulfonation and chloromethylation, can take place. Nucleophilic reactions such as lithiation or reaction after lithiation with aldehydes or ketones can be conducted on the diaryl part .



**Figure 2.9 :** Post-modification of polysulfones-General approach.

### 2.1.2.3 End chain approach

End groups of polysulfone polymers can be modified or directly used in reaction with other functional materials such as epoxy resins. If the end groups are bifunctional they can take part in polymerization reactions, resulting block and/or graft copolymers or networks.



**Figure 2.10 :** End chain modification of polysulfones.

Polysulfone oligomers terminated aryl chloride groups were condensed with hydroxyl functional poly(ethylene oxide) to prepare poly(ethylene oxide)-PSU multiblock copolymers [113]. Polysulfone-block-polydimethylsiloxane block copolymers has been prepared by the condensation reaction of chloro-terminated polysulfone oligomers and  $\alpha,\omega$ -dihydrogensilyl-polydimethylsiloxane in the existence of urea as a hydrogen chloride accepting molecule [114]. End-capped

polysulfones with acid or anhydride groups (PSU-PhAHs) was prepared from chlorine and phenol ended-polysulfone [115]. A series of block copolymers containing bisphenol A polysulfone and poly (vinylidene fluoride) (PSU-*b*-PVDF) was prepared by polycondensation of dihydroxybisphenol A polysulfone precursors and dibromopoly(vinylidene fluoride) in the presence of sodium hydride (NaH) at room temperature and sulfonated [116]. Mannich polycondensation among phenolic hydroxyl-terminated polysulfone, aminopropyl-terminated polydimethylsiloxane, and paraformaldehyde was utilized to prepare polysulfone-block-polydimethylsiloxane multiblock copolymer (PSU-*b*-PDMS) [117]. Hydroxyl groups of polysulfone were reacted with 12-bromo-1-dodecanol. Then, the replacement of the resulting hydroxyl groups by chlorine; and final substitution of chlorine atoms by (4R)-hydroxy-L-proline was resulted (4R)-hydroxy-L-proline ended polysulfones [118]. Epoxy hybrid nanocomposites using different ratios of nanoclays was mixed with hydroxyl terminated polysulfone modified with diglycidyl ether of bisphenol-A type epoxy resin [119]. Hydroxy functional polysulfones was reacted with ethylene carbonate to afford telechelic aliphatic hydroxyethyl groups. Cationic polymerization of 2-ethyl-2-oxazoline was achieved after tosylation of hydroxyl ethyl groups in order to afford amphiphilic triblock poly(2-ethyl-2-oxazoline-*b*-sulfone-*b*-2-ethyl-2-oxazoline) and poly(2-ethyl-2-oxazoline-*co*-ethyleneimine-*b*-sulfone-*b*-2-ethyl-2-oxazoline-*co*-ethyleneimine) copolymers [120]. The hydroxy functional polysulfone was modified with phthalic anhydride by addition of 4-fluorophthalic anhydride to the polymerized solution of polysulfone. PSU-PhAHs have been mixed with non-reactive polysulfone and polyamide to get block or graft copolymers [121]. PSU-PhAHs were also condensed with an amorphous polyamide in DMF to form PSU-PA block copolymers [122]. Hydroxy functional polysulfone was modified with (meth) acrylates in the presence of triethyl amine by mixing with (meth) acryloyl chlorides at 0 °C and used in the formation of crosslinked networks [123]. Benzoxazine ended polysulfones were synthesized by refluxing the phenol- terminated polysulfone (PSU-OH) with aniline and paraformaldehyde in chloroform [124].

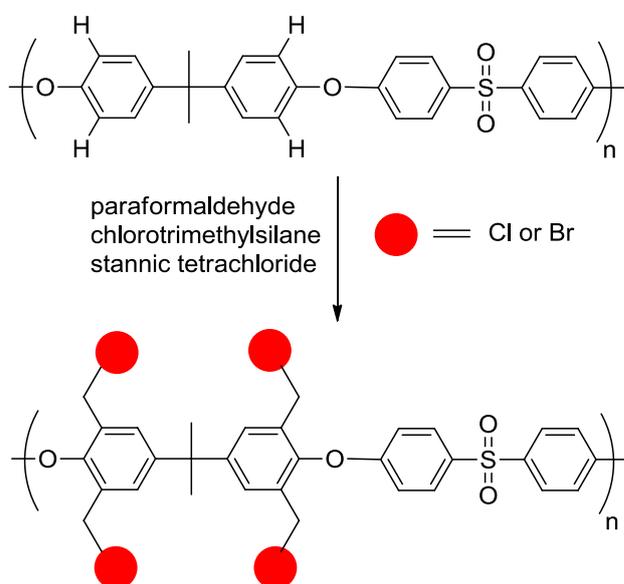
#### **2.1.2.4 Side chain modification of polysulfones approach**

Side chain modification of polymers are very important approach in order to add functional groups or polymers. Firstly, activation of the groups on the side chain and then chemical reaction with other groups results the modified polymers with superior

properties as compared to neat polymer. Activated side chain may be used as the initiating points that can be used as the point a polymerization takes place. By this way, graft polymers may easily be prepared. Below several studies related to side chain modifications of polysulfones are classified and organic reactions that many researchers have been conducted are listed.

### Halomethylation

Avram et.al. used the mixture of paraformaldehyde/chlorotrimethylsilane as the chloro-methylation agent, stannic tetrachloride as the catalyst, and chloroform as the solvent for the chloromethylation of polysulfone and investigated the effects of catalyst, polymer structural unit mol ratio and reaction time on the preparation. The reaction temperature was 50-52 °C [125].



**Figure 2.11** : Halomethylation-General approach.

Other researchers have benefitted from this work and published many articles by addition of new groups to the chloromethylated group or by blending with other polymers. Optical properties and the conformational behavior of chloromethylated polysulfone (CMPSU) were also studied experimentally and theoretically for further usage of CMPSU in other applications [126, 127]. Liquid crystalline azomethine groups were reacted to chloromethylated polysulfones in DMF solution containing anhydrous potassium carbonate at 82 °C for 24h [128]. CMPSU was modified with 2-(*N,N*-dimethylamino)ethanol or triethylamine groups by the nucleophilic bimolecular substitution reaction in *N,N*-dimethylformamide (DMF) to form polysulfones with pendent groups of dimethylethanolammonium or triethylammonium chloride,

respectively . The reactions were performed at 60 °C for 40 h by using a 1:2 molar ratio functional groups CH<sub>2</sub>Cl:amine [129]. Quaternized polysulfones was also prepared from chloromethylated polysulfones CMPSU by stirring CMSPU and *N,N*-dimethylethanolamine (DMEA) mixture dissolved in DMF for 48 h at 60°C [129, 130]. Phosphonation of chloromethylated polysulfone was achieved by Michaelis–Arbuzov reaction. Chloromethylated PSU, diethyl carbitol and triethyl phosphite was dissolved in NMP. The reaction mixture was mixed at 140 °C for 8 h. Polymers with phosphonic acid functional groups were obtained after hydrolysis of resulting phosphonic acid ester polymers by refluxing in aqueous hydrochloric acid [129, 131]. Bromo methylated groups on the polysulfone was prepared in the reaction media containing bromomethyl octyl ether, tin(IV) chloride, 1,2-dichloroethane and converted to quaternarymethylammonium units by immersing the bromo-methylated membrane in a solution containing 27% trimethylamine, 20% methyl alcohol, and 53% deionized water [128, 132]. CMPSU was reacted by dipping into the thiourea of anhydrous ethanol solution and the reaction was conducted at 50 °C for 8 h. In order to prepare polysulfone modified with mercapto group (PSU-SH), hydrolysis of the methyl(iso-thiourium) polysulfone (MTUPSU) was achieved by stirring at 80°C for 10 h in 1 mol/L of sodium hydroxide solution [133]. Methylene methacrylate groups were substituted with chlorine moiety in CMPSU by reacting CMPSU with methacrylic acid in the presence of potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) and tetra-*n*-butylammonium bromide (TBAB) in DMF. The reaction mixture was stirred for 24 h at 40 °C under a nitrogen atmosphere [128, 134]. Chloromethylated polysulfone (CMPSU) was chemically modified by reacting the chloromethyl group with P-H bond of 9,10-dihydro-oxa-10-phospho-phenanthrene-10-oxide (DOPO). CMPSU and DOPO was stirred at 165–170 °C under nitrogen for 6 h [128, 135]. Pyridine units have been incorporated into PSUs by using click chemistry strategy. Chloromethylated groups of CMSPF were firstly converted to azides by using NaN<sub>3</sub> in DMF at 60 °C for 24 h and then propargyl pyrene groups was reacted with PSU-azides in DMF solution containing 2, 2'-dipyridyl as ligand and CuBr as catalyst [136]. CMPSU was reacted with 1-methylimidazole in *N,N*-dimethylacetamide (DMAc) as solvent and the mixture was stirred at room temperature for 12 h. Then, NaOH solution was used for the alkalization [137]. A series of imidazolium chloride-functionalized polysulfone (PSU-ImCl) were successfully synthesized from CMSPU by the reaction of CMSPU with 1-methylimidazole at 80 °C for 30 minutes.

Imidazolium hydroxide-functionalized polysulfone (PSU-ImOH) was obtained from PSU-ImCl by soaking it into the KOH solution [138]. CMPSU was grafted with cinnamic structures by the nucleophilic chloro-displacement reaction with cinnamic acid and p-hydroxycinnamic acid, respectively. The reaction of chloromethylated polysulfone with cinnamate type aromatic carboxylic acids was carried out using 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) as catalyst at 70 °C for 12 h in DMF as solvent [139]. Poly(2-gluconamidoethyl methacrylate) was grafted onto the CMPSU via surface-initiated ATRP (SIATRP). CMPSU was dissolved in 1,2-dichloromethane and reacted with chloromethyl methyl ether in the presence of the catalyst, zinc chloride anhydride, at 40 °C for 4 h. Then, 2-gluconamidoethyl methacrylates, CuCl<sub>2</sub>, PMDETA were dissolved in 50 mL of deionized water and introduced into a flask. Then, CMPSU was added into the flask purged with nitrogen gas and the addition of CuCl started the polymerization [140]. Chloromethylation of the polysulfone membranes (Cl-PSU) was achieved by immersing in a solution of chlorodimethyl ether, hexane and SnCl<sub>4</sub> as the Friedel Crafts catalyst at 25 °C for 15 min and then by immersing the chloromethylated membranes into ethylenediamine solution for 15 min at 25 °C were resulted aminated polysulfones that further reacted with aspartic acid to prepare aspartic-acid functionalized polysulfones (ASP-PSU) [141]. Chloromethylation and subsequent quaternization of polysulfones with triethyl amines was performed. The blends of quaternized polysulfone (QPSU) and benzoyl guar gum (BGG) with various contents (10-80 wt%) were prepared by solution casting technique [142]. Quaternized polysulfone was also prepared from CMPSU by reacting with *N,N*-dimethylethanol-amine (DMEA) or triethyl amine (TEA) in DMF for 48 h at 60 °C [143]. Phosphoric acid containing quaternary 1,4-diazabicyclo-[2.2.2]-octane (DABCO) polysulfone was synthesized with various degrees of substitution. Non-crosslinked quaternary 1,4-diazabicyclo-[2.2.2]-octane (DABCO) polysulfone was obtained by incorporating chloromethylated PSU and DABCO in DMAc in a molar ratio of 1(CH<sub>2</sub>Cl):5(DABCO). The mixture was mixed at 80 °C for 14 h [144]. A polytetrafluoroethylene (PTFE)/quaternized polysulfone (QNPSU) composite membrane is made by immobilizing a QNPSU membrane that prepared from chlorinated PSU (Cl-PSU) by immersing into trimethylamine solution at 25 °C for 7 days [129, 145]. Polysulfones containing phosphonate and aldehyde groups were utilized in forming a crosslinked polysulfone by using phase transfer catalysis (PTC) method. Functionalization of polysulfones was achieved from

chloromethylated polysulfone [128, 146]. CMPSU was reacted with a tertiary amine (DMOA) in DMF with a CMPSU/tertiary amine molar ratio of 1:1.5 for 24 h to produce polysulfone with *N*-dimethyloctylammonium chloride groups (PSU–DMOA) [147].

### **Sulfonation**

Polysulfones were sulfonated by using as a sulfonation agent, chlorosulfonic acid, at room temperature in 1,2-dichloroethane as the solvent and blended with polyamide (PA) [128, 148] or polybenzimidazole (PBI) [149]. Sulfonated polysulfone (SPSU) was achieved from UDEL polysulfone dissolved in chloroform with trimethylsilyl chlorosulfonate at room temperature in the reaction time of 24 to 48 h to form a silyl sulfonate polysulfone. Sodium methoxide was then added to separate the silyl sulfonate moiety to result sulfonated polysulfone [150]. The sulfonated polysulfones were prepared from direct sulfonation method by adding chlorosulfonic acid at -10 °C [151]. Sulfonation of chloromethylated polysulfones was achieved by stirring the mixture of CMPSU and Na<sub>2</sub>SO<sub>3</sub> in water-ethanol at the temperature of 70 °C [152, 153]. Polysulfone was sulfonated by employing chlorosulfonic acid as the sulfonating agent in dichloromethane at a temperature of 4°C. The obtained polysulfone sulfonic acid was neutralized by immersing into sodium methoxide/methanol solution [154]. A sulfonating agent prepared by mixing triethyl phosphate and sulfuric acid at 4 °C for 48 h was used in the formation of sulfonated polysulfone by mixing it with appropriate ratios of commercial polysulfone dissolved in 1,1,2,2-tetrachloroethane at the temperatures of 25,50,75 and 125 °C for 4h or 8h time periods [155]. Sulfonated polysulfones (SPSU) were prepared via addition of chlorosulfonic acid (HSO<sub>3</sub>Cl) and chlorotrimethylsilane ((CH<sub>3</sub>)<sub>3</sub>SiCl) as sulfonating agent, respectively, into the solution of dichloromethane containing dried polysulfone at 35 °C for 12h [156]. Sulfonation of polysulfone was achieved by addition of chlorosulfonic acid into the chloroform solution of polysulfone. Twenty minutes of stirring vigorously was resulted the sulfonated polysulfone [157]. SPSU with different degree of sulfonation (DS) have been synthesized by using trimethyl silyl chlorosulfonate as a mild sulfonating agent at room temperature for 24 h or 48 h [84, 158, 159]. Polysulfone was dissolved in 1,2-dichloroethane (DCE) or chloroform under a reaction temperature of 60 °C and a solution containing chlorosulfonic acid in DCE/chloroform was slowly added dropwise. The reaction

mixture was stirred for 6 h [160]. Polysulfone was sulfonated with sulfuric acid and blended with chitosan (CS) [161].

### **Lithiation/Amination**

The polysulfones with pendant sulfophenylated groups was prepared by titration of polysulfone with enough amount of n-butyl lithium under argon atmosphere and anionic reaction with 2-sulfobenzoic acid cyclic anhydride [162]. Lithiated polysulfones was achieved by adding n-butyl lithium into the polysulfone dissolved in tetrahydrofuran at 0 °C [243, 244]. Dipyrindyl functionalized polysulfones were formed by the reaction of lithiated polysulfone with excess 2,2—vinylidenedipyridine in tetrahydrofuran (THF) at -78 °C [163]. Polysulfone was lithiated in THF at -78 °C and was mixed with 4-fluorobenzoic acid chloride to incorporate 4-fluorobenzoyl side chains to the polymer backbone. The activated fluoro groups were substituted by 4-sulfophenoxy or 7-sulfo-2-naphthoxy in a potassium carbonate-mediated nucleophilic substitution reaction [164].

Polysulfones containing benzoyl(difluoromethylenephosphonic acid) side chains were formed by CuBr-mediated cross-coupling reactions between the iodinated polymer and [(diethoxyphosphinyl)difluoromethyl] zinc bromide [91, 165]. Sulfophenylation of polysulfone was achieved via lithiation by BuLi at -50 °C in THF and following reaction with 2-sulfobenzoic acid cyclic anhydride [166, 167]. Polysulfone with aldehyde was synthesized from lithiated PSU by adding a cooled (-60 °C) mixture of DMF as a masked electrophile and freshly distilled THF into the reaction flask under stirring vigorously [168]. Aminated polysulfones was obtained after lithiation at -60 °C by addition of n-butyl lithium and azidation by using tosyl azide. Azidated polysulfone was reduced to aminated polysulfone by using sodium borohydrate as reducing agent in tetrahydrofuran/ethanol mixture at -50 °C followed by 12 h stirring at room temperature [169]. Modification of polysulfones with amine were achieved from phthalimides by using Friedel-Craft catalyst, AlCl<sub>3</sub>, in CCl<sub>4</sub>/MeOH mixture and reduction with hydrazine hydrate [170]. An aminated polysulfone was prepared from chloromethylated polysulfone by stirring it with ethylenediamine at room temperature [171]. PSU containing pendant bis-(phenyldimethylamine) substituents was prepared by functionalization with tertiary amines via lithiation chemistry. The PSU containing pendant bis-(phenyldimethylamine) substituents were subsequently quaternized with CH<sub>3</sub>I and

ion exchange reaction to provide bis(phenyltrimethylammonium) (PTMA) polymer [172, 173]. Synthesis of aminomethyl-polysulfone was achieved by firstly reacting chloromethylphthalimide with polysulfone in the presence of  $\text{SnCl}_4$  as the catalyst and subsequent cleavage of phthalimide groups by hydrazine hydrate [174].

### **Carboxylation**

The surface of PSU polymer were carboxylated and then heparin (HE) or endothelial cell surface heparan sulfate (ESHS) was covalently linked by the reaction of amino groups and a coupling reagent. Carboxyl groups were incorporated into polysulfone backbones using different reactions, i.e. UV, heat or redox activation by nitrene or radical species [175]. Guiver et.al synthesized carboxylated polysulfone by the procedure in which polysulfone dissolved in THF was lithiated at  $-50\text{ }^\circ\text{C}$  and then several 1-lb blocks of dry-ice were freshly prepared from  $\text{CO}_2$  was added slowly while mixing the solution vigorously. 4-nitro phenol was reacted with the carboxylated polysulfones by mixing it with CPSU in the presence of DCC and DMAP for 20 h time period at room temperature [176]. Carboxylated polysulfone was blended with polyurethanes at  $40\text{ }^\circ\text{C}$  for 3-4 h [147, 148, 149]. Carboxylated polysulfones were prepared by incorporating carboxyl groups into polysulfone backbone and after that the preparation of ultrafiltration membranes was achieved by blending them with cellulose acetate [177].

