SYNTHESIS AND CHARACTERIZATION OF NEW POLYMERIC MATERIALS FROM ELEMENTAL SULFUR

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AT

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MAY 2015

Approval of the Graduate School of Natural and Applied Sciences, Atilim University

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Prof. Dr. Ibrahim K. Akman

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

_____

Prof. Dr. Atilla Cihaner

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This is to certify that we have read the thesis "Synthesis and Characterization of New Polymeric Materials From Elemental Sulfur" submitted by "MOHAMED KHALIFA SALMAN" and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF NEW POLYMERIC MATERIALS FROM ELEMENTAL SULFUR

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M.S., Chemical Engineering and Applied Chemistry

Supervisor: Prof. Dr. Atilla Cihaner

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New elemental sulfur based polymeric materials called poly(sulfur-*random*-divinylbenzene) (poly(S-*r*-DVB)) were synthesized by ring opening polymerization in the presence of a mixture of o-, m- and p-diviniylbenzene (DVB) as a crosslinker. In order to get the copolymers, the elemental sulfur was melted at 160 ^{o}C and therefore ring-opening polymerization of the S_8 was promoted and a clear yellow/orange colored liquid was obtained. Then, various amounts of DVB were added to this liquid directly via a syringe and continued to further mixing at 200 ^{o}C for 10 minutes to get viscous reddish brown polymeric materials. The copolymers are soluble in common solvents like tetrahydrofuran, dichloromethane and chloroform, and they can be coated on any surface as thin film. The characterization of the materials were performed by using nuclear magnetic resonance, fourier transform infrared and Raman spectroscopies. The morphological properties were monitored via scanning electron microscope technique. Thermal analysis showed that an increase in the amount of DVB in the copolymers resulted in an increase in the termal decomposition temperature.

On the other hand, poly(S-*r*-DVB) copolymers exhibited good percent transmittance as 50 %T between 1500 and 13000 nm in electromagnetic radiation spectrum, which make them good candidates to be amenable use in military and surveillance cameras.

Keywords: Inverse vulcanization, IR-transmittance materials, IR cameras, elemental sulfur, divinylbenzene.

ÖZ

ELEMENTEL KÜKÜRTTEN YENİ POLİMERİK MALZEMELERİN SENTEZİ VE KARAKTERİZASYONU

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Tez Yöneticisi: Prof. Dr. Atilla Cihaner

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Çapraz bağlayıcı olarak kullanılan o-, m- ve p-divinilbenzen (DVB) karışımı varlığında halk açılma polimerizasyonu ile poli(kükürt-düzensiz-divinilbenzen) (poli(S-*r*-DVB) olarak adlandırılan yeni elementel kükürt esaslı polimerik malzemeler hazırlanmıştır. Kopolimerleri elde etmek için, elementel kükürt 160 ^{o}C'de eritilmiş ve böylece halka açılması tepkimesi başlatılarak berrak sarı/turuncu renkli bir sıvı elde edilmiştir. Daha sonra, farklı miktarlarda DVB bir şırınga yardımı ile bu sıvıya eklenmiş ve 200 ^{o}C'de devamlı karıştırılarak yoğun kırmızımsı kahverengi polimerik malzemeler elde edilmiştir. Kopolimerler tetrahidrofuran, diklorometan ve kloroform gibi yaygın çözücülerde çözünür olup herhangi bir yüzeye ince film olarak kaplanabilmektedirler. Malzemelerin karakterizasyonu nükleer magnetik rezonans, forier kızılötesi ve Raman spektroskopileri ile yapılmıştır. Morfolojik özellikler taramalı elektron mikroskobu ile görüntülenmiştir. Termal analizler, kopolimer içerisindeki DVB miktar artışının bozunma sıcaklığının artmasına sebep olduğunu göstermiştir.

Diğer bir taraftan, poli(S-*r*-DVB) kopolimerleri elektromanyetik radyasyon spektrumunda 1500 and 13000 nm aralığında % 50 gibi iyi bir geçirgenlik yüzdesi göstermiştir. Bu özellik malzemeleri askeri amaçlı kameralar ve gözetleme kameraları için iyi birer aday yapmıştır.