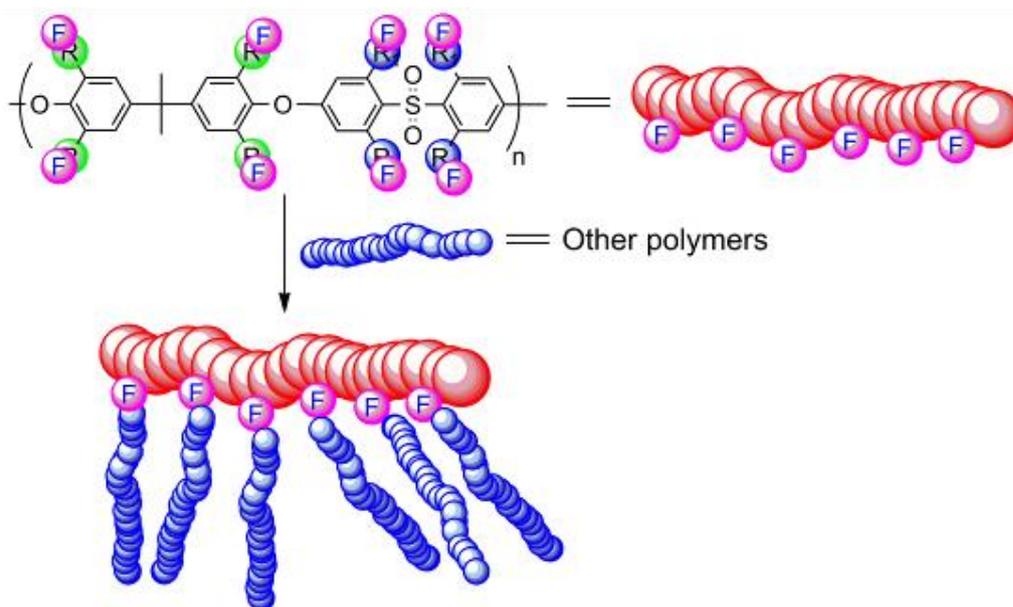
### **Others**

Polysulfones were treated with ozone in order to change gas sorption properties of the resulting membranes [178]. Ozone-treatment was also applied to introduce peroxides on the polysulfone membranes, and chemical modification was continued by grafting with either acrylic acid or chitosan, followed by the immobilization of heparin [179]. Optical and electronic properties of quaternized polysulfone with triphenylphosphonium pendant groups was analyzed [180]. Polysulfone (PSU) was modified by Friedel-Crafts alkylation of PSU with 4- (chloromethyl) benzoic acid (CMBA) as reaction reagent, and benzoic acid (BA) ligand was linked to the side chains of PSU, leading to the aromatic carboxylic acid-functionalized PSU [181].

### 2.1.2.5 Grafting of polysulfones with other polymers

#### Grafting Onto

PEG azides were immobilized by UV irradiation and brushes on PSU support membranes were prepared. This membrane was complexed with silver salt [182]. Low temperature plasma technique was used for grafting of poly (ethylene glycol) on chloromethylated polysulfone [183]. Photochemically grafting of polysulfone films with methoxypoly (ethylene glycol) (MPEG) derivatives on its surface was done by UV irradiation [184]. Maleic anhydride grafted polysulfone (PSU-g-MAH) was prepared and used in blends of thermotropic liquid crystalline polymer (TLCP) [185]. Chloromethylation and azidation were applied to form (PSU-N<sub>3</sub>). Independently, atom transfer radical polymerization (ATRP) was used to get poly(tert-butyl acrylate) (PtBA) with an alkyne-end-group. After that, click chemistry strategy is applied to combine two polymers to obtain polysulfone-graft-poly(tert-butyl acrylate), (PSU-g-PtBA) [186].

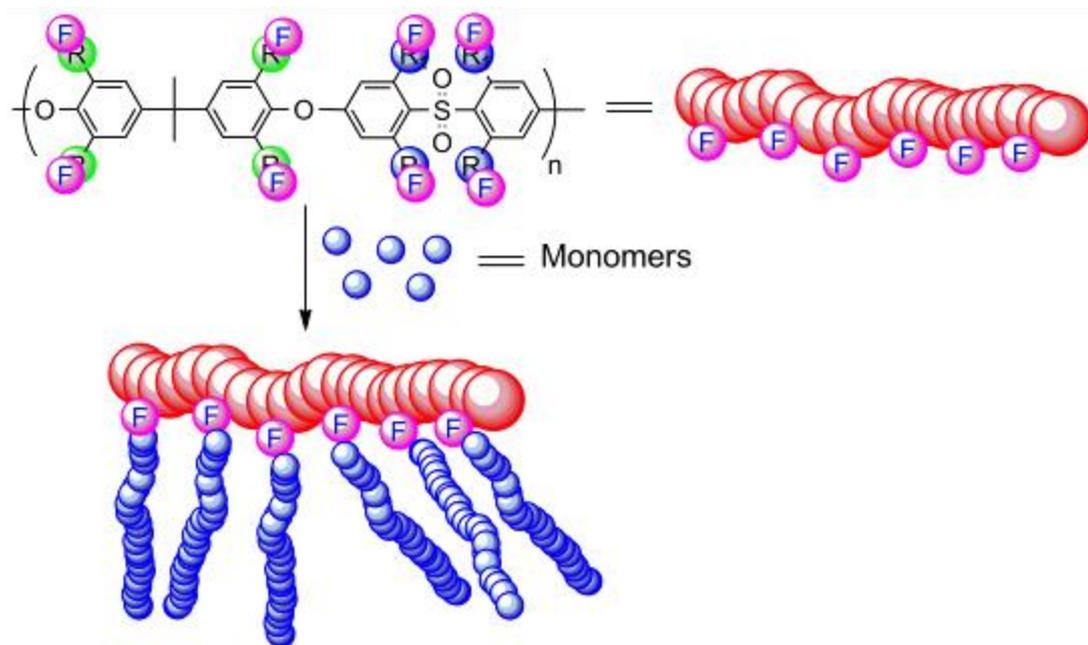


**Figure 2.12 :** “Grafting onto” approach.

#### Grafting From

Plasma modification of polysulfone films were reported by grafting of 2-hydroxyethylmethacrylate and a model protein (hen egg-white lysozyme, Lz) [187]. UV-assisted graft polymerization of *N*-vinyl-2-pyrrolidinone from poly (ether sulfone) and sulfonated poly (sulfone) was utilized to prepare nanofiltration membranes (NVP) [188]. The syntheses of PSU-g-PS and PSU-g-(PS-*b*-PMMA) in

DMF were achieved *via* ATRP by using chloromethylated polysulfone as a macroinitiator. ATRP was catalyzed by  $\text{FeCl}_2$ /isophthalic acid [273, 274]. Chitooligosaccharides (COS) was synthesized by the coupling reaction of acrylic acid grafted polysulfone with chitosan oligomer. Activation of PSF surface was achieved by ozonolysis and acrylic acid polymerization was achieved in the presence of  $\text{FeSO}_4$  [189]. The preparation of polysulfone-graft-poly(acrylic acid) (PSU-g-PAA) and polysulfone-graft-poly(tetraalkylammonium acrylate) (PSU-g-P(AA-TAA)) membranes from polysulfone-graft-poly(tert-butyl acrylate) (PSU-g-PtBA) was reported [190]. Surface initiated atom transfer radical polymerization (SI-ATRP) technique was utilized to graft polyacrylamide units from the chloromethylated polysulfone surface [191]. The technique (SI-ATRP) was also used to prepare hydrophilic poly((poly(ethylene glycol) methyl ether methacrylate) (P(PEGMA)) and poly(glycidyl-methacrylate) (PGMA) brushes grafting from chloromethylated polysulfone (CMPSF) membrane surfaces [192]. Fridel Craft alkylation reaction was utilized to get polysulfone grafted poly(styrene sulfonic acid) (PSU-g-PSSA) from chloromethylated polysulfone. Atom transfer radical polymerization (ATRP) technique was used for grafting [193]. PEG-OH was directly bound to chloromethylated polysulfone to achieve polysulfone-g-poly-ethylene glycol (PSU-g-PEG) polymers [194]. Polysulfone-graft-poly (ethylene glycol) methyl ethermethacrylate (PSU-g-POEM) was prepared by ATRP technique and blended with neat polysulfone [195]. Click chemistry strategy for grafting PEG into polysulfone backbone was reported. Chloromethylated groups were converted to azides and then PEG-alkynes were chemically bound to azidated polysulfone [196]. Densely grafting novel sulfonic acid polymers, poly(styrene-sulfamide acid) (PSA) and poly(vinylsulfonic acid) (PVS), were achieved from the azo-initiator-modified poly(ethersulfone) (PSU). Lithiated polysulfones was reacted with azo initiator units and then radicals formed to initiate the radical polymerization [197]. Reversible addition-fragmentation chain transfer (RAFT) polymerization was benefitted to synthesize polysulfone-g-poly(styrenesulfonic acid) (PSU-g-PSSA) copolymers [198].



**Figure 2.13 :** “Grafting from” approach.

### 2.1.3 Properties and applications of polysulfones

Polysulfone offers highest temperature service usage available among the melt-processable thermoplastics. Also it has high hydrolysis stability up to 200 °C. Because of these properties, they can be used in medical applications that need autoclave and steam sterilization. But the problems related to its low resistance to some solvents and weathering limit their usages. It has also good mechanical and electrical properties, acid/caustic stability, excellent creep resistancy, transparency and high heat deflection temperature. Polysulfones have low flammability (limiting oxygen index typically 38), and burn with little smoke production. For these reasons, they have been used in various applications such as, printed circuit boards, integrated circuit carriers, coil bobbins, television and stereo components, under-the-hood and aircraft components, microwave cookware, cooking appliances, pacemakers, refrigerators, filtration membranes, and pipes.

Because of its biocompatibility and porosity, polysulfone is used in hemodialysis membranes. Polysulfone is also used as membrane supporting material for gas separation, reverse osmosis and ultrafiltration. The composite materials made from polysulfone and zirconia ( $ZrO_2$ ) have found usages in aerospace nickel-hydrogen batteries for large satellites and in nickel-cadmium cells for applications both in space and on the ground [199]. Polysulfone presenting high durability and stability is

used as polymer exchange membrane material in fuel cell applications [200]. Also polysulfones has been widely used in last years in the field of sensors [201].

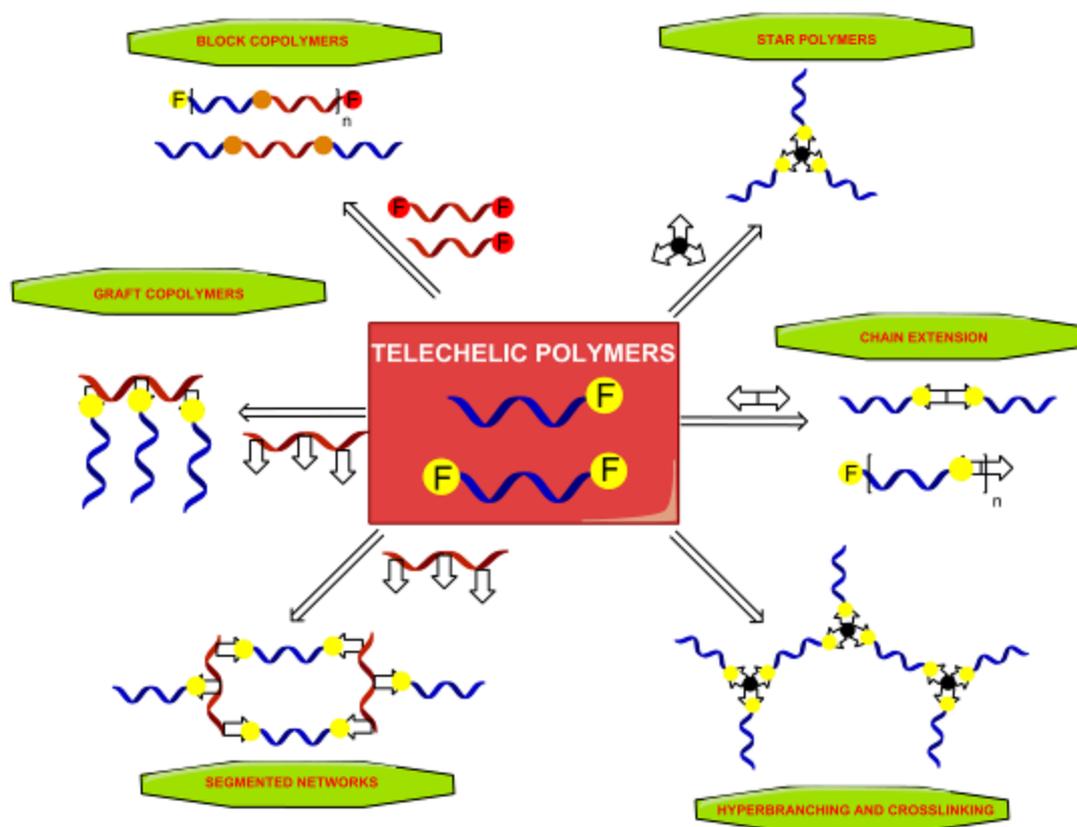
## 2.2 Telechelic Oligomers

The term 'telechelic' originates from the junction of two Greek words: tele means 'end' while chele means 'claw'. Although the studies on telechelics began in 1947 [202], the concept of telechelic polymers was introduced to describe polybutadienes having carboxyl and hydroxyl endgroups in the 1960 [203]. According to the IUPAC, telechelic polymers or oligomers are defined as prepolymers capable of entering into further reactions by their reactive end groups which come from the initiator or the terminating or chain-transfer agents in chain polymerizations [204].

A polymer having functional groups that can be reacted with other molecules can be seen as a telechelic. Upon the number of end-functional groups it has, the telechelics may be divided into mono or semi, di, tri, and multifunctional telechelics (polytelechelics) [205].

Developing strategies to the synthesis of telechelic oligomers is an important area of research because they can be used as the building blocks for the formation of block copolymers [206]. The short polymer chains having end functional chain ends can be defined as telechelic oligomers. They are generally used as building blocks for the production of materials that have improved properties and they are used as spacers or scaffolds for introducing chemical functionality. More specifically they can be used as precursors for the formation of ; (i) long polymer chains by chain extension of short polymer chains, (ii) network and (iii) block copolymers [207].

The term "telechelic" is mostly referred to linear polymers containing chain ends with the same functionalities. The functionality means the number of functional groups per number of polymer chains. If the polymer has two different functional groups, it is referred as "heterotelechelic". The telechelic oligomers can also be used in many different fields as crosslinking agents, curatives, star and precursors for hyper branched dendritic polymers, graft polymers or networks [208-210]. They have been used in many different industrial areas such as paints, inks, adhesives, rubbers, composites, biotechnology and nanotechnology [211, 212].



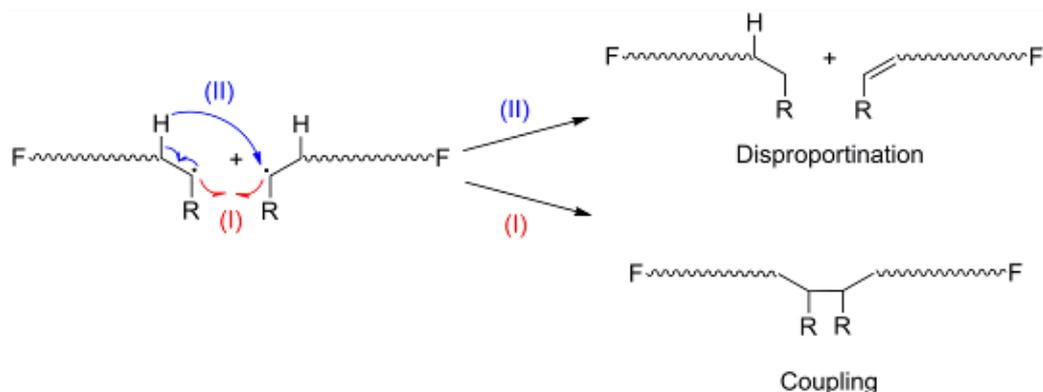
**Figure 2.14 :** Structures obtained by the reaction of telechelics.

Monofunctional and multifunctional telechelics may be coupled in a suitable environment to obtain star and hyper-branched or dendritic (or hyper-branched) structures as shown in Figure 2.14. The type of functionality of the end group is important. When they are bifunctional, they are defined as macromolecular monomers, macromonomers, or macromers. They can take place in polymerization resulting graft copolymers or networks. After the development of ABA block and multiblock copolymers, telechelics have received much attention in industry especially in thermoplastic elastomers [213].

Several polymerization techniques have been used in preparation of telechelics: conventional and controlled radical, anionic, carbocationic, ring-opening, metathesis, chain scission and step-growth.

Free radical polymerization is the most used one because of its easeness, suitability to most types of monomers, insensitivity to impurities and functional groups as compared to the other polymerization techniques. In conventional radical polymerization the end groups may be controlled by a functional initiator with a high concentration or polymerization can be driven with a suitable transfer agents [213].

Disproportionation or coupling (combination) reactions of propagating radicals with primary or macroradical leads to the formation of telechelics as shown in Figure 2.15.



**Figure 2.15 :** Disproportionation and coupling reactions of propagating radicals.

Disproportionation results in monofunctional telechelics whereas coupling reaction produces bifunctional telechelics. Monomers show some characteristics that some monomers choose the disproportionation and the some choose coupling reactions. Table 2.2. indicates the percentages of terminations by combination (coupling) [11].

**Table 2.2 :** Termination percentage by combination of different monomers at 25 °C.

Monomer	Percent	Monomer	Percent
styrene	100	methyl methacrylate	33
<i>p</i> -chlorostyrene	100	ethyl metacrylate	32
<i>p</i> -methoxystyrene	81	<i>N</i> -butyl methacrylate	25
methyl acrylate	100	acrylonitrile	100
ethyl acrylate	100	methacrylonitrile	35

Telechelics may be prepared by using azoinitiators having thermally labile azo groups in their backbones. The carbon-nitrogen bonds are broken when heating and results in two radicals that may be used as polymerization centers.



**Figure 2.16 :** Radical formation by cleavage of carbon-nitrogen bonds with heat.

If  $R^1$  and  $R^2$  are aliphatic groups, the activation energies for this reaction is very suitable to achieve with low energy requirements. It is between 60 and 160  $\text{kJ} \cdot \text{mol}^{-1}$ . Azo groups are also photoactive, too. Despite their low absorbance, aliphatic azo groups evolve nitrogen with quantum yields as high as = 0.44 (AIBN). For the formation of telechelics azo compound should consist one or more functional moieties other than azo group [214].

Functional telechelics can be prepared directly from other telechelics beforely prepared. As an example, carboxyl terminated oligostyrenes are obtained from the oligostyrenes with terminal isocyanate groups by hydrolysis [215]. Amine terminated telechelics are prepared by photolysis and hydrolysis processes using imino azoinitiators as telechelic precursors [216]. Also hydrogen peroxide is used for preparation of radicals initiating the polymerization.  $\text{H}_2\text{O}_2$  is very well hydroxy radical source that is used in industry to prepare hydroxt-terminated butadienes [217].

Monofunctional telechelics can be prepared by using chain transfer agents. Hydrogen abstraction plays an important role in chain reactions. Polymerizable vinyl groups incorporated into polyvinyl chloride by employing 3-mercaptopropionic acid as chain transfer agent [218].

Photo-chemically and thermally activated iniferter of thiuram disulfides resulted some telechelic derivatives. On the alkyl group of the thiuram disulfide, a functional group is added and used in thermal or photo polymerization [219].

Despite its suitability to the most type of polymers and insensitivity towards impurities and functional groups, conventional radical polymerization suffers from the fact that the control over molecular weight and end groups is impossible resulting polydisperse polymers with unknown end groups. Well-defined polymers can be obtained by controlled/living radical polymerization methods [220]. Telechelics were obtained by using atom transfer radical polymerization (ATRP) [221], nitroxide mediated polymerization (NMP) [222], and reversible addition–fragmentation chain transfer polymerization (RAFT) [223].

ATRP use the halogens as the initiating sites and monomers can be added to these sites to form polymers. Styrene and acrylate type polymers were prepared by ATRP using sulfonyl chlorides as initiators [224]. Fast deactivation results always in formation of halogen ends leading to formation of heterotelechelic. Halide groups may be catalyzed by Lewis acids to change to other functional groups. Halogens may

be reacted with sodium azide and then azides may convert to amine to get amino functional telechelics [225].

Nitroxide mediated living radical polymerization can be used. NMP offers two possibilities for the formation of telechelics: functional groups can be put on the initiating chain end, or the nitroxide mediated chain end [223].

Anionic polymerization can be utilized to obtain telechelics. This method is very suitable to obtain polymers with narrow dispersity [226]. Negatively charged species are the propagating sites. Depending on the monomer, initiator, solvent, and termination agent telechelics may be obtained. It is very sensitive to the humidity as water plays a role of nucleophile that stops the reaction [227].

Because of no control of molecular weight and end groups carbocationic polymerization is not preferable. Some researchers made the polymerization of vinyl monomers by this technique [228].

Ring opening polymerization of oxiranes yielded bifunctional polyethylene glycols that has wide applications in industry [229].

The telechelics may also be formed by chain scission of high molecular polymers. Oxidation, reduction, rearrangements and irradiation can be applied. The reaction of polybutadiene with controlled amounts of ozone can be used to prepare hydroxy-terminated telechelic polybutadienes [230].

### **Step-Growth (Condensation) Polymerization**

Step-growth polymerization is very convenient method to obtain multifunctional oligomers if other types of polymerization techniques is not possible. It is called also condensation polymerization because it results small molecules such as methanol, water, or hydrogen chloride, condensed during polymerization. Multifunctional monomers are the basis for these reactions. All functional groups may be utilized. Generally, active bifunctional groups of different groups are reacted. Condensation begins with the formation dimers, then dimers react with each others to get oligomers and finally all oligomer and dimers react to form high molecular weight polymers. Increase in the chain length results in the concentration of active groups are lower. Therefore, more time is needed to reach high molecular weight polymers. Thermoplastic elastomers with high glass-transition temperatures may easily be

prepared by this method. Commercially available polymers such as polyethers, polyesters, polyamides and polyurethanes are achieved.

Several differences of step-growth polymerization in comparison with addition polymerization are listed in Table 2.3.

**Table 2.3 :** Differences between addition and step-growth polymerizations [231].

<b>Addition Polymerization</b>	<b>Step-growth Polymerization</b>
Chain growths only occur on the active centers	Chain growth occurs when any two molecules react
Sequential addition of monomers onto the active centers	Every chains without any size limit can react with each other
Monomers are consumed but a little is presence at the end of the reaction	All monomers are consumed after reaction begins
The reaction proceeds rapidly and high molecular weight polymer is formed at the beginning and after that no change in molecular weight	By time the weight of the polymer increases
Reaction time and conversion are proportional and time never affects the mass of the polymer	Time detemines the molecular weight of the polymer. The shorter times result low molecular weights
During the polymerization monomer, polymer and growing active chains are found in the media	Chains of every length are found in the media during the polymerization

As well as the time affects the condensation reaction strongly another parameter playing an effective role is the amount of the monomers used. Condensation of two monomers obey the rules of Carother's equation that before the experiment a researcher may theoretically calculate the molecular weight of the polymers which will be synthesized. According to Carother's equation [232], linear polymers can be obtained by two approaches: (i) monomers with equimolar quantities, and (ii) one

monomer in excess. In the first approach, generally high molecular weight polymers are obtained by a high monomer conversion. The number-average value of the degree of polymerization describing the the average number of monomer units in a polymer can be calculated by the formula (2.1) where p is the conversion to polymer and can be calculated by the formula  $p = (N_0 - N)/N_0$ .  $N_0$  shows the number of molecules present initially and N is the number of molecules at any time.

$$\bar{X}_n = \frac{1}{1-p} \quad (2.1)$$

In the second approach, one monomer is used in excess to arrange the molecular weight of the polymer. The formula becomes (2.2).

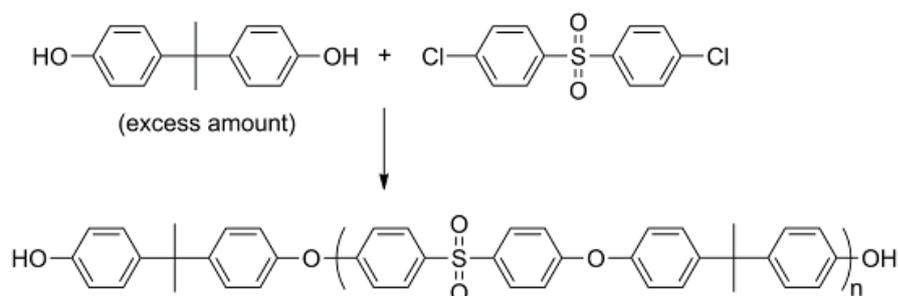
$$\bar{X}_n = \frac{1+r}{1+r-2rp} \quad (2.2)$$

R is defined as the stoichiometric ratio of reactants and it is smaller than 1 in that case. If it is equal to 1, above case where the moles of monomers are equal.

If the conversion of the minor reactant is 100%, then the equation becomes (2.3).

$$\bar{X}_n = \frac{1+r}{1-r} \quad (2.3)$$

The end groups of the obtained telechelic is the end groups of the major reactant. Polysulfone oligomers have been obtained successfully with controlling the end group functionalities [233]. In this case, the bis-phenols are the major component and after full conversion of minor group, 1,4-dichlorosulfone, phenol ended polysulfones are obtained and is shown in Figure 2.17.

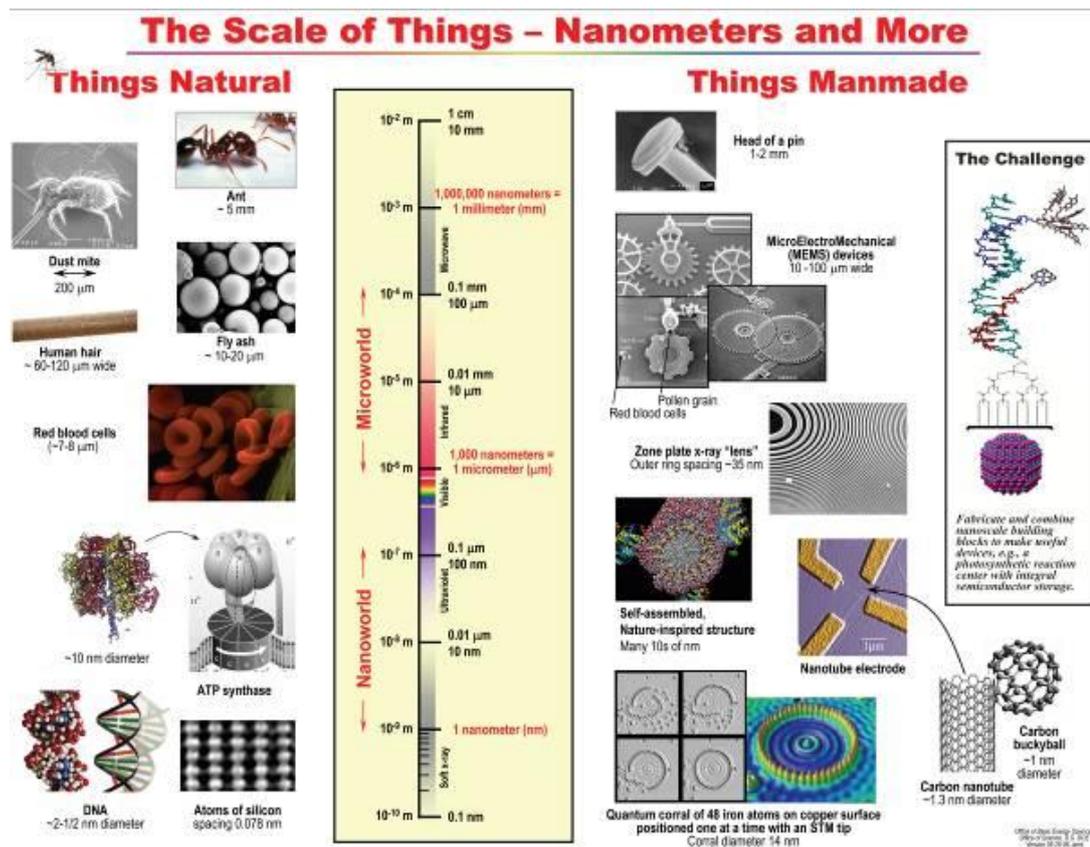


**Figure 2.17 :** Polysulfone telechelics obtained by one monomer excess case.

### 2.3 Polymer Layered Nanocomposites

A composite can be defined as any material made from two or more components. The difference of the composite materials from the blends or alloys comes from the fact that the components having different chemical, physical and structural properties combine to get a solid multiphase material. The continuous phase is called “matrix” and the other is the “filler” phase that is dispersed in the matrix phase. Matrix phase can be polymer, ceramic, or metal. Polymers are preferred to be used in many applications because of many reasons such as flexibility, dielectric, processability, light weight, ductility, easy fabrication, etc. But there are many disadvantages such as lower mechanical, strength and modulus properties etc... in comparison with ceramics and metals. The trend in composite technology is to make polymer composites having improved properties without losing the positive properties of the polymer [234].

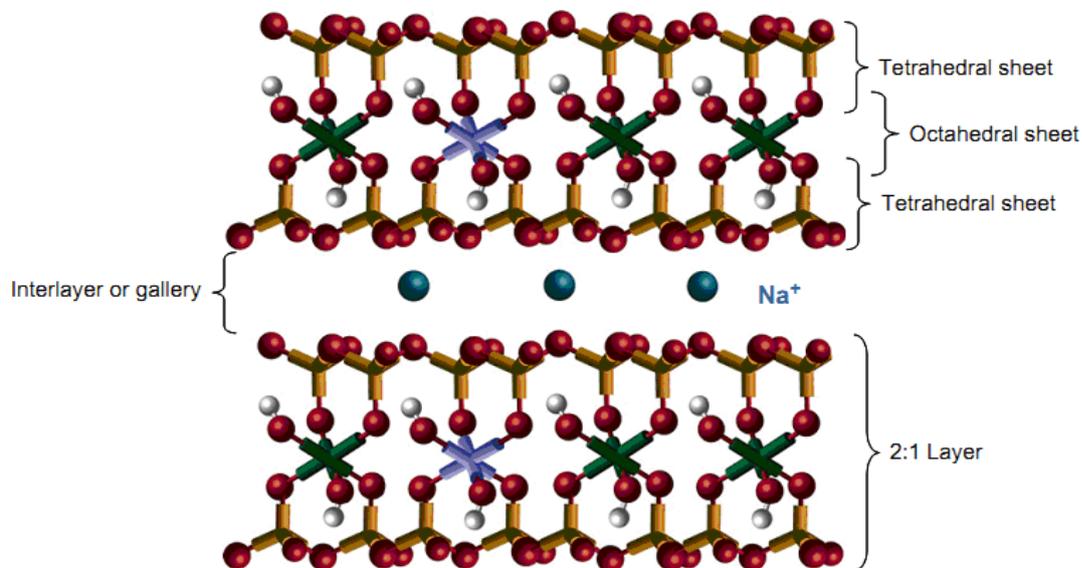
Polymer composites have two components: a polymer and inorganic filler. Conventionally, inorganic fillers are generally talc, calcium carbonate, fibers, etc. They are generally used for two purposes. First one is to add these fillers into polymers in order to gain enhanced properties such as mechanical, thermal, barrier and fire retarding etc. The second is to decrease the cost. But too much addition of these fillers to get increased properties leads to unacceptable results such as higher brittleness and opacity decrease etc. In a polymer composite the interaction of polymer matrix with the fillers and aspect ratio of filler are very important as well as the properties of the filler. Nano-fillers with high aspect ratio such as clays, nanofibers and nanotubes, have been used in polymer composite materials because of their appreciable enhancements in the polymer features at very low filler loadings. Due to the small size of the nano fillers they exhibit small mechanical, electrical and optical defects compared to the micron size fillers [235]. Size comparison of macro, micro and nano materials is shown in Figure 2.18.



**Figure 2.18 :** Size comparison of macro, micro and nano materials [283].

Polymer nanocomposites have been researched for many years to replace with conventional fillers that have been used with high amount as additives to polymers. The nano-sized structures are defined as those that have at least one dimension in the range 1 to 100 nm. IUPAC is defined the nanocomposites in which at least one of the phases has at least one dimension of the order of nanometers [236]. In another definition, polymer nanocomposites are defined as the polymer matrix in which nano-sized inorganics less than 5 % as reinforcing materials are dispread. Because small quantities of inorganic fillers are used, polymers properties, such as processability, toughness, are retented [237]. Due to their enhanced optical, electrical, thermal, magnetic, physical, chemical, conductive and other smart functionalities, polymer nanocomposites are valuable materials used in structural and biomedical applications [238]. Polymer-layered clay nanocomposites have received much attention in industry and in academia because they show significant enhancements in materials features such as, thermal, flame and solvent resistancy, lower gas permeabilities and mechanical properties in comparison with neat polymer or micro and macro-composites.

Nano-sized clay layers having a large surface area interact with the polymer matrix. Therefore, the use of suitable clay types and modification of the clays are very important. Montmorillonite is commonly used because other types of clays such as 1:1 structures, 2:1 pyrophyllite and mica are not useful from the reason that it is not easy to separate their layers leading not to achieve intercalation. The MMT consists of 1 nm thin layers that is parallel to each other forming stacks with van der Waals forces. The gap between the stacks is called interlayer or gallery. Montmorillonite (MMT) is the mostly applied clay with hydrophilic nature, because it can be converted to hydrophobic nature by ion exchange process to enhance the compatibility of polymer with the clay layers. Also, MMT is very useful because of its high surface area and reactivity and well known chemistry explaining the separation of the layers. The surface area of MMT is about  $750 \text{ m}^2/\text{g}$  [239].



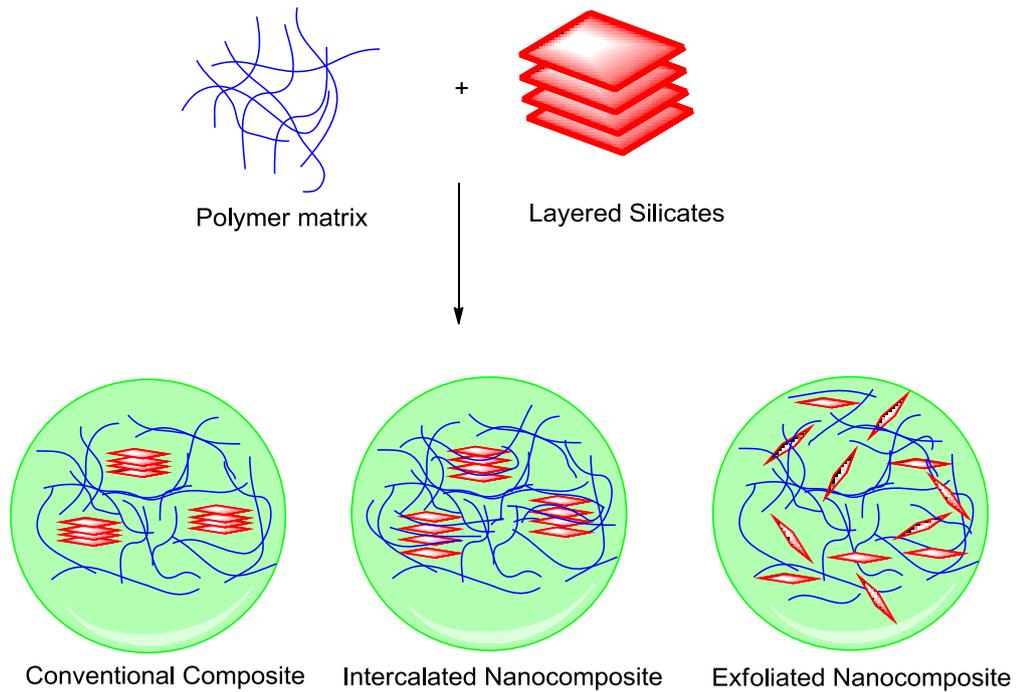
**Figure 2.19** : Representative scheme of montmorillonite (MMT) [239].

Generally, polymer/layered nanocomposites can be classified into two types.

(i) Intercalated nanocomposites: in which polymer chains are inserted in the layered structures and polymer/layer ratio is fixed. They are generally interested for their charge and electronic properties.

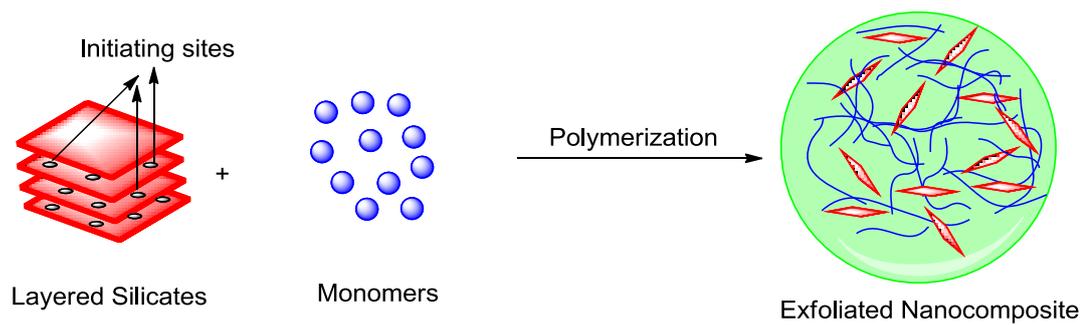
(ii) Exfoliated nanocomposites: in which polymer chains separate the layers apart completely and individual layers are obtained. Improvements in the polymer properties such as, high storage modulus, increased tensile and flexural properties and mechanical properties are observed as compared to the intercalated or composite

materials. Representative scheme of conventional composites, intercalated and exfoliated nanocomposites are shown in Figure 2.20.