Anahtar Kelimeler: Ters vulkanizasyon, IR geçirgen malzemeler, IR kameralar, Elementel kükürt, divinilbenzen.

TO MY PARENT

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LIST OF ABBREVIATIONS

Au^{I}	-	Gold(I)
AuNPs	-	Gold Nanoparticales
$ClAu^{I}CO$	-	Gold(I) chlorocarbonyl
$ClAu^{I}PPh^{3}$	-	Gold(I) triphenylphosphine chloride
CS_2	-	Carbon disulfide
DCM	-	Dichloromethane
DCS	-	Differential Scanning Calrimetry
DIB	-	Diisopropenylbenzene
DMF	-	Dimetylformamide
DMSO	-	Dimetylsulfoxide
DVB	-	Divinyl benzene
FTIR	-	Fourier Transform Infrared
GPC	-	Gel Permeation Chromatography
HER	-	Hydrogen Evolution Reaction
HRIP	-	High Refractive Index Polymers
Li-S batteries	-	Lithium Sulsur batteries
Mn	-	Number average molecular weight
Mw	-	Weight average molecular weight
n	-	Referactive index
NaCl	-	Sodium Chloride
NMR	-	Nuclear Magnetic Resonance

PC	-	Propylene Carbonate
PDI	-	Polydispersity Index
PDVB	-	Polydivinyl benzene
Poly(S-r-DIB)	-	Poly(Sulfur-random-1,3-diisopropenylbenzene)
Poly(S-r-DVB)	-	Poly(Sulfur-random-Divinyl benzene)
ROP	-	Ring Opening Polymerization
S_8	-	Elemental Sulfur
SBR	-	Styrene-butadine rubber
SCE	-	Saturated Calomel reference Electrode
SEM	-	Scanning Electron Microscope
T_g	-	Glass transition temperature
T_m	-	Melting transition temperature
TGA	-	Thermal Gravimetric Analysis
THF	-	Tetrahydrofuran
1,2-DCB	-	1,2-dichlorobenzene

CHAPTER 1
INTRODUCTION

1.1 Sulfur

Sulfur is a chemical element with atomic number 16 and shown by symbol S in the periodic table. Within regular circumstances, sulfur atoms form cyclic octatomic molecules with a chemical formula S_8. At room temperature sulfur has a shiny yellow-colored crystalline with solid state (**Figure 1.1**). It acts chemically as either an oxidant or reducing agent. It oxidizes major of metals and a number of nonmetals like carbon, which cause to its negative charge in the majority of organosulfur substances, however it reduces various strong oxidants such as oxygen and fluorine. Additionally it is the least heavy element to quickly generate constant exclusions to the octet rule.

Naturally, sulfur can be discovered as the pure element or as sulfide and sulfate minerals. Being several in local type, sulfur was known in olden days, described for its uses in historical Greece, China and Egypt. Fumes of sulfur were used as fumigants, and sulfur-containing therapeutic mixes were used as balms and antiparasitics [1]. Sulfur was regarded essential enough to get its own alchemical symbol. It was required to create dark gunpowder, and the shiny yellow-colored powdered was hypothesized by alchemists to have some properties of gold, which they desired to synthesize from it. In 1777, Antoine Lavoisier assisted persuade the scientific community that sulfur was an element rather than a substance [2].

Elemental sulfur was once created from salt domes where it in some cases happens in nearly pure form, however this technique has become outdated since the delayed Twentieth century. Nowadays, nearly all of elemental sulfur is created as a by-product of eliminating sulfur-containing pollutants from organic gas and oil refineries.