**Figure 2.20 :** Conventional, intercalated and exfoliated polymer/layered silicates.

Exfoliated nanocomposites can also be obtained by polymerization of monomers from the initiating sites found in the interlayers of the clays as shown in Figure 2.21. Polymerization results in the opening of the interlayers that after a time the interlayers are far apart to form exfoliated polymer nanocomposites.



**Figure 2.21 :** Formation of exfoliated polymer/layered silicates by polymerization of monomers in the layers.

For the preparation of polymer layered nanocomposites, first of all, hydrophobic clay is modified by exchanging the  $\text{Na}^+$  or  $\text{K}^+$  with an alkyl ammonium cation to prepare a media that accepts an organic monomer or polymer. Cation exchange capacity of a clay is a very important parameter affecting the clay properties. It is defined as the

maximum amount of cations a clay can take up. It is measured in milliequivalents per gram (meq/g) or more frequently per 100 g (meq/100g) performed in pH of 7. The CEC of montmorillonite is between 80 to 150 meq/100g. [240]

Several methods are used for the preparation of polymer layered nanocomposites: (i) solution exfoliation, (ii) melt intercalation, and (iii) *in situ* polymerization [240, 241].

(i) Solution exfoliation: In this method, organically modified clay and polymer are dissolved in a polar solvent. Disorption of solvent molecules on polymer chains lead to the polymer chains intercalate between the layers. Then, solvent is removed resulting intercalating polymer layered silicates. Epoxy-clay nanocomposites are prepared by this way. The disadvantage of this system is the use of large amount of solvents.

(ii) Melt intercalation: In this method, polymer and layered silicates are mixed at elevated temperatures. Polymer intercalated layered silicates can be prepared easily by injection molding and extrusion.

(iii) *In situ* polymerization: This method is similar to solution exfoliation except that instead of solvent polar monomers are used. After organically modified clay is swollen in the monomer or monomer solution, a curing agent (catalyst or initiator) is added to start polymerization in clay layers by an externally stimulation, heat or light [242]. Polymerization results in lower polarity and this causes polar monomers diffuse in the clay layers easily resulting exfoliation of layers. The disadvantage of this system is the difficulty to arrange the polymerization degree that should be controlled to get nanocomposites with the same property in every case.

Latter is the best and mostly used way to prepare the nanocomposites because of the types of nanofillers and polymer precursors can be varied in a wide range to get the enhanced properties [243].

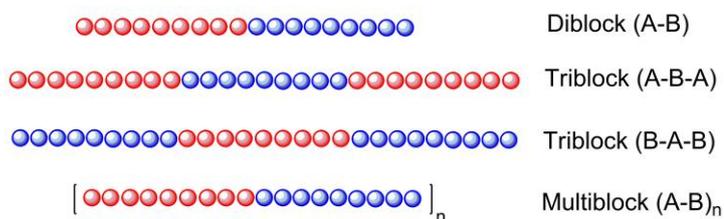
## **2.4 Block Copolymers by Macroazoinitiators**

Recently, there is high interest to develop novel polymeric materials displaying improved physical and chemical properties to meet the needs of the industry for high-tech applications. Such improvements might be achieved by either combination of two homopolymers mechanically by blending that generally result immiscible polymer blends or chemically linking of the homopolymers by preparing block or

graft copolymers [244]. Block copolymers are commonly applied as supporter for immobilization of proteins and cells, thermoplastics, thermoplastic elastomers, fibres, surfactants, adhesives, modifiers for polymers, compatibilizer for polymer blends and etc. [245-251]. Block copolymer synthesis have been performed mostly by anionic or cationic polymerization methods. By these methods polymers with a narrow polydispersity index and well-defined end groups can be obtained. Main disadvantages of these methods are the requirement of extraordinarily high purity, sensitivity to environmental conditions and limitations to ionically polymerizable monomers. Radical polymerization techniques in which the reaction is less sensitive toward impurities and is applicable to a great number of monomers, have become common after the discovery of controlled radical polymerization techniques including ATRP, RAFT and NMRP [221, 222, 252]. In recent decades, mechanistic transformation techniques, in which a polymer chain synthesized by a certain mechanism is functionalized either by initiation or termination steps for the initiation of another polymerization mechanism, has been proposed to extend the range of monomers for the synthesis of block copolymers [253-255]. The main benefit of this methodology is that it offers a straightforward route to obtain block copolymers that cannot be made by a single polymerization mode [54, 208, 256, 257].

By using bifunctional initiators ABA symmetric triblock copolymers can be prepared. Also, AB diblock or ABA triblock copolymers can be prepared by combining end-functionalized chains of A and B homopolymers or AB blocks, respectively.

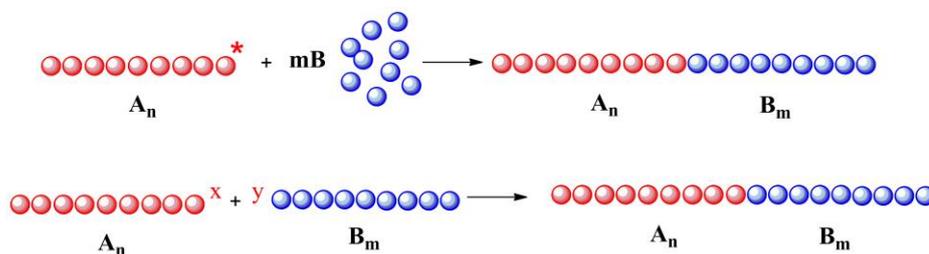
Incompatible blocks obtained from different monomers can be combined in a linear arrangement by covalent binding. It is possible to form diblock (A-B), triblock (A-B-A or B-A-B) and segmented polymers as shown in Figure 2.22.



**Figure 2.22 :** Different types of block copolymers.

Two main methods utilized in the formation of block copolymers contain step and chain polymerizations [240, 258]. In the first, two polymers with functional end

groups are reacted while in the later, sequential polymerization involving initiation of other monomers on the active site of a macromolecular chain of one monomer is done (Figure 2.23.)

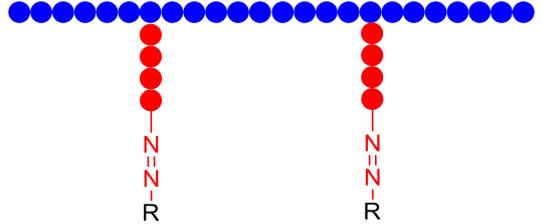


**Figure 2.23 :** Synthetic ways for block copolymers.

Several transformation approaches have been developed by combining free radical systems with other polymerization techniques such as anionic [259], active monomer [260], cationic [257], radically promoted cationic [261], and condensation [262]. In some cases, same polymerization mechanisms but different initiating systems were also employed [263]. Macroinitiator technique is the mostly used technique to prepare block or graft copolymers by conventional free radical polymerization. This technique is advantageous since the preparation of macroinitiator before use in the free radical step can be achieved by various types of polymerization including cationic [264], anionic [265] and free radical polymerization [266] methods.

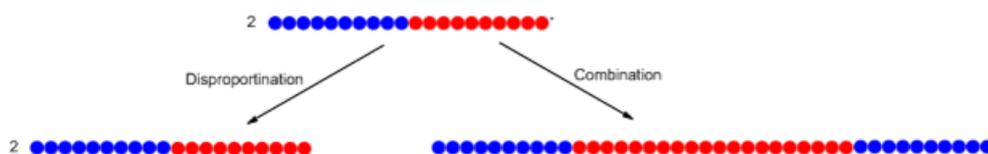
Macroazoinitiators (MAIs) carrying labile azo functional groups exhibit a most versatile way of preparing block copolymers via conventional radical polymerization [47, 50, 267, 268]. In this method polymerization is initiated in the radical sites. If this groups are at the end chain of a polymer a block copolymer is formed. If it is in the side chain of the polymer a graft polymer can be obtained. According to type of MAI, whether contains one or more azo group in the terminal or side chain, and termination step, diblock (AB), triblock (ABA), multiblock (AB)<sub>n</sub> copolymers or graft polymers can be synthesized. The locations of azo bonds in a macroazoinitiator are shown in Table 2.4.

**Table 2.4 :** Types of macroazoinitiators (MAIs).

Location of the azo bond	Structure
Central azo bond	
Azo groups in the main chain	
One terminal azo bond	$R-N=N-$ 
Two terminal azo bonds	$R-N=N-$  $-N=N-R$
Side chain azo bonds	

Block copolymerization is initiated from the radical generated by the cleavage of the azo group from the polymer backbone thermally or photochemically. Aliphatic azo compounds evolve nitrogen leading to the formation of two radicals. Either condensation or addition mechanisms can be employed in preparation of MAIs [51, 52, 269]. There are several reports on the preparation of novel block copolymers composed of a condensation polymer segment (e.g, polyether, polyester, polyamide, polyurethane, and polysiloxane) with vinyl polymer segments [54, 55, 270-272].

The mode of chain termination affects the type of block copolymer formed. For example, if a MAI (based essentially on the first monomer A) possessing one central azo bond is decomposed in the presence of monomer B, the growing chain B<sub>n</sub> can terminate either by disproportionation or combination as shown in Figure 2.24., leading to AB and ABA type copolymers, respectively.



**Figure 2.24 :** Formation of AB or ABA block copolymers by disproportionation or combination.

Which mechanism of termination will be preferably applied depends largely on the monomer used. Thus, methyl methacrylate chains terminate to a large extent by disproportionation, whereas styrene chains tend to termination by combination. According to types of initiators, disproportionation or combination results different types of block copolymers as shown in Table 2.5.

**Table 2.5 :** Types of block copolymers.

<b>Types of MAI</b>	<b>Disproportionation</b>	<b>Combination</b>
One central azo bond	AB	ABA
Azo bonds in the main chain	BAB, AB	(AB) <sub>n</sub>
One terminal azo bond	AB	ABA
Two terminal azo bonds	BAB	(AB) <sub>n</sub>

Termination of radical chains by additives is an important method to get AB type block copolymers. Radical chains may easily be terminated with thiols. Regarding the block copolymer formed, one would obtain AB blocks, provided that a growing block of monomer B is attached to a block of A and no other blocks are present. The termination by additives gives exactly the same type of block copolymers as if all growing chains would terminate by disproportionation .

### 3. EXPERIMENTAL WORK

#### 3.1 Materials and Chemicals

*Bisphenol A (Hallochem Pharma Co. Ltd, China)*

It was used without further purification.

*Bis(p-chlorophenyl) sulfone (Hallochem Pharma Co. Ltd, China, 99%)*

It was used without further purification.

*N, N-dimethyl acetamide (Acros, 99.5%):*

It was utilized as received.

*Potassium carbonate (Merck, >99%):*

It was utilized as received.

*Toluene (Alfa Aesar, 99.5%):*

It was utilized as received.

*Chloroform (Alfa Aesar, 99,5%):*

It was utilized as received.

*Methanol (Merck, >99%):*

It was utilized as received.

*Dichloromethane (Aldrich, 99%):*

It was utilized as received.

*Chloroform (Aldrich, 99%):*

It was utilized as received.

*Acryloyl chloride (Merck, 97%):*

It was utilized as received.

*Methacryloyl chloride (Merck, 97%):*

It was utilized as received.

*2,2-Dimethoxy-2-phenylacetophenone(DMPA) (Across, 99%):*

It was utilized as received.

*Cloisite 30B [MMT-(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>] (Southern Clay Products):*

It was purchased from (Gonzales, TX, USA). The clay is a MMT modified by methylbis(2-hydroxyethyl)(tallow alkyl)ammonium ions. The organic content of the organo-modified MMT, determined by TGA, was 21 wt%.

*Tetrahydrofuran (THF) (Fluka, 99%):*

It was dried over sodium metals and distilled over just before use.

*Triethylamine (TEA) (Aldrich, HPLC grade):*

It was used without further purification.

*Benzene (Aldrich):*

It was used without further purification.

*4,4-Azobis(4-cyanopentanoic acid) (ACPA)( Fluka, 98%):*

It was used without further purification.

*Styrene (St)( Aldrich, 99%):*

It was passed through basic alumina column to remove the inhibitor.

*4-(Dimethylamino) pyridine (DMAP) (Aldrich, 99%):*

It was used without further purification.

*P-toluenesulfonic acid (PTSA) ( ACS Reagent Aldrich, 98.5%):*

It was used without further purification.

*N,N'-dicyclohexylcarbodiimide (DCC) (Aldrich, 99% ):*

It was used without further purification.

*Anhydrous N,N-dimethylformamide (DMF) (Aldrich, 99%):*

It was used without further purification.

## **3.2 Characterization**

### **3.2.1 Nuclear magnetic resonance spectroscopy (NMR)**

<sup>1</sup>H NMR spectra of 5-10% (w/w) solutions of the intermediates and final polymers in CDCl<sub>3</sub> with Si(CH<sub>3</sub>)<sub>4</sub> as an internal Standard were recorded at room temperature at 250 MHz on a Bruker DPX 250 spectrometer.

### **3.2.2 Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectra**

Fourier transform infrared-Attenuated Total Reflectance (FTIR-ATR) spectra were recorded on a Perkin-Elmer FT-IR Spectrum One B spectrometer with a Universal ATR accessory equipped with a single reflection diamond crystal. Solid oligomers were placed over the ATR crystal and maximum pressure was applied using the slip-clutch mechanism.

### **3.3.2 Differential scanning calorimetry (DSC)**

Differential scanning calorimetry analyses were performed on a Perkin-Elmer Diamond DSC in the range of 30-300 °C with a heating rate of 10 °C min<sup>-1</sup> under nitrogen flow.

### **3.2.4 Photo-differential scanning calorimetry (Photo-DSC)**

The photo-differential scanning calorimetry (Photo-DSC) measurements were carried out by means of a modified Perkin-Elmer Diamond DSC equipped with a high pressure mercury arc lamp (320–500 nm). A uniform UV light intensity was delivered across the DSC cell to the sample and reference pans. The intensity of the light was measured as 53 mW cm<sup>-2</sup> by a UV radiometer capable of broad UV range coverage.

### **3.2.5 Gel permeation chromatography (GPC)**

Molecular weights and polydispersities of the linear telechelics were measured by gel permeation chromatography employing an Agilent 1100 instrument equipped with a differential refractometer by using tetrahydrofuran as the eluent at a flow rate of 0.3 ml min<sup>-1</sup> at 30 °C. Molecular weights were determined using polystyrene standards.

### 3.2.6 Thermal gravimetric analyzer (TGA)

Thermal gravimetric analysis was performed on Perkin-Elmer Diamond TA/TGA under nitrogen flow. Approximately 3 mg of samples were heated at a rate of 10 °C min<sup>-1</sup>.

### 3.2.7 X-ray diffraction (XRD)

The powder XRD measurements were performed on a PANalytical X'Pert PRO X-ray diffractometer equipped with graphite-monochromatized Cu K $\alpha$  radiation ( $\lambda$ = 1.54 Å).

### 3.2.8 Transmission electron microscopy (TEM)

TEM imaging of the samples was carried out by FEI Tecnai™ G2 F30 instrument operating at an acceleration voltage of 200 kV. Each sample was dispersed in methanol and drop-cast onto carbon coated grid for the TEM imaging.

## 3.3 Preparation Methods

### 3.3.1 Synthesis of polysulfone oligomers (PSU-2000 and PSU-4000)

General procedure for the synthesis of polysulfone oligomer Bisphenol A (40 g, 175 mmol), bis (p-chlorophenyl) sulfone (25.16 g, 87.6 mmol) and dried potassium carbonate (25.39 g, 83.6 mmol) were added to 400 mL DMAC (dimethyl acetamide) and 50 mL toluene in a 2000 mL, 2 necked round bottom flask, fitted with a condenser, nitrogen inlet, a Dean and Stark trap and an overhead mechanical stirrer. The reaction mixture was heated under reflux at 150 °C for 4 h with water removal. The reaction was stopped after about 2 h and cooled to room temperature. The solution was filtered to remove most of the salts and poured into a mixture of methanol and water (4:1). The precipitated polymer was filtered, and washed several times with water in order to remove the remaining salts and impurities. Finally, the polymer was washed with methanol and dried in a vacuum oven at 60 °C for about 12 h to give PSU-2000 oligomer (42.2 g).

IR (ATR, cm<sup>-1</sup>): 3435 (-OH), 3200–3000 (Ar), 2975 (-CH<sub>3</sub> sym-), 2945 (-CH<sub>3</sub> asym-), 1322 and 1293 (O=S=O asym-), 1240 (C-O-C), 1175 and 1151 (O=S=O sym-) and 1014 (Ar). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta$  = 7.85 (16H), 7.26 (16H), 7.07 (4H), 7.00 (16H), 6.94 (16H), 6.75 (4H), 1.69 CMe<sub>2</sub> (30H).

A similar procedure using 6:5 ratios of the monomers instead of 2:1 resulted PSU-4000 ( $M_{n,GPC} = 4360 \text{ g mol}^{-1}$ ,  $M_{n,NMR} = 4000 \text{ g mol}^{-1}$ )

### 3.3.2 Synthesis of polysulfone diacrylate (PSU-DA)

PSU-2000 (5 g, 2.86 mmol) was added to 20 mL  $\text{CH}_2\text{Cl}_2$  in a 50 mL, two necked round bottomed flask fitted with a condenser and argon inlet. The flask was placed in an ice bath and the contents stirred for about 5 min. Excess triethylamine ( $\text{Et}_3\text{N}$ ) 2.0 mL was added followed by excess acryloyl chloride (1.15 mL, 14.3 mmol) dissolved in 5 mL  $\text{CH}_2\text{Cl}_2$  which was added slowly to the reaction flask over a 10 min period. The reaction mixture was stirred for 24 h then filtered to remove the salts formed and poured into methanol to precipitate the acrylate oligomer. The precipitated oligomer was filtered and washed several times with water to remove the remaining salts and impurities. Finally, the polymer was washed with methanol and dried in a vacuum oven at room temperature for about 12 h to give PSU-DA-2000 macromonomer (5 g). IR (ATR,  $\text{cm}^{-1}$ ): 3200–3000 (Ar), 2968 ( $-\text{CH}_3$  sym-), 2875 ( $-\text{CH}_3$  asym-), 1739 ( $-\text{C}=\text{O}$ ), 1322 and 1293 ( $\text{O}=\text{S}=\text{O}$  asym-), 1238 (C-O-C), 1175 and 1151 ( $\text{O}=\text{S}=\text{O}$  sym-) and 1014 (Ar).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta = 7.76$  (16H), 7.16 (16H), 7.02 (4H), 6.94 (16H), 6.86 (16H), 6.84 (4H), 6.53–6.51 (2H) and 6.24–6.22 (2H) ( $\text{CH}_2=$ ), 5.94–5.92 (2H) ( $=\text{CH}-$ ), 1.62  $\text{CMe}_2$  (30H).

The same procedure was applied for the synthesis of PSU-DA-4000.

### 3.3.3 Synthesis of polysulfone dimethacrylate (PSU-DMA)

For the preparation of PSU-DM-2000, a similar procedure as described for the synthesis of acrylate functional macromonomers was followed with methacryloyl chloride instead of acryloyl chloride.

IR (ATR,  $\text{cm}^{-1}$ ): 3200–3000 (Ar), 2969 ( $-\text{CH}_3$  sym-), 2875 ( $-\text{CH}_3$  asym-), 1735 ( $-\text{C}=\text{O}$ ), 1323 and 1295 ( $\text{O}=\text{S}=\text{O}$  asym-), 1243 (C-O-C), 1175 and 1151 ( $\text{O}=\text{S}=\text{O}$  sym-) and 1014 (Ar).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta = 7.78$  (16H), 7.17 (16H), 6.94 (16H), 6.87 (16H), 6.26 (2H) and 5.76 (2H), 1.98 ( $\text{C}=\text{Me}$ ) (6H), 1.63  $\text{CMe}_2$  (30H).

The same procedure was applied for the synthesis of PSU-DMA-4000.

### 3.3.4 Preparation of photo-curable formulations

Formulations containing macromonomers (0.003 g) and DMPA (2 mol %) in 250  $\mu$ L chloroform were prepared from appropriate stock solutions. The mixture was then dropped onto an aluminum pan and the solvent allowed to evaporate completely. The film samples were placed into the sample cell of photo-DSC instrument.

### 3.3.5 Modification of MMT with methacryloyl chloride

Methylbis (2-hydroxyethyl) (tallow alkyl) ammonium organomodified clay [MMT-(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>], 2.25 g, 2.75 mmol and TEA (1.85 mL, 13.25 mmol) were added in THF (50 mL) and cooled to 0 °C. Methacryloyl chloride (1.1 mL, 13.3 mmol) was added dropwise while stirring. The reaction mixture was allowed to heat up to room temperature and stirred overnight. After cooling to room temperature and removing the solvent by rotary evaporation, ether (200 mL) was added to the crude reaction mixture and washed three times with a saturated NaCl aqueous solution. The clay was then filtered off on a cold silica filter, washed with water, and finally dried in vacuum.

IR (ATR):  $\nu$ = 3612 (-OH), 3380 (-NR), 2965 (-CH<sub>3</sub> sym), 2872 (-CH<sub>2</sub> sym), 1724 (C=O), 1625 (-C=C-), and 1210 (C-O-C) cm<sup>-1</sup>.

### 3.3.6 Preparation of the PSU/MMT nanocomposites (NCs)

The organomodified clay (1, 3, and 5 wt% monomer) and DMPA (1 wt% oligomer) was mixed with PSU-DMA oligomer dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (2 mL) in Pyrex tubes via a magnetic stirrer at room temperature for 12 h and degassed with nitrogen prior to irradiation by a merry-go-round type reactor equipped with 16 Philips 8W/06 lamps emitting light at  $\lambda > 350$  nm and a cooling system. At the end of 4 h, polymers were precipitated into methanol, filtered, dried, and weighed. Conversions, the percentage of the macromonomer converted into insoluble network were determined gravimetrically.

### 3.3.7 Synthesis of 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS)

Firstly, the condensing agent, 4-(dimethylamino) pyridinium 4-toluene sulfonate (DPTS), was synthesized according to the modified procedure in which an equimolar solution of DMAP in benzene was added to the anhydrous benzene solution of PTSA

and mixed thoroughly with heating. The suspension was cooled to room temperature and the white powder was collected by filtration.

### **3.3.8 Synthesis of polysulfone macroazoinitiator (PSU-MAI)**

The PSU-MAI was prepared with a direct polycondensation reaction between HO-PSU-OH and ACPA. HO-PSU-OH (0.44 g, 0.20 mol), ACPA (0.028 g, 0.10 mol), and DPTS (0.012 g, 0.04 mol) were dissolved in a mixture of 2 g of dichloromethane and 1 mL of DMF at room temperature. Then, the DCC solution (0.255g, 1.2 mmol) (dissolved in 3 mL of dichloromethane) was added slowly and stirred at room temperature for 24 h. The resulting viscous suspension was filtered to eliminate the dicyclohexylurea (DCU) formed, which was washed with dichloromethane twice. The filtrate was slowly poured into a large volume of methanol to precipitate the polymer. This process was repeated two times to purify the polymer.

### **3.3.9 Polysulfone-*b*-polystyrene block copolymers by conventional free radical polymerization technique**

PSU-MAI and styrene were dissolved in DMF in a Schlenk tube equipped with a magnetic stirring bar. The tube was degassed by three freeze–pump–thaw cycles, left under nitrogen, and placed in an oil bath at 70 °C. After the reaction, the mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and precipitated into ten-fold excess methanol. The final product was washed with methanol and dried for 24 h in a vacuum oven at 60 °C.

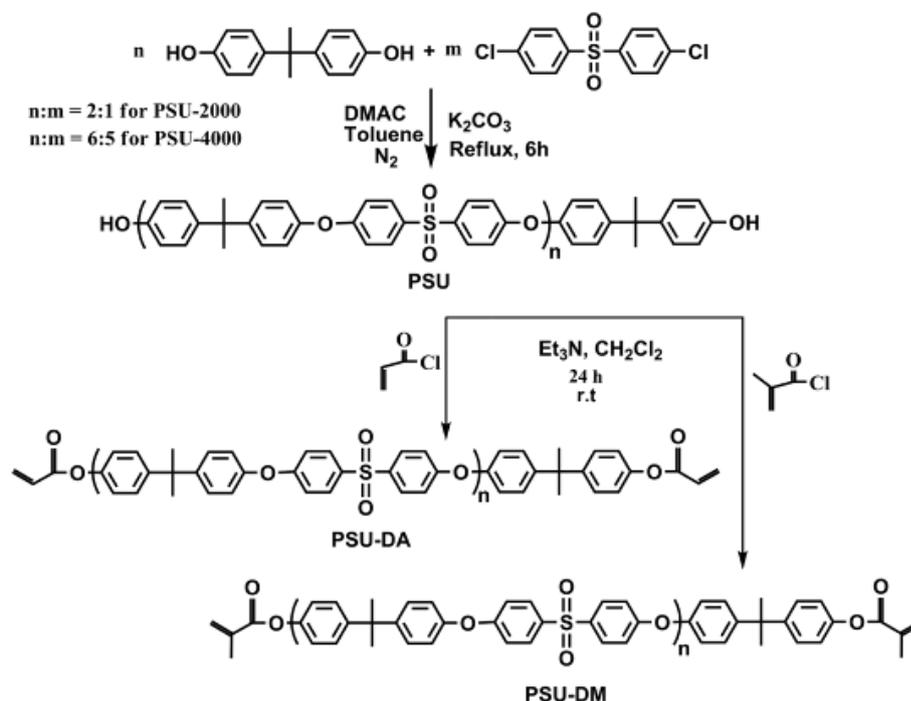


## 4. RESULTS AND DISCUSSION

### 4.1 Synthesis, Characterization and Photoinduced Curing of Polysulfones with (Meth)acrylate Functionalities

#### 4.1.1 Synthesis of (meth)acrylate functional PSU telechelics

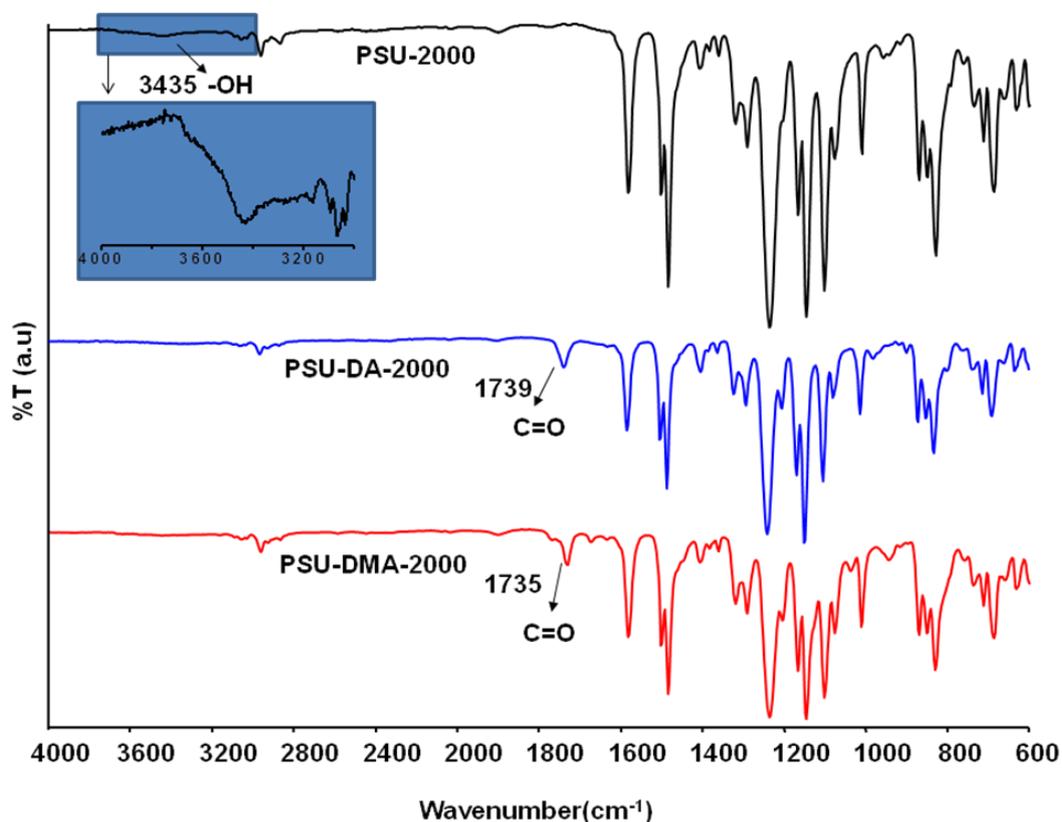
UV-Curable PSU telechelics were synthesized by condensation polymerization and subsequent esterification. First of all, PSU-2000 and PSU-4000 were synthesized by condensation polymerization according to the procedure described in the literature [273]. Monomer concentrations were adjusted to yield oligomers possessing phenolic groups at both ends. Polysulfone macromonomers were then synthesized by esterification of the oligomers obtained with acryloyl chloride and methacryloyl chloride in the presence of Et<sub>3</sub>N as the base. The overall procedure is presented in Figure 4.1.



**Figure 4.1** : Synthesis of (meth)acrylate functional PSU telechelics.

The characterization of the synthesized oligomers was carried out by using FTIR-ATR, <sup>1</sup>H NMR, GPC, DSC, photo-DSC and TGA. FTIR-ATR data shows the

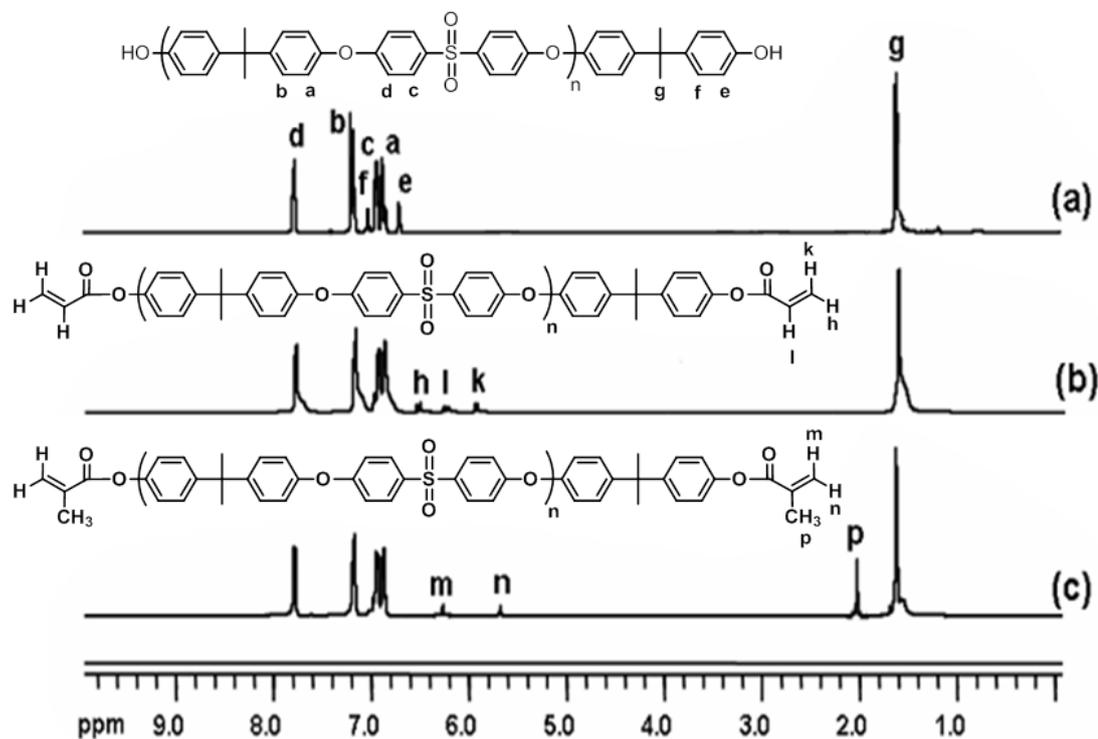
characteristic bands for the polyether sulfone backbone. The new broad but weak peak around  $3435\text{ cm}^{-1}$  indicates the presence of phenolic end groups. Attachment of polymerizable acrylate and methacrylate functional groups through the esterification process was evidenced by the disappearance of this peak and the formation of the new ester carbonyl peak at around  $1735\text{ cm}^{-1}$  (Figure 4.2.).



**Figure 4.2 :** FT-IR spectra of PSU-2000, PSU-DA-2000 and PSU-DM-2000.

The structures of the macromonomers were further confirmed by  $^1\text{H}$  NMR analysis. As can be seen from Figure 4.3., where the  $^1\text{H}$  NMR spectra of the precursor polymer and telechelics are presented, the methyl group belonging to bisphenol A appears in all the spectra at 1.69 ppm. The shifts between 6.70 and 7.86 ppm correspond to the aromatic protons of the poly(ether sulfone) backbone. The phenolic protons were not observed, probably due to the relatively high molecular weight of the precursor polymers. Distinctively, the aromatic protons of the terminal benzene ring appeared at 6.77 and 7.07 ppm as relatively weak signals. Successful macromonomer formation was confirmed by the appearance of the new peaks at around 6.15 (d), 6.50 (t) and 6.75 (d) ppm for the acrylate and 6.15 (s) and 6.45 (s) ppm for methacrylate groups, respectively. Notably, in both cases, the aromatic protons were down field shifted. End chain aromatic protons overlap with the other

aromatic protons. The signal at 2.02 (s) ppm was assigned to the methyl group of the methacrylate functionality.



**Figure 4.3 :** <sup>1</sup>H NMR spectra of PSU-2000 (a), PSU-DA-2000 (b) and PSU-DM-2000 (c) in CDCl<sub>3</sub>.

The molecular weight characteristics of the polymers with respect to the synthesis conditions are presented in Table 4.1. As the functionalized PSUs were intended to be used in the ultimate photocuring step, the conditions of polycondensations were chosen so as to obtain relatively low molecular weight polymers with phenolic end group functionality combined with a satisfactory conversion. The efficiency of functionalization was confirmed by <sup>1</sup>H NMR spectrum by using the integration ratio of the protons corresponding to the (meth)acrylic groups to that of the methyl protons of the repeating unit. Almost quantitative functionalization was attained in both cases. Notably, the molecular weights calculated by <sup>1</sup>H NMR in general agree well with the measured values. Moreover, general agreement between the molecular weight of the final telechelic polymers and that of the precursor PSU obtained by GPC also confirms efficient esterification. The observed increase in the molecular weight is due to the additional acrylate and methacrylate moieties incorporated.

**Table 4.1** : Synthesis<sup>a</sup> and molecular weight characteristics of polysulfones.

Polymer	Bis-A/ DCDPS (mol/mol)	Yield <sup>b</sup> (%)	$M_n^c$ (GPC) (g/mol)	PDI	$M_n^d$ (NMR) (g/mol)	Acrylates		Methacrylates	
						$M_n^c$ (GPC) (g/mol)	$M_n^d$ (NMR) (g/mol)	$M_n^c$ (GPC) (g/mol)	$M_n^d$ (NMR) (g/mol)
PSU-2000	2/1	65	1900	1.45	2200	2200	2400	2100	2300
PSU-4000	6/5	71	4400	1.51	4000	4600	4200	-	-

<sup>a</sup> Reaction Temperature: 170 °C, Time: 6h.

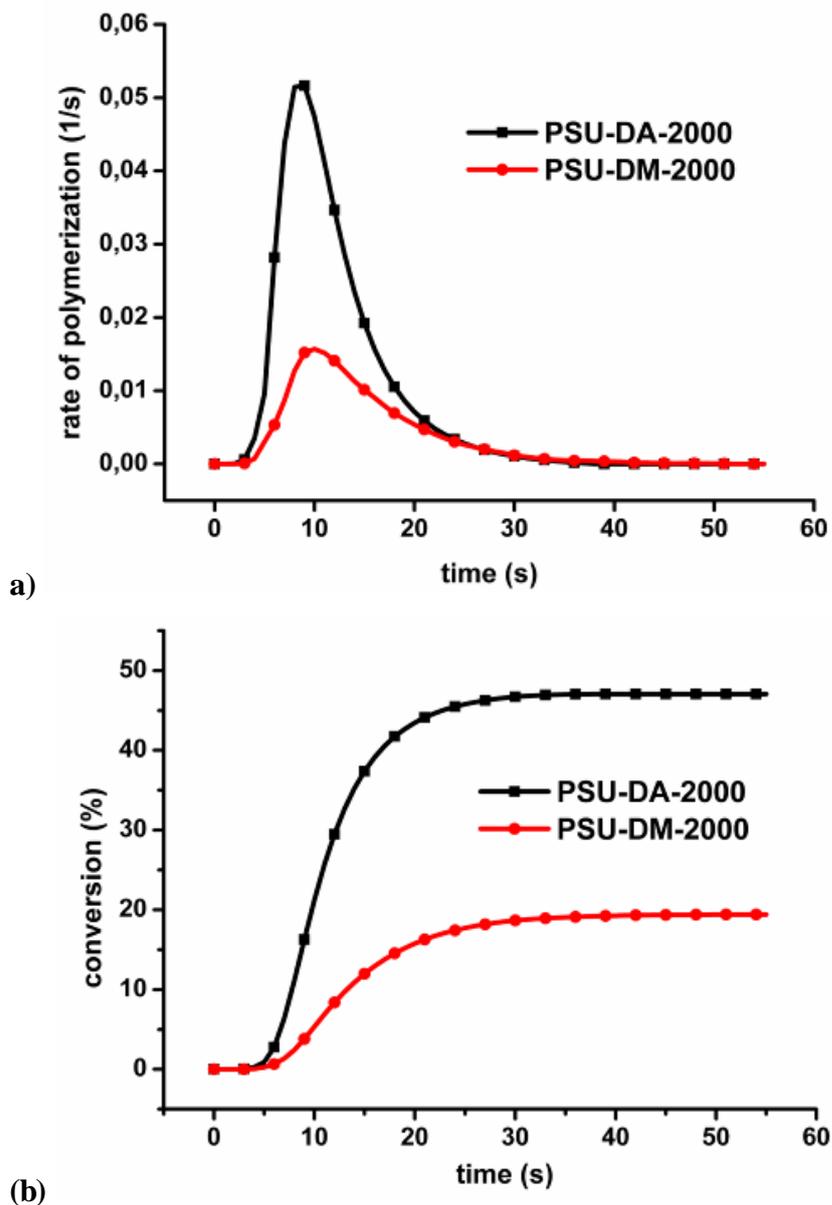
<sup>b</sup> Determined gravimetrically.