Figure 1.1 Sulfur crystals, Khanegiran, Iran [10]

1.1.1 Allotropes of Sulfur

There are a huge number of allotropes of sulfur. The common forms identified in nature are:

- Yellow orthorhombic α-sulfur, it contains creased rings of S_8, with the best-known allotrope being octasulfur. Octasulfur is a sleek bright-yellow solid as shown in **Figure 1.2(a)** and it burns with a blue flame attendant with the creation of sulfur dioxide, strong with only a weak smell just like that of matches as shown in **Figure 1.2(b,c)**. It melts at 115.21 ^{o}C, boils at 444.6 ^{o}C and sublimes easily. It is insoluble in water and soluble in carbon disulfide. It is stable at room temperature and its specific gravity is 208 g/cm^3 [1].
- Monoclinic sulfur: It is the allotropic form of sulfur which is stable between 96 ^{o}C and 119 ^{o}C. It has a melting point at 119 ^{o}C and it is also soluble in carbon disulfide. It is one molecule consists of 8 atoms and it is found as pale yellow needle shaped crystals [1].

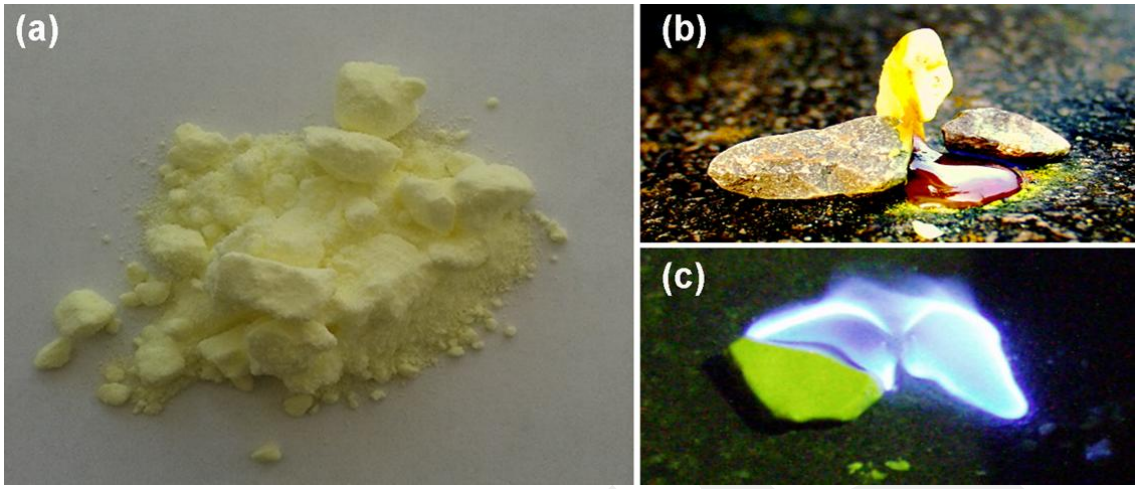


Figure 1.2 (a) bright-yellow solid sulfur (b) Red liquid of burned sulfur and (c) Produces a glowing blue fire which is best seen in the dark [10].

1.1.2 Production of Sulfur

Sulfur could be found by itself and traditionally acquired in this way, whilst pyrite has been a source of sulfur by means of sulfuric acid [3]. The Sicilian method was utilized in previous times to acquire sulfur from stones present in volcanic places of Sicily. Nowadays sulfur manufacturing is as a part item of other commercial procedures like oil refining; during these operations, sulfur usually happens as unwanted or damaging substances which are produced and transformed to elemental sulfur. As a nutrient, local sulfur within salt domes is considered to be a non-renewable nutrient source, created via activity of historical bacteria on sulfate remains. It had been eliminated from such salt-dome mines mainly by the Frasch method [4]. During this technique, superheated water was injected down into a local sulfur to burn the sulfur, after which compressed air came back the 99.5% genuine dissolved product to the outer lining area. All over the Last millennium this process created elemental sulfur without additional refinement. Nevertheless, because of a small variety of those sulfur remains and the heavy price of operation, this procedure for exploration sulfur will not be applied in a significant way everywhere on the world since 2002 [5,6].