<sup>c</sup> Number average molecular weight determined from GPC measurements based on polystyrene standards.

<sup>d</sup> Calculated by using <sup>1</sup>H NMR spectra.

#### 4.1.2 UV curing of (meth)acrylate functional PSU telechelics

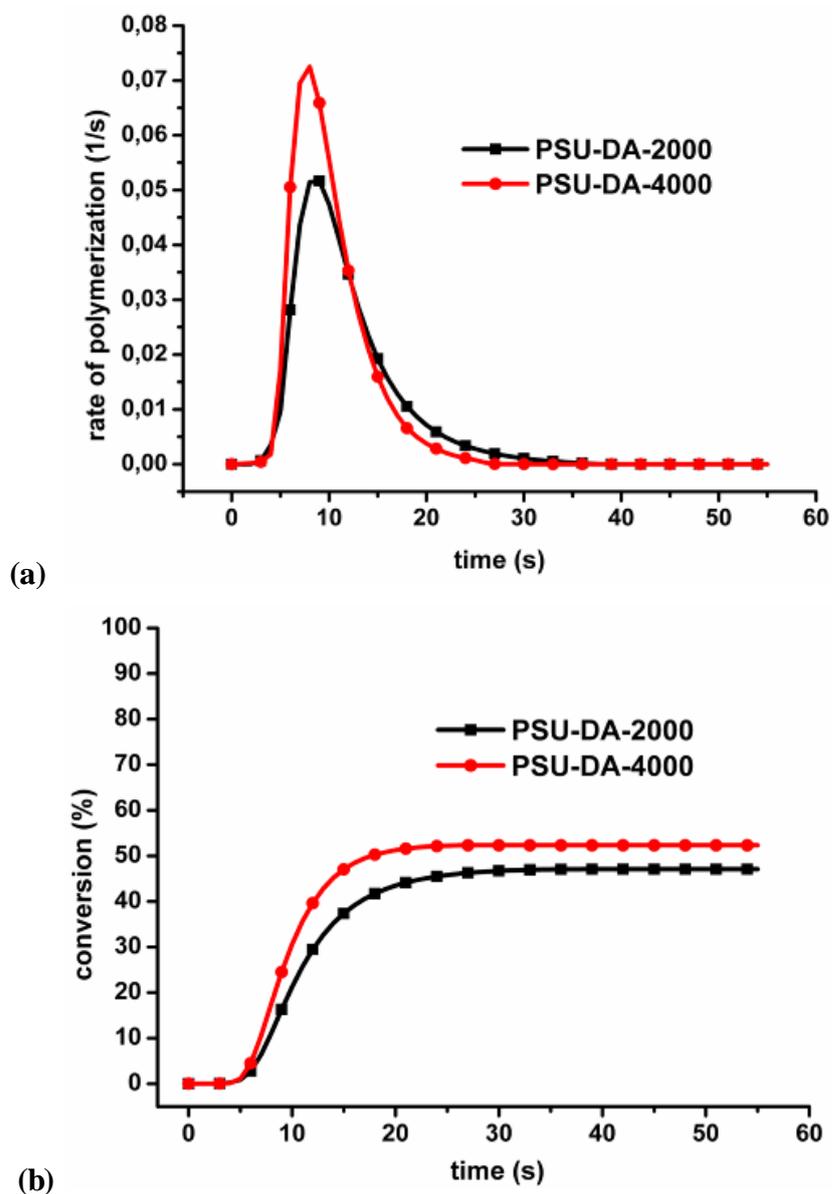
The polysulfone oligomers can undergo photo induced curing via radical polymerization of (meth) acrylate groups in the presence of a photoinitiator, DMPA. Kinetic studies concerning photopolymerization of the macromonomers were performed by photo-DSC. The results are shown in Figure 4.4 and exhibit no plateau region indicating the absence of the rapid auto acceleration at the very beginning of the reaction.



**Figure 4.4 :** Rate (a) and conversion (b) of photo induced polymerization of PSU-DA-2000 and PSU-DM-2000 in presence of DMPA (2%) as initiator, cured at 30 °C by UV light with an intensity of 53 mW cm<sup>-2</sup> under nitrogen flow of 20 mL min<sup>-1</sup>.

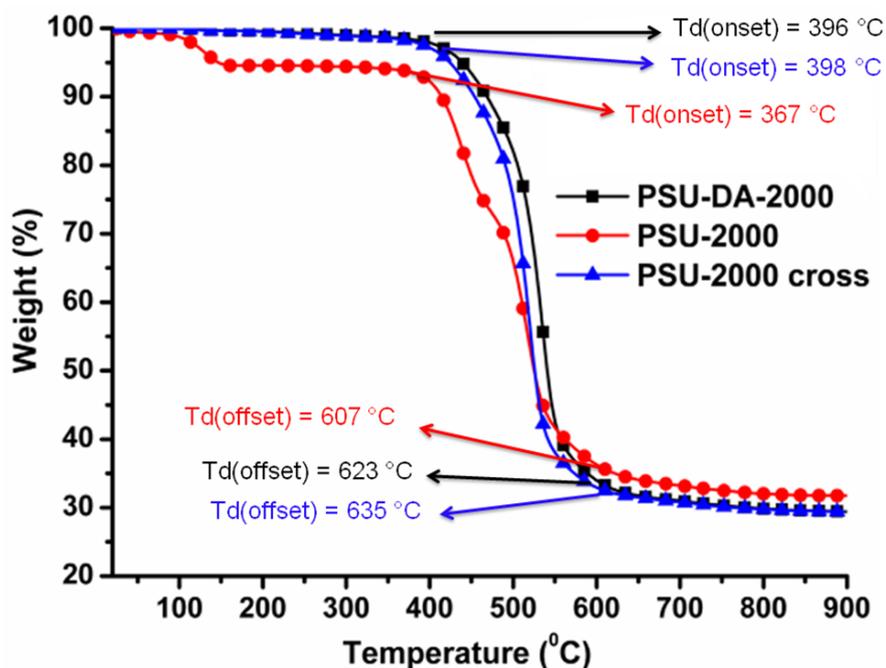
This behavior may be due to factors related to the cross-linking nature of the samples and solid-state measurements. Since the obtained telechelics exhibit high melting points and are solid at room temperature, free standing films can easily be prepared. The photopolymerization under these conditions leads to a suppressed center of coil diffusion resulting in rapid auto acceleration [274]. The results also indicate that conversions are lower than 50%. Although the oligomers possess long flexible chains, due to their vitreous nature dense cross-linked network formation occurs

which decreases the amount of reacted double bonds significantly [275]. Figure 4.4. shows also that the conversion and polymerization rate of the acrylate derivative is considerably higher than that of the methacrylate macromonomer. This difference may be due to the  $\alpha$ -methyl group present in the monomer which stabilizes the propagating radical. These results are consistent with the literature data for the thermal initiated polymerization that gives a difference by a factor of approximately 5 in the polymerization rates at room temperature [276]. The cross-linking capability of the oligomers increased with the molecular weight of the macromonomer as a result of the increased flexibility of the longer chains. Therefore, PSU-DA-4000 displays a slightly higher conversion and a faster rate of polymerization (Figure 4.5.) [277].



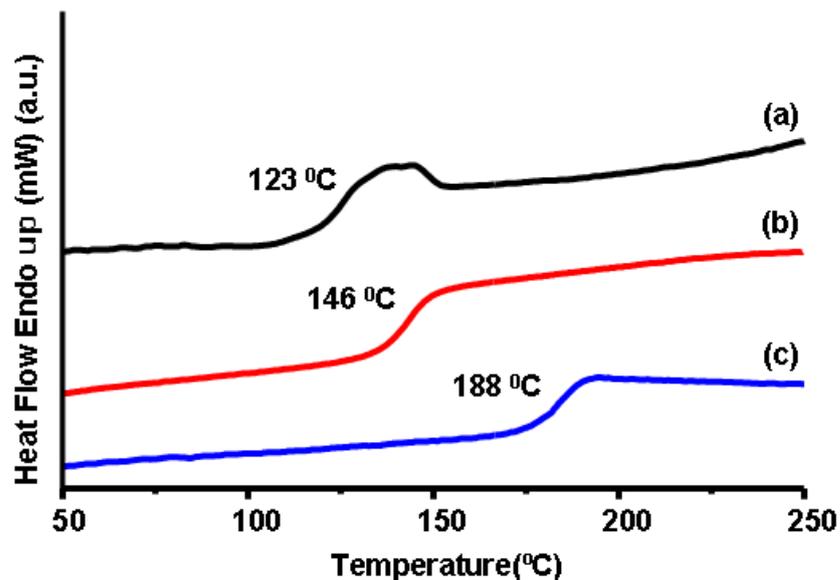
**Figure 4.5 :** Rate (a) and conversion (b) of photo induced polymerization of PSU-DA-2000 and PSU-DA-4000 in presence of DMPA (2%) as initiator, cured at 30 °C by UV light with an intensity of 53 mW cm<sup>-2</sup> under nitrogen flow of 20 mL min<sup>-1</sup>.

TGA thermograms of photochemically cured and precursor oligomers were shown in Figure 4.6. As can be seen, the initial oligomers show some but small weight loss up to 200 °C. This degradation can be attributed to the water elimination reaction. Similar weight losses have been observed for other hydroxyl-containing polymers [278]. The main degradation of the oligomers began at nearly 400 °C. The overall thermal stability of the polymers is similar.



**Figure 4.6 :** TGA thermograms of the precursor oligomers (PSU-2000) (a), and macromonomer, PSU-DA-2000 before (b), and after curing PSU-DA-2000 cross)(c).

As can be seen from Figure 4.7, the acrylate macromonomer shows more than 20 °C higher glass transition temperature ( $T_g$ ) than that of its precursor polymer because of the structural compatibility between end groups and inner backbone. Interestingly, the corresponding UV-cured macromonomer exhibits much higher  $T_g$  (188 °C) which is almost the same  $T_g$  of the commercially available high molecular weight PSU such as UDEL-PSU ( $M_n = 30000$ ). This behavior indicated that the properties of the high molecular weight PSUs can be attained even with oligomeric macromonomers as a result of extended chain length by UV induced crosslinking.

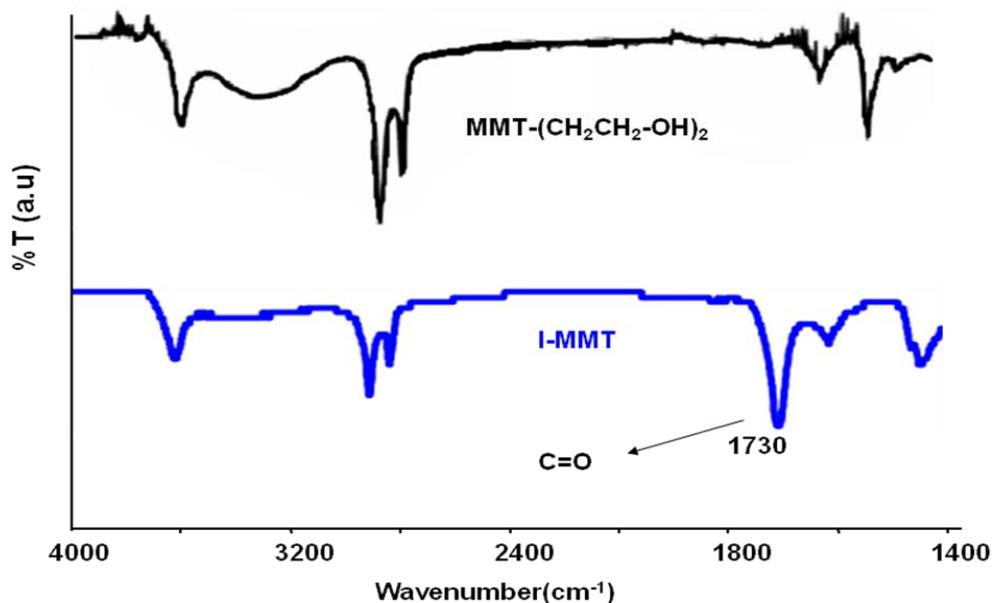


**Figure 4.7 :** DSC results of the precursor oligomer (PSU-2000) (a), and macromonomer, PSU-DA-2000 before (b), and after curing (PSU-DA-2000 cross) (c).

## 4.2 Polysulfone/Clay Nanocomposites by in situ Photoinduced Crosslinking Polymerization

### 4.2.1 Modification of MMT with methacryloyl chloride

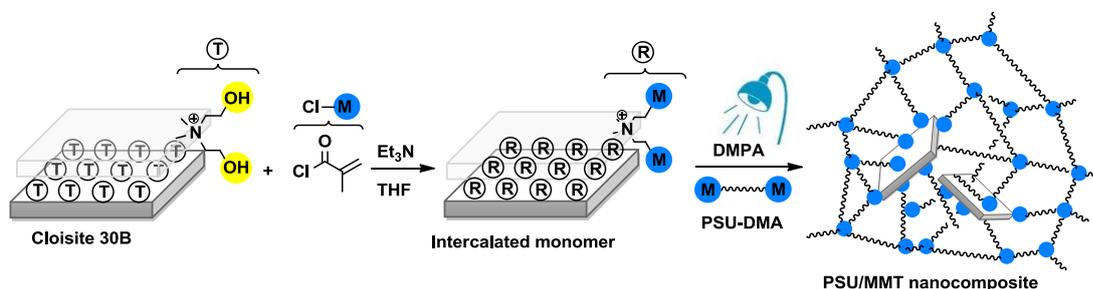
Intercalated methacrylate functionalized montmorillonite (I-MMT) clay was prepared from commercial montmorillonite clay containing two hydroxyl groups (Closite 30B) by using esterification reaction with methacryloyl chloride. The FT-IR spectrum of resulting MMT clay showed that a characteristic carbonyl peak at  $1730\text{ cm}^{-1}$  corresponding to (meth) acrylate moiety, whereas a broad peak at around  $3400\text{ cm}^{-1}$  indicates that small amount of nonfunctionalized hydroxy groups on the surface of the layers is still remained.



**Figure 4.8 :** FT-IR spectra of Cloisite 30B and I-MMT.

#### 4.2.2 Preparation of the PSU/MMT nanocomposites and characterization

Polysulfone/montmorillonite (PSU/MMT) nanocomposites were prepared by *in situ* photoinitiated crosslinking polymerization of I-MMT and PSU-DMA monomers. Photochemically generated radicals can allow polymer molecules to grow inside the clay galleries upon irradiation and consequently form covalent bonds between organic and inorganic phases. Attachment of monomeric sites into clay layers and subsequent photoinduced crosslinking of immersed monomers with PSU-DMA macromonomers facilitate propagation and exfoliation processes concomitantly, leading to the formation of homogeneous clay-polymer nanocomposites (N1, N3 and N5) (Figure 4.9).



**Figure 4.9 :** Preparation of polysulfone/montmorillonite clay nanocomposites by *in situ* photoinitiated crosslinking polymerization.

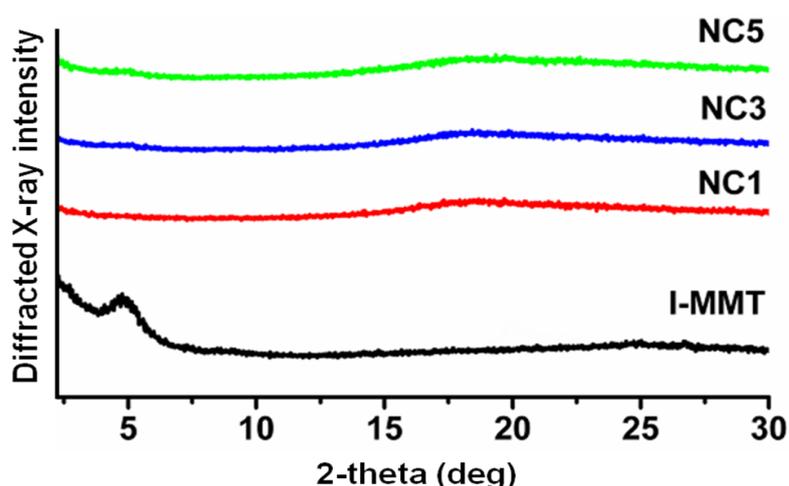
The characteristic data for I-MMT, PSU-DMA and PSU/MMT nanocomposites synthesized with different clay loadings were given in Table 4.2.

**Table 4.2 :** Photoinitiated crosslinking polymerization of PSU-DMA in the presence and absence of organomodified I-MMT, and thermal properties of neat PSU, I-MMT and resulting nanocomposites.

Samples	MMT Conv. <sup>b)</sup>		$d_{001}$ <sup>c)</sup>	$T_g$ <sup>d)</sup>	Weight loss temperature <sup>e)</sup>		Char yield <sup>e)</sup>
	(wt%)	(%)			(°C)	(°C)	
I-MMT	-	80	1.8	-	726.3	-	78.6
PSU-DMA <sup>a)</sup>	-	67	-	136.7	456.1	526.2	21.2
NC1 <sup>a)</sup>	1	81	-	146.3	467.1	530.1	24.1
NC3 <sup>a)</sup>	3	85	-	144.4	484.0	536.9	30.0
NC5 <sup>a)</sup>	5	75	-	143.1	497.1	551.3	34.1

<sup>a)</sup>[Photoinitiator] : 1 % of the monomer by weight; <sup>b)</sup>determined gravimetrically; <sup>c)</sup>basal spacing ( $d_{001}$ ) is calculated by XRD analysis; <sup>d)</sup>determined by DSC analysis; <sup>e)</sup>determined by TGA analysis.

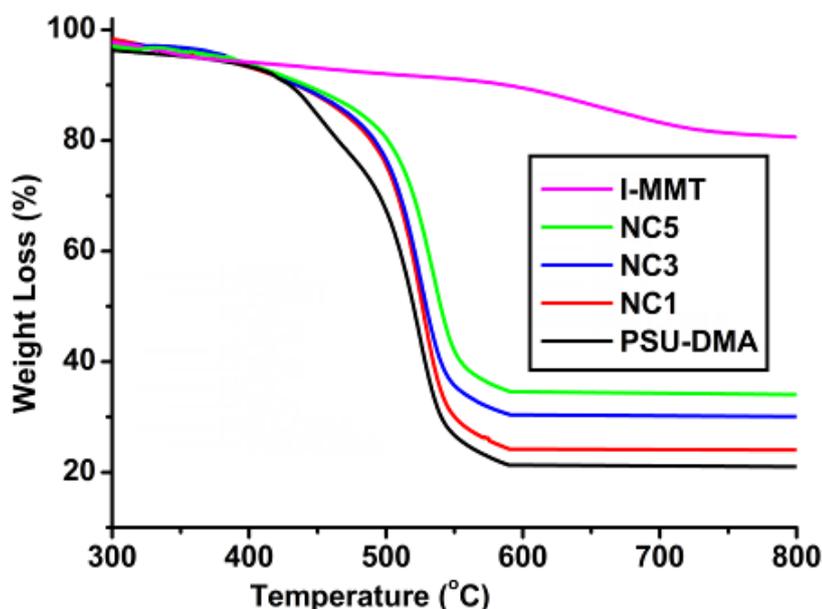
XRD curves of the intercalated MMT and polysulfone nanocomposites are illustrated in Figure 4.9. According to the XRD diffraction pattern, changes in the value of  $2\theta$  reflect changes in the gallery distance of the clay. The organo-modified clay sample exhibits a peak at  $4.95^\circ$ , which corresponds to a basal space ( $d_{001}$ ) of 1.78 nm. As can be seen in Figure 1, after the polymerization, it is completely disappeared in all nanocomposite samples. Although, these results indicate that the silicate layers are likely to be exfoliated in the matrix, XRD measurements alone are not conclusive for determining the true structures and distributions of the silica platelets; thus, we turned our attention to by transmission electronic microscopy (TEM) measurements.



**Figure 4.10 :** X-ray diffractions of organo-modified clay I-MMT, NC1, NC3 and NC5 nanocomposites.

TGA thermograms of neat PSU-DMA and its nanocomposites are shown in Figure 4.10. It is quite obvious that the decomposition temperatures of the nanocomposites

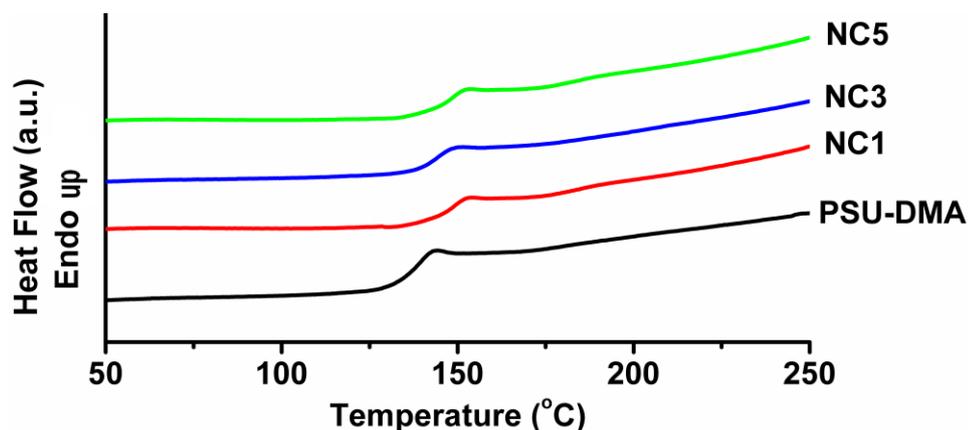
are higher than the neat oligomer. Notably, the final char yield of nanocomposites is increased with increasing organo-clay concentrations. Approximate decomposition temperatures of neat PSU-DMA and NC1, NC3 and NC5 were 485, 494, 496 and 504 °C, respectively. In the nanocomposites, the enhancement in the thermal stability could be explained by the barrier properties attributed to the clay mineral layers which hampered the diffusion of oxygen molecules into the nanocomposites and also the diffusion of the combustion products outside the system. The same trend was also observed by previous studies, which were prepared the PSU/MMT nanocomposites via solution exfoliation method [279].



**Figure 4.11 :** TGA thermograms of neat PSU-DMA, organo-modified clay I-MMT, NC1, NC3 and NC5 nanocomposites.

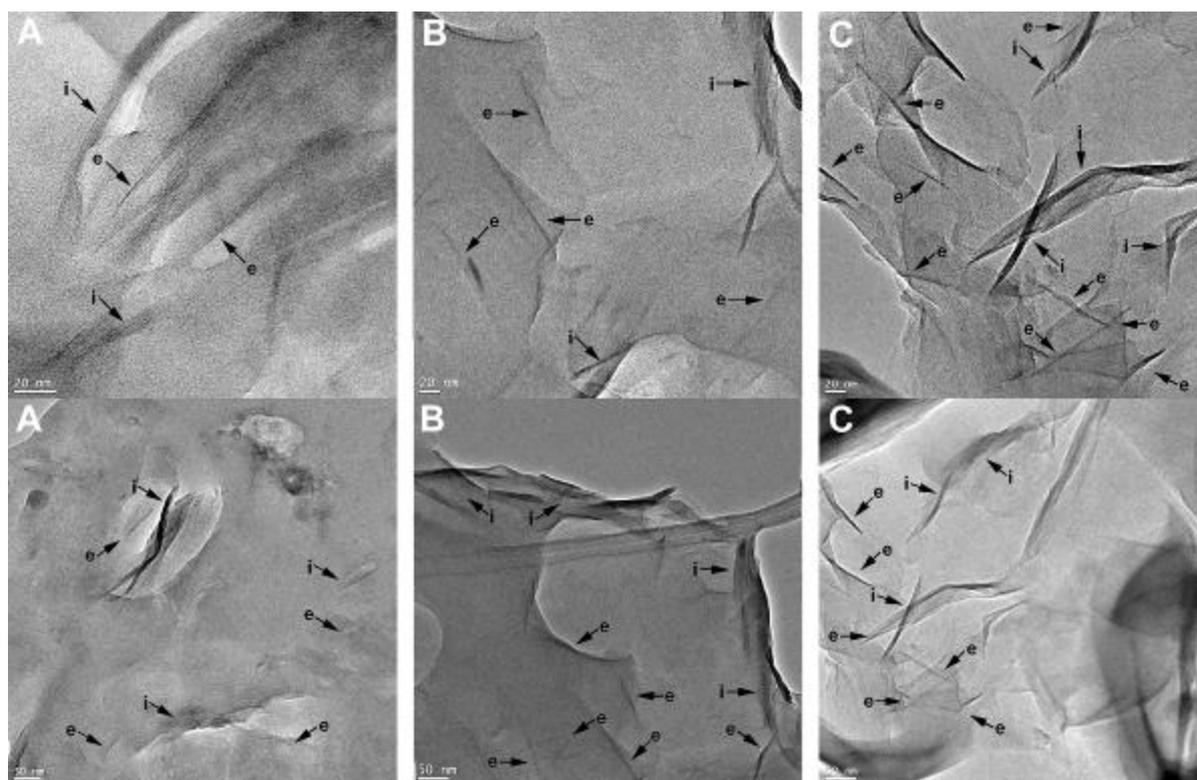
DSC traces of neat PSU-DMA and corresponding nanocomposites are shown in Figure 4.11. The  $T_g$  of polymers depends mainly on the molecular structure of the polymer (chain stiffness, number, and bulkiness of the side groups, and the inter- and intra-molecular interactions) and on the crosslink density of the polymer [280]. All the nanocomposites show a higher  $T_g$  value compared to pure polysulfone. The highest increment in  $T_g$  of NC1 nanocomposite can be ascribed to its exfoliation morphology with fine dispersion of silicate layers in the polymer matrix that provides large surface area for clay interacting with polymer matrix which can be lead to the restricted segmental motions near the organic-inorganic interfaces [45,

46]. Conclusively, with the increase of the clay content to PSU chains, leading to a slight decrease of  $T_g$ .



**Figure 4.12 :** DSC traces of neat PSU-DMA, NC1, NC3 and NC5 nanocomposites.

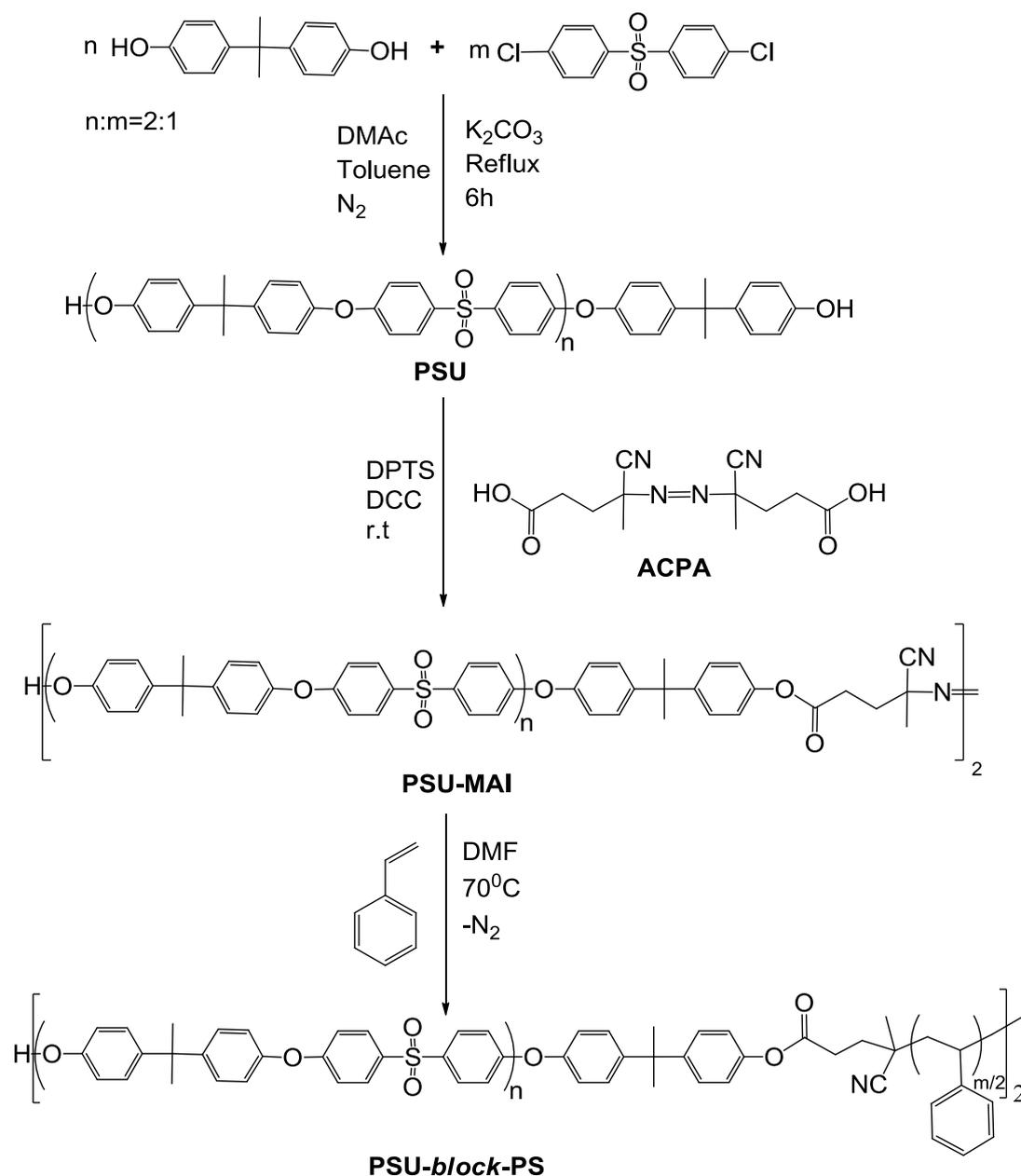
A direct evidence for the nanocomposite formation is obtained TEM observation with two different magnification scales as displayed in Figure 4.12. for NC1, NC3 and NC5 samples. In the powdery PSU/MMT nanocomposites, the dark line represents individual silicate layers, whereas the brighter area represents the PSU matrix. In the both magnifications, TEM analysis indicates that all nanocomposites have a mixed morphology. The observed individual clay layers (highlighted by black arrows (e)) are well dispersed (delaminated) in the polymer matrix. In addition, large intercalated tactoids (highlighted by black arrows (i)) can also be visible in the all samples. The small stacks of intercalated structure may be described as the incomplete activation of intercalated MMT monomer in the polymerization due to the high loading degree or limited mobility of PSU macromonomer within the layers. TEM analysis also confirms that the concentration of clay in the nanocomposites increased with increasing clay loading in the process (Figure 4.12.).



**Figure 4.13 :** TEM micrographs of PSU/MMT nanocomposites (A, NC1), (B, NC3) and (C, NC5) in high (scale bar: 20 nm, upper images) and low magnification (scale bar: 50 nm).

### 4.3 Novel Polysulfone Macroazoinitiator to Prepare Polysulfone-*b*-Polystyrene Block Copolymers

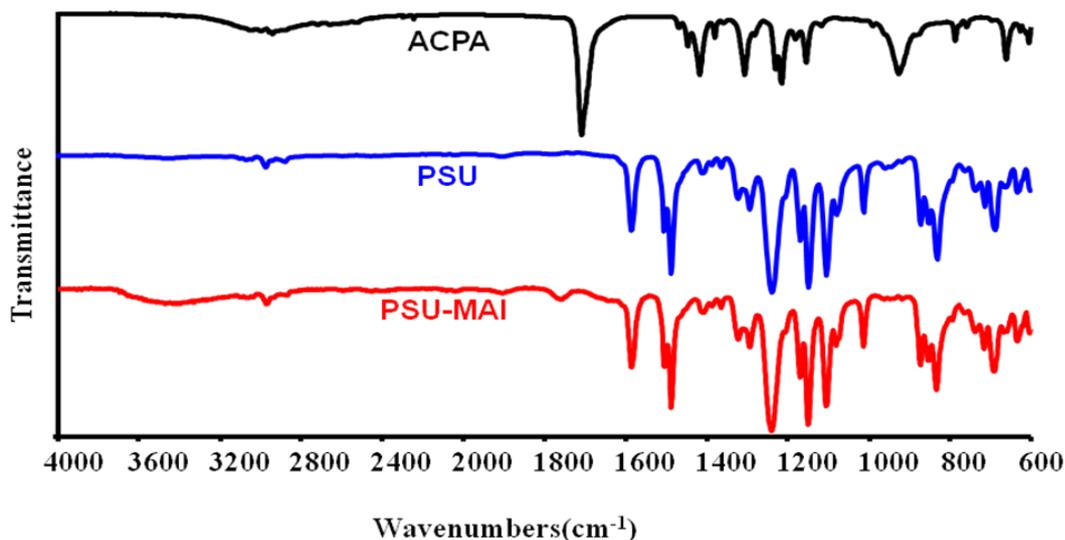
The overall procedure involving the synthesis of  $\alpha,\omega$ -dihydroxyl polysulfone (HO-PSU-OH), polysulfone macroazoinitiator (PSU-MAI) and block copolymer is shown in Figure 4.13. Characterization of the synthesized PSU-MAI and block copolymers were carried out with FTIR-ATR,  $^1\text{H-NMR}$ , and GPC.



**Figure 4.14** : Synthesis of PSU, PSU-MAI and PSU-*block*-PS copolymer.

### 4.3.1 Preparation of PSU-MAI macroazoinitiator and its characterization

PSU-MAI was synthesized by condensation reaction of carboxylic groups of 4,4'-azobis(4-cyanopentanoic acid) (ACPA) with hydroxyl moieties of the PSU at room temperature in the presence of a condensing agent, DPTS. FTIR spectrum of PSU with hydroxyl end groups shows the characteristic bands for polyether sulfone backbone as shown in Figure 4.14.

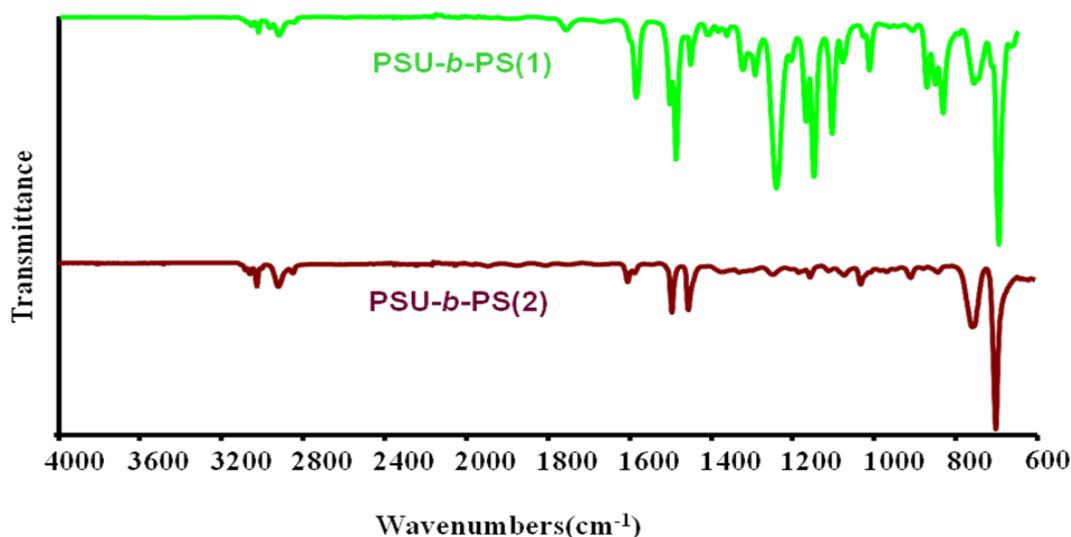


**Figure 4.15 :** FT-IR spectra of ACPA, PSU and PSU-MAI.

The broad but weak peak around  $3435\text{ cm}^{-1}$  indicates the presence of phenolic end groups. In the IR spectrum of PSU-MAI, the disappearance of the acidic carbonyl band at  $1710\text{ cm}^{-1}$  showing the absence of the ACPA and emergence of new ester carbonyl peak at around  $1751\text{ cm}^{-1}$  proves the formation of ester linkage.