Nowadays, sulfur is created from oil, natural gas and relevant non-renewable source, where it is acquired mostly as hydrogen sulfide. Organosulfur substances as

unwanted pollutants in oil could be eliminated by submitting them to hydrodesulphurization, which cleaves the C-S bonds [5, 6].

$$R\text{-}S\text{-}R + 2\,H_2 \rightarrow 2\,RH + H_2S$$

The obtained hydrogen sulfide from this method, as it happens in natural gas, is also turned into elemental sulfur by the Claus method. The method requires oxidation of some hydrogen sulfide to sulfur dioxide then the comproportionation of these two [5,6].

$$3O_2 + 2H_2S \rightarrow 2SO_2 + 2H_2O$$
$$SO_2 + 2H_2S \rightarrow 3S + 2H_2O$$

Due to the great sulfur material of the Athabasca Oil Sands, stockpiles of elemental sulfur from this method are available throughout Alberta, Canada **(Figure 1.3)** [7]. A different way of saving sulfur is as a binder for concrete, the producing products have a lot of suitable features [8]. The price of sulfur improved from 2007 to 2008, and reduced after that [9].

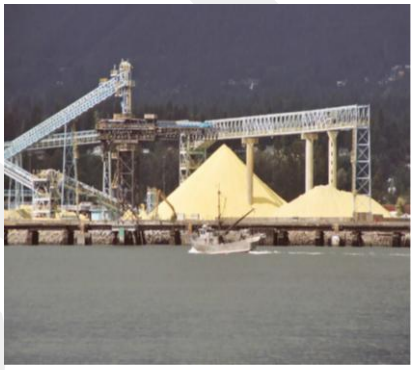


Figure 1.3 Stored sulfur retrieved from hydrocarbons in Alberta. [10].

1.1.3 Application Area of Sulfur

Elemental sulfur can be used in many of applications as a forerunner for some other substances. Nearly 85% (1989) is changed to sulfuric acid:

$$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4$$

Sulfur is progressively used as a part of manure. Probably the most essential from sulfur for manure is the mineral calcium sulfate. Important sulfur is hydrophobic (which is, does not dissolvable in water) and as a consequence, it cannot be straight used by vegetation. Eventually, ground bacteria can turn it to dissolvable types, which may then be used by vegetation.

Organosulfur substances are used in medication, dyestuffs, and agrochemicals, such as fungicide and pesticide, and tyre industry [10].

1.2 The Use of Elemental Sulfur as an Alternative Feedstock for Polymeric Material

The planning of novel polymers and nanocomposites straight from elemental sulfur provides an awesome new route in material makeup, components technology and chemical engineering to make novel components from a substitute content feedstock. Above 60 million tons a lot of important sulfur are developed yearly, almost all that are a by-product of the hydrodesulfurization method used to decrease sulfur dioxide pollutants through the dropping of non-renewable sources of power in oil refining. Most of elemental sulfur is used for manufacturing of sulfuric acidity and phosphates for position fertilizers. More compact niches for specialized chemicals, especially artificial rubberized (such as, tyres) via vulcanization process and beauty products, also utilize elemental sulfur straight [11]. Even so, these current techniques have a restricted requirement for sulfur, so massive excess of elemental sulfur nearly seven million tons is produced yearly. Hence, the actual variety of elemental sulfur provides a clear and strong inspiration to create impressive chemical makeup and processing techniques due to the usage as a new feedstock for features of new polymeric materials.

Even though it is known that sulfur provides a wide range of interesting features, that is great electrochemical capacities [12,13], as well as indices [14,15], manufactured and managing techniques to get prepared well-defined elements with great sulfur are very losing.

1.3 Polymerization of Elemental Sulfur

Elemental sulfur displays limited solubility in many organic solvents, with exemption of sparing in aromatic media, as well as carbon disulfide and a number of ionic liquids [16]. There are lengthy been regarded that under normal circumstances elemental sulfur prevails mainly by means of an eight-membered ring (S_8) that melts into an obvious yellow-colored liquid stage at 120-124 ^oC. Rings with 8-35 atoms are established and additional warming of the liquid sulfur stage higher than 159 ^oC outcomes in stability ring-opening polymerization (ROP) of the S_8 monomer into a straight line polysultane with diradical sequence finishes, that consequently polymerizes into polymeric sulfur of large molecular weight as shown in **Figure 1.4**. This diradical way of polymeric sulfur displays a deep-red color and depolymerizes back again to the monomeric ring types.

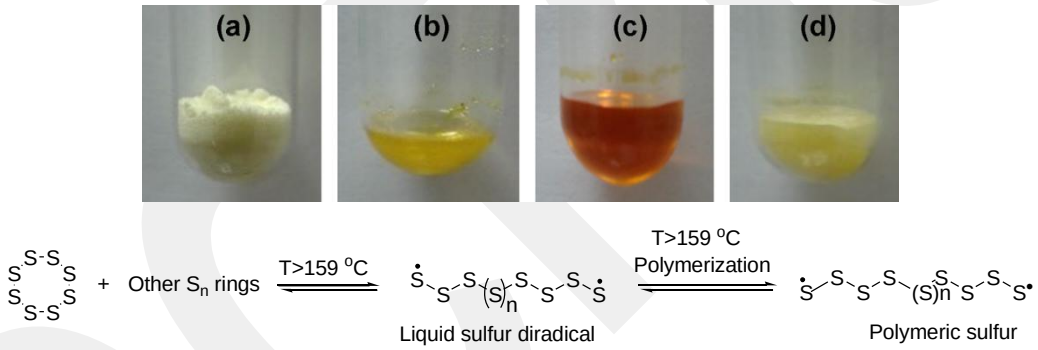
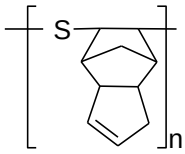


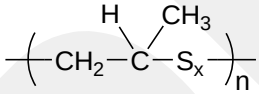
Figure 1.4 Thermal ROP of S_8 into polymeric sulfur diradical scheme. (a) molten of sulfur (b) sulfur diradical (c) polymeric sulfur (d) depolymerization.

1.3.1 Copolymers Containing Elemental Sulfur

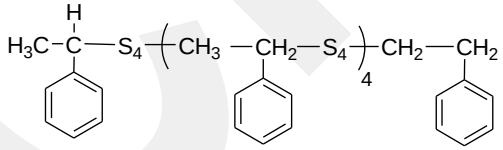
Polymeric sulfur produced by heat ROP forms a semicrystalline, intractable solid with inadequate technical qualities and is not responsive to melt or solution processing. Stabilizing of the diradical polymeric sulfur way with this content can be carried out by quenching of the radical chain ends via copolymerization with dienes, such as dicyclopentadiene, that chemical balances the polymer, however offers a weak crystalline material [11].



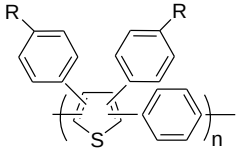
Copolymerization techniques are already researched to alter the properties of elemental sulfur by development into polymeric components. The seminal perform of Penczek and co-workers illustrate the capability to copolymerize S_8 anionically with propylene sulfide to get ready straight line polysulfide with about nine S-S bonds [17, 18].



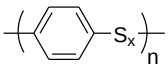
Stillo and co-workers analyzed the free radical copolymerization of S_8 with styrene, which provided mainly oligomeric products, unless divinyl monomers were used to stability the depolymerization process with crosslinking [19].



Tsuda and Takeda revealed the copolymerization of diynes with S_8 to form regiorandom polythiophenes [20].



More lately, Ding and Hay confirmed the copolymerization of cyclic disulfide with S_8, which provided intractable copolymers with improving sulfur nourish percentages [21].



Even though all of these reviews factor towards the prospective for sulfur usage, these components either have low level of sulfur content into the ultimate copolymer or form polymeric components with restricted processability and tenability of properties.

1.4 Structure and Properties of Polymer Sulfur

Furthermore, slowly quenching of sulfur vapour at room temperature results in flowers of sulfur which involve an assortment of rhombic, monoclinic and polymeric sulfur, where polymeric sulfur can be separated by CS_2-extraction of cyclooctasulfur. The professional item known as "Crystex", employed in rubberized industry, is usually known as supersublimation sulfur and connected for this type of sulfur [11, 22].

Each of the described types of polymeric sulfur are not stable at room temperature and gradually return to cyclooctasulfur, that is thermodynamically more constant in normal circumstances. This change from polymeric sulfur to cyclooctasulfur is known as reversion and is temperature-dependent based to the Arrhenius law. Consequently, at greater heat range the reversion is significantly multiplied.