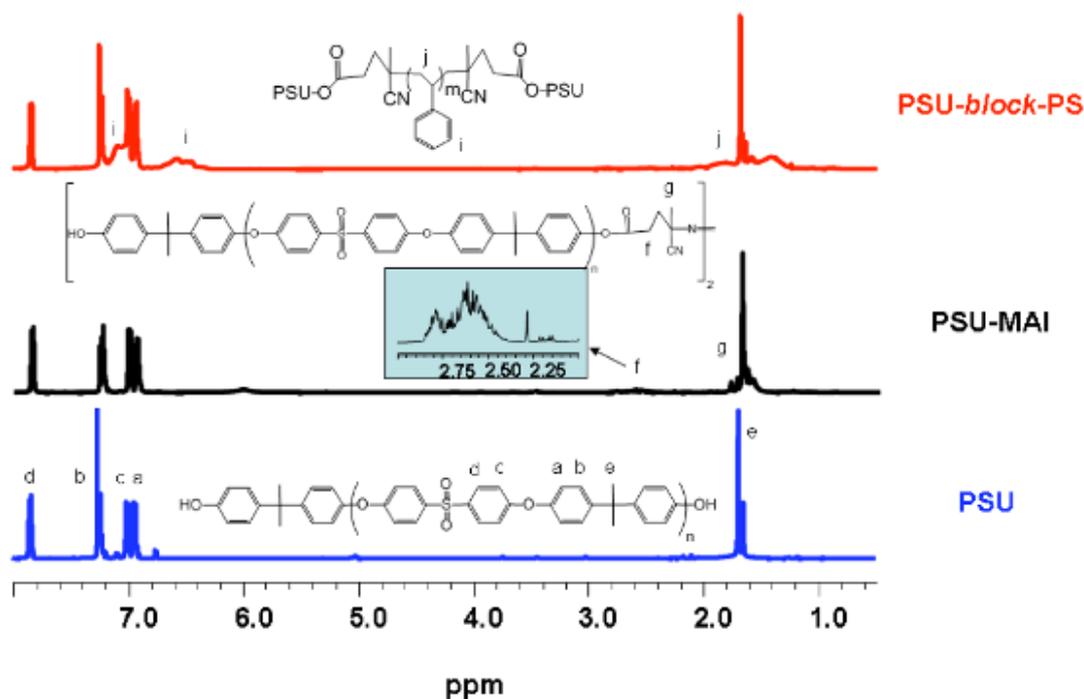
#### 4.3.2 Preparation of PSU-PS block copolymers

Block copolymerizations were achieved by radical polymerization of styrene initiated from the radicals formed through the scission of the azo units. In the spectra of block copolymers as shown in Figure 4.15., the aromatic ring vibrations observed at around  $3081$ ,  $3056$ , and  $1601\text{ cm}^{-1}$  and the aliphatic backbone of the polystyrene at  $1452\text{ cm}^{-1}$  indicate the addition of the styrene monomers into the polysulfone backbone. The change of the polystyrene content in the block copolymers of PSU-*b*-PS may easily be followed by comparison of the peaks  $1584\text{ cm}^{-1}$  (corresponding to polysulfone) and  $1452\text{ cm}^{-1}$  (corresponding to polystyrene).



**Figure 4.16 :** FT-IR spectra of PSU-*block*-PS copolymers, (1) and (2).

The structures of the MAI and block copolymers were further confirmed by  $^1\text{H-NMR}$  analysis. As can be seen from Figure 4.16. where the  $^1\text{H-NMR}$  spectra of the precursor PSU oligomer, the macroazoinitiator (PSU-MAI) and the block copolymer are presented, peaks corresponding to the methyl group of bisphenol A and aromatic protons of the poly(ether sulfone) backbone appears in all spectra at 1.69; 6.70 and 7.86 ppm, respectively.. The chemical shift of phenolic proton was detected at around 5.02 ppm with a relatively small intensity due to the relatively high molecular weight of the precursor polymers. Successful MAI formation was confirmed by appearance of the new peaks at around 2.30-2.75 ppm and an increase in intensity of the peak around 1.65 ppm due to ethylene and methyl protons from ACPA moieties, respectively. The ratio of peak area due to the aromatic hydrogens adjacent to the sulfoxide group to ethylene peak area of ACPA (4:1) indicates that the polysulfones bounded to the two sides of an ACPA molecule. The presence of polystyrene block in the copolymers is evidenced by the presence of aromatic peaks between 6.5-7.1 ppm and aliphatic  $-\text{CH}_2-$  at around 1.6-2.0 ppm.



**Figure 4.17 :**  $^1\text{H}$  NMR spectra of ACPA, PSU-MAI and PSU-*block*-PS copolymer.

Molecular weight characteristics of the MAI and the block copolymers with respect to copolymerization conditions are presented in Table 4.3. As can be seen from the GPC chromatogram of the PSU-MAI, molecular weight of the precursor PSU oligomer was doubled after a successful esterification reaction. This may be due to formation of PSU-MAI ( $M_n=3746$  g/mol) by attachment of two PSU chains ( $M_n=1811$  g/mol) to both sides of an ACPA molecule. Homolytical cleavage of azoinitiators and generation of carbon-centered free radicals upon heating to  $70^\circ\text{C}$  is well-known process and have been employed in synthesis of block copolymers [281]. The molecular weights of the copolymers ranging from 3800 to 20000 g/mol were observed after block copolymerization, in which PSU-MAI was heated at  $70^\circ\text{C}$  in the presence of styrene under various reaction conditions. In the process addition of styrene monomers onto these macro-radicals yields the copolymer as in the form of AB or ABA-type block copolymers, since polystyryl radicals mainly prefer recombination type of termination process, thus a greater proportion of ABA is expected [282].

As expected, lower amount of PSU-MAI used in the formulations gave rise block copolymers with higher molecular weight but lower level of conversion (Table 4.3, Run 1 and 2). This means decrease in amount of the macroinitiator obviously resulted in formation of longer styrene segments in the block copolymer but less

number of polymer chains. These results perfectly correlate with the FTIR spectra. Longer polymerization time also caused increase in molecular weight of resulted block copolymers and thus styrene content (Run 1 and 2). Higher concentrations of PSU-MAI give rise higher amount of macro-radicals leading to higher conversion values and thus lower molecular weights (Run 3 and 4).

**Table 4.3 :** Block copolymerization of styrene with PSU-MAI at 70 °C in 2 ml DMF under N<sub>2</sub> atmosphere.

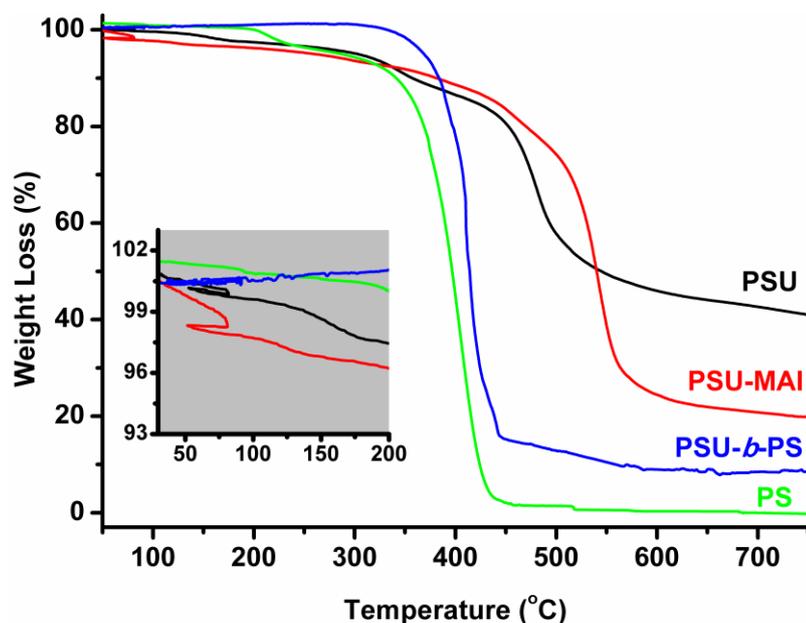
Run No.	PSU-MAI Conc. (mol/L)	Reaction Time (h)	Conv. <sup>a</sup> (wt.%)	$M_n^b$ (g/mol)	$M_w/M_n^c$
1	$9.15 \times 10^{-4}$	24	12.8	13310	3.07
2	$9.15 \times 10^{-4}$	48	15.4	19360	2.96
3	$4.57 \times 10^{-3}$	24	41.9	9090	3.31
4 <sup>d</sup>	$7.65 \times 10^{-2}$	24	70.0	3860	2.75

<sup>a</sup> Determined gravimetrically.

<sup>b,c</sup> Number average molecular weights as determined from GPC measurements based on polystyrene standards.

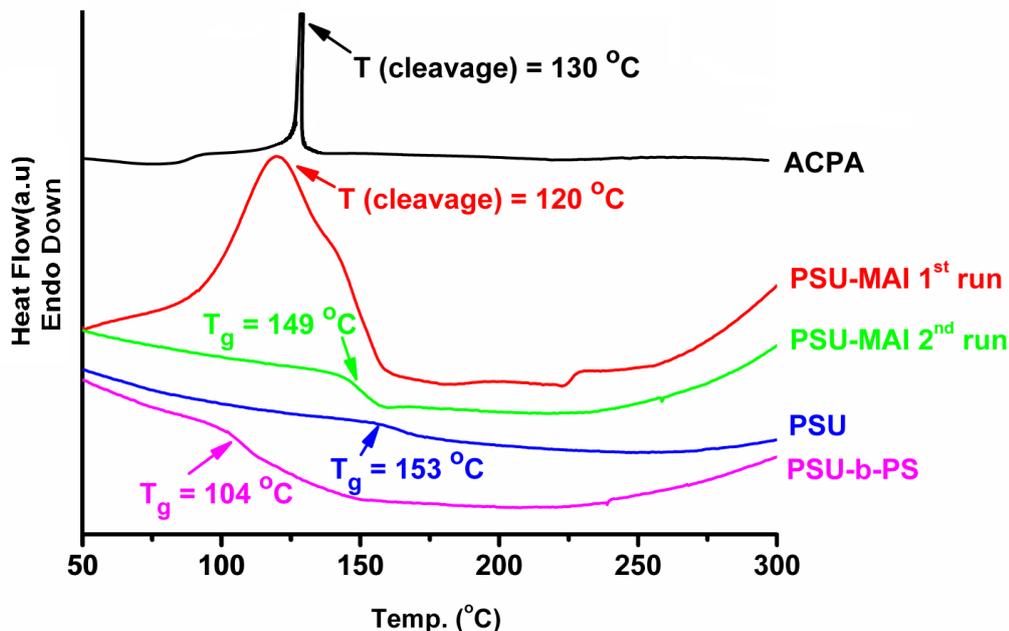
<sup>d</sup> 0.5 ml DMF used instead of 2 ml.

TGA thermograms of PSU oligomer, PSU-MAI and PSU-*b*-PS block copolymer are shown in Figure 4.17. The thermograms involve preheating cycle in which the samples were heated up to 100 °C, allowed to stay at this temperature for 10 minutes and then cooled down to ambient temperature followed by heating to 900 °C. As a result of preheating only PSU-MAI lost a little weight due to the decomposition of the diazo moiety and, in turn, release of N<sub>2</sub> at around 70 °C. The char yield increases with the increase in the amount of polysulfones. At high temperatures PSU-MAI shows greater stability towards the precursor PSU oligomer. This may be due to recombination of PSU radicals to form higher molecular weight oligomer that results higher thermal stability. By the addition of the polystyrene units to polysulfones, the thermal stability and char yield of block copolymers were dramatically decreased.



**Figure 4.18 :** TGA thermograms of the precursor oligomer (PSU), polystyrene (PS), macroazoinitiator (PSU-MAI), and block copolymer (PSU-*b*-PS).

The DSC analysis of the initial diazo compound and the prepared polymers are presented in Figure 4.18. In the first run thermogram of PSU-MAI, the PSU-MAI macroazoinitiator shows a broad exothermic peak centered at 120 °C due to scission of the diazo moiety. This behavior is consistent with the thermogram of ACPA, in which a sharp exotherm, attributed to thermal decomposition of diazo group again, was observed at 130 °C. The glass transition temperature ( $T_g$ ) of the polymers are in good agreement with literature and each polymer segment displayed its characteristic  $T_g$  value.



**Figure 4.19** : DSC results of ACPA, the precursor oligomer (PSU), macroazoinitiator (PSU-MAI), and copolymer (PSU-*b*-PS).

For further confirmation of expected structure and the mechanism, an acid hydrolysis of PSU-*b*-PS block copolymer (Mn: 9,090 g/mol) using TFA was performed and molecular weights of the resulted polymers were measured. After hydrolysis, the block copolymer was degraded into two main segments with molecular weights of 1,420 and 6,500 g/mol corresponding to those of the precursor segments. This result shows expected block copolymers were obtained by this simple block copolymerization approach with little effort.



## 5. CONCLUSIONS AND RECOMMENDATIONS

As a conclusion, functional phenol-ended polysulfone telechelics with low and high molecular weights have been prepared simultaneously by condensation reaction of bisphenol-A and bis (p-chlorophenyl) sulfone with different ratios in the presence of potassium carbonate. After that the obtained telechelics have been modified with acrylate or (meth) acrylate groups in order to be used as polymeric precursors for preparation of cross linkable networks. The effects of the molecular weight of the PSU precursor and type of functionality on the rate of polymerization and conversion were evaluated. The thermal stability of the photochemically cross-linked polymers indicates that these oligomers may be important components of UV curable formulations for obtaining networks that could have application in coatings and membranes. Thus we thought the use of these telechelics for the formation of polysulfone based nano composites with improved properties.

In the second part of the study, a new class of photo cross linkable oligomers consisting of polysulfone structure as backbone with methacrylate functional groups connected to both ends has been successfully applied for the preparation of polysulfone/clay nanocomposites. Polysulfone/montmorillonite (PSU/MMT) nanocomposites are prepared successfully dispersing the inorganic nanolayers of MMT clay in an organic PSU matrix via *in situ* photoinduced crosslinking polymerization. Thermogravimetric analysis results confirms that the thermal stability and char yield of PSU/MMT nanocomposites increases with the increase of clay loading. Exfoliation/intercalation structures were found to be related to the loading degree and limited mobility of macromonomer. DSC and TGA analyses showed that the all nanocomposites have higher Tg value and thermal stabilities relative to that of the neat PSU. Polymerization through the interlayer galleries of the clay was achieved by crosslinking of methacrylate functionalized MMT clay and PSU-DMA macromonomer. The random dispersion of silicate layers in the PSU matrix was confirmed by XRD and TEM measurements. Exfoliation/intercalation

structures were found to be related to the loading degree and limited mobility of macromonomer.

Finally, a macroazoinitiator (MAI) having polysulfone (PSU) units was synthesized from 4,4'-azobis(4-cyanopentanoic acid) (ACPA) and PSU oligomer by direct esterification process at ambient conditions. It was used for the preparation of block copolymers by conventional free radical polymerization method. The block copolymers were achieved by free-radicals generated from the cleavage of the azo group from macroazoinitiator in the presence of styrene monomer in dimethylformamide (DMF) solution by heating. The polysulfone macroazoinitiator (PSU-MAI) and polysulfone-*b*-polystyrene block copolymers were characterized by spectral analysis using FT-IR, <sup>1</sup>H-NMR, GPC, TGA and DSC. By the synthetic procedure described in this work, it has been possible to obtain block copolymers composed of PSU and vinyl blocks. The approach clearly demonstrates the convenience and applicability of PSU end-capping for the synthesis of polymers having appropriate functionality for a subsequent vinyl polymerization. While the chain length of PSU is deliberately kept low so as to achieve efficient functionalization, the molecular weight of the polystyrene block can be adjusted by the polymerization time, concentrations of macroinitiator and monomer.

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## CURRICULUM VITAE



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### List of Publications and Patents:

- **Dizman, C., Kahveci M.U., Yagci, Y.** (2013). Synthesis of Polysulfone-*b*-Polystyrene Block Copolymers by Mechanistic Transformation from Condensation Polymerization to Free Radical Polymerization, *Polymer Bulletin*. Submitted.
- **Dizman, C., Uyar, T., Tasdelen, M. A., and Yagci, Y.** (2012). Synthesis and Characterization of Polysulfone/POSS Hybrid Networks by Photoinduced Crosslinking Polymerization, *Macromolecular Materials and Engineering*, doi: 10.1002/mame.201200351.
- **Dizman, C., Ates, S., Uyar, T., Tasdelen, M.A., Torun, L., Yagci, Y.** (2011). Polysulfone/Clay Nanocomposites by in situ Photoinduced Crosslinking Polymerization. *Macromolecular Materials and Engineering*, 296, 1101-1106.
- **Sangermano, M., Roppolo, I., Camara, V.H.A., Dizman, C., Ates, S., Torun, L., Yagci, Y.** (2011). Polysulfone/Metal Nanocomposites by Simultaneous Photoinduced Crosslinking and Redox Reaction. *Macromolecular Materials and Engineering*, 296, 820-825.

- **Dizman, C., Demirkol, D.O., Ates, S., Torun, L., Sakarya, S., Timur, S., Yagci, Y.** (2011). Photochemically prepared polysulfone/poly(ethylene glycol) amphiphilic networks and their biomolecule adsorption properties. *Colloids and Surfaces B: Biointerfaces*, 88, 265-270.
- **Ates, S., Dizman, C., Aydogan, B., Kiskan, B., Torun, L., Yagci, Y.** (2011), Synthesis, characterization and thermally activated curing of polysulfones with benzoxazine end groups. *Polymer*, 52, 1504-1509.
- **Dizman, C., Ates, S., Torun, L., Yagci, Y.** 2010, Synthesis, characterization and photoinduced curing of polysulfones with (meth)acrylate functionalities. *Beilstein Journal of Organic Chemistry*, No: 56.
- **Metin Tulu \*, Mehmet Senel, Naz M. Aghatabay, Tezcan Parali, Cemil Dizman, Basaran Dulger,** "Synthesis, characterization and antimicrobial activity of water soluble dendritic macromolecules ", *European Journal of Medicinal Chemistry*, Jun. 2008

#### PUBLICATIONS/PRESENTATIONS ON THE THESIS

- **Dizman, C., Kahveci M.U., Yagci, Y.** (2013). Synthesis of Polysulfone-*b*-Polystyrene Block Copolymers by Mechanistic Transformation from Condensation Polymerization to Free Radical Polymerization, *Polymer Bulletin*. Submitted.
- **Dizman, C., Ates, S., Uyar, T., Tasdelen, M.A., Torun, L., Yagci, Y.** (2011). Polysulfone/Clay Nanocomposites by in situ Photoinduced Crosslinking Polymerization. *Macromolecular Materials and Engineering*, 296, 1101-1106.
- **Dizman, C., Ates, S., Torun, L., Yagci, Y.** 2010, Synthesis, characterization and photoinduced curing of polysulfones with (meth) acrylate functionalities. *Beilstein Journal of Organic Chemistry*, No: 56.