The rubberized technologist differentiates amongst dissolvable and insoluble sulfur as the typical items typically managed as vulcanizing providers of rubberized substances. Dissolvable sulfur represents cyclooctasulfur or rhombic sulfur which is soluble in CS_2 and even in rubberized hydrocarbons like cis-polyisoprene, and styrene-butadiene copolymers. When cyclooctasulfur is integrated in a rubberized substance the combining heat range gets to 105 ^{o}C. At this heat range relatively considerable amounts of this sulfur are dissolvable in rubberized. The insolubility sulfur is usually used as the initial sign of its extremely high molecular weight. Getting insoluble in the rubberized hydrocarbon, insoluble sulfur is just allocated and therefore "suspended" in the rubberized substance. During cooling no flourishing is noticed even at relatively high amounts of sulfur, given that dumping temperature lastly will not surpass 105 ^{o}C to prevent reverse reactions.

1.4.1 FT-IR Study on Polymeric Sulfur

At greater temperature range (200 ^{o}C) band expanding is noticed and the essential unique band of cyclooctasulfur at 463 cm^{-1} disappears as shown in **Figure 1.5**; despite liquid sulfur at 200 ^{o}C includes a certain percentage of polymeric sulfur, its IR spectrum continues to be absolutely different from that of insoluble sulfur [23].

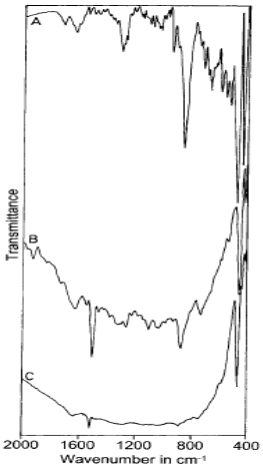


Figure 1.5 FT-IR spectra of (A) rhombic sulfur, (B) Insoluble polymeric sulfur, (C) Insoluble polymeric sulfur heated at 65 ^{o}C for 12 h [23].

1.4.2 Thermal Properties of Polymeric Sulfur

Differential scanning calorimetry (DSC) is another method that enables distinguishing rhombic sulfur type polymeric insoluble sulfur. The samples warmed at 5 ^{o}C min^{-1} and, as shown in **Figure 1.6(a)**, rhombic sulfur reveals an endothermic peak at 104 ^{o}C that as a result of the conversion from rhombic sulfur to monoclinic allotrope. The endothermic peak at 116 ^{o}C is the crystalline combination of monoclinic sulfur. At about 113 ^{o}C a quick warming amount is implemented in order that the rhombic type does not have a chance to be turned into the other allotrope.

With a heating ratio of 5 ^{o}C min^{-1}, insoluble polymeric sulfur reveals a wide endotherm which facts its thermoplastic and polymeric properties. As shown in **Figure 1.6(b)**, it is usually noticed that polymeric sulfur begins to make softer at about 90 ^{o}C. At 112 ^{o}C a small peak is noticed which might be as a result of the combination of cyclooctasulfur established by heat reversion. The combination peak is centred at 120 ^{o}C

followed by an exothermal rearrangement at 127 ^{o}C. From this information it indicates that DSC is an efficient technique that is capable to distinguish soluble sulfur from insoluble sulfur [23].

Past researchers have recommended that the T_g (glass transition temperature) of insoluble sulfur can be found at +75 ^{o}C, although that of plastic/elastic sulfur acquired by quenching melted sulfur at -78 ^{o}C can be found at -30 ^{o}C. They recommend that plastification of polymeric chains of sulfur by cyclooctasulfur decreases the T_g at -30 ^{o}C from the preliminary +75 ^{o}C. This speculation is affordable, even so, depending on X-ray it can be said that those variations in T_g might be as a result of various superstructures. Actually, which measured at -30 ^{o}C connected to fibrous sulfur while that measured at +75 ^{o}C is a part of laminar sulfur [23].

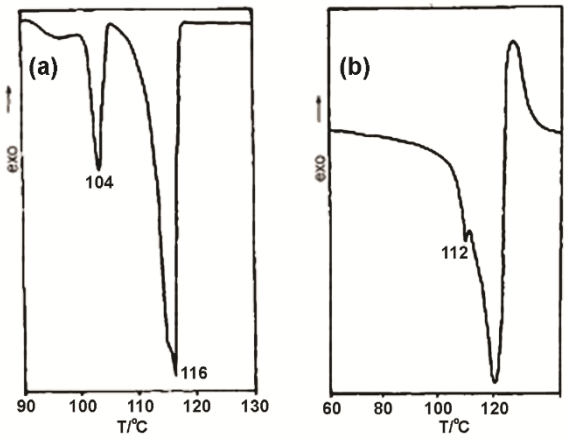
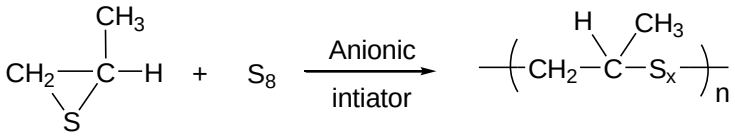


Figure 1.6 (a) DSC of rhombic and monoclinic sulfur (b) DSC of indissoluble polymeric sulfur [23].

1.5 Anionic Copolymerization of Elemental Sulfur with 2,2-Dimethylthiirane

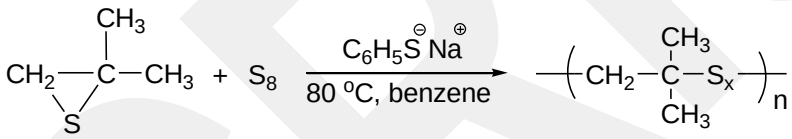
This method revealed on the anionic copolymerization of elemental sulfur (S_8) with 2-methylthiirane.



This reaction produce polysulfides with high molecular weight ($M_n > 10^4$), including about 85% of sulfur, mainly in polysulfide units. The polymerization was conducted less than floor temperature of the homopolymerization of S_8 [24].

The growth of actual copolymers with a statistical distribution of the polysulfide units was identified by ^1H and ^{13}C NMR studies [25], and more lately by laser Raman spectra, obviously displaying that in copolymers containing about 85% of sulfur no elemental sulfur is existing (the loss of bands at 217 cm^{-1} and at 475 cm^{-1} via sulfur) [25].

The growth of a copolymer from sulfur and 2,2-dimethylthiirane in an immediate anionic copolymerization. The copolymerization was started by sodium thiophenolate (cation crowned with dibenzo-18-crown-6) [25].



1.6 Vulcanization

Vulcanization is a chemical method which convert natural rubber or relevant polymers into more strong materials due to the sulfur addition [26] or other comparative curatives or accelerators. These preservatives change the polymer by developing cross-links (bridges) involving individual polymer chains [27, 28]. Vulcanized components are fewer difficult and possess outstanding mechanical properties.

1.6.1 Natural Rubber versus Vulcanized Rubber

Untreated natural rubber is difficult, deforms simply during heating, and is weak when cool. With this condition, it is a bad content if a high level of elasticity is needed. The purpose for inelastic deformation of un-vulcanized rubber is usually discovered in its substance structure rubber is made up of long polymer chains. The chains can shift individually comparative to one another, that allows the content modify form.

Crosslinking presented by vulcanization stops the polymer chains from shifting individually as shown in **Figure 1.7**. Consequently, when pressure is used the vulcanized rubber deforms, but after launch of the pressure it goes back for their initial form.

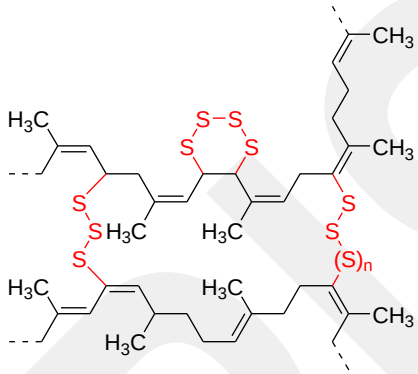


Figure 1.7 Scheme demonstrate the strands of natural rubber vulcanized with sulfur.

1.6.2 The Process

In comparison with thermoplastic process, vulcanization is usually irreversible. The cross-linking is often obtained due to inclusion of sulfur. The primary polymers exposed to vulcanization are polyisoprene (natural rubber) and styrene-butadiene rubber (SBR), which are utilized for major of traveler car wheels. The "cure package" is modified particularly for the substrate and the application. The sensitive sites "cure sites" are allylic hydrogen atoms. These C-H bonds are close to carbon-carbon double bonds. Through vulcanization, some of these C-H bonds are changed by chains of sulfur atoms which connect with a treat site of another polymer chain. These bridges includes of one and eight atoms. In the crosslink number of sulfur atoms strongly impacts the physical properties of the produced rubber content. Small crosslinks provide the rubber better heated level of resistance. Crosslinks contain high number of sulfur atoms provide the rubber excellent dynamic properties but less warm level of resistance. Dynamic properties are significant to bending motions of the rubber content, e.g., the movement

of a side-wall of a running tire. Devoid of excellent bending properties these motions quickly produce breaks and, eventually, make the rubber content fail.

1.7 Inverse Vulcanization

Inverse vulcanization existing the employment of elemental sulfur for the features of polymeric materials with a very high feed ratio of sulfur by inverse vulcanization. In traditional vulcanization, polydienes are cross-linked with a little amount of sulfur to create artificial rubber. The inverse vulcanization method, explains the stabilizing of polymeric sulfur against depolymerization by copolymerizing at a huge unwanted of sulfur with a moderate quantity of small-molecule dienes. By using copolymerization this method allowed, for initially, the adjustment of elemental sulfur into processable polymeric components where molten sulfur, serving as a solvent, was copolymerized with 1,3-diisopropenylbenzene (DIB) to produce a chemically stable and processable sulfur plastic as shown in **Figure 1.8**.

This method is known as a bulk free radical copolymerization conducting in molten sulfur. Furthermore, this facile, solvent-free technique allowed the planning of multigram-scale copolymers with sulfur that have tunable thermomechanical properties. As an immediate impact of copolymerization sulfur with divinylic styrenic comonomers, this process was capable of get ready dissoluble prepolymer sulfur resins with a very high feed ratio of sulfur (up to 90 wt% sulfur), that might be prepared into micropatterned films using polydimethylsiloxane moulds via imprint lithography. Using these artificial improvements, this process maintains many of the suitable properties of elemental sulfur (for example electrochemical activity), but changing sulfur into a copolymer type with enhanced chemical and processing properties [29].

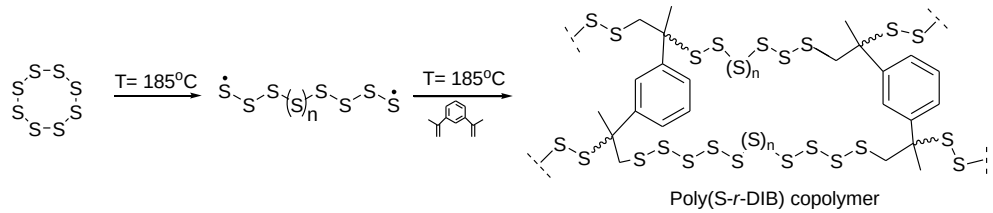


Figure 1.8 Scheme of the copolymerization S_8 with DIB to produce chemically stable sulfur copolymer called poly(sulfur-carbon-random-1,3-diisopropeylbenzene) (poly(S-*r*-DIB)) [29].

1.7.1 Copolymerization Conditions and Requirements

The preparing of poly(sulfur-random-1,3-diisopropenylbenzene) poly(S-r-DIB) copolymers by using inverse vulcanization, the copolymerization of DIB with liquid sulfur was conducted at 185 ^{o}C to enhance efficient ROP of S_8 as well as manage chemical stable copolymers which could not be easily depolymerize. Massive copolymerization of liquid sulfur at 185 ^{o}C was performed to make sure a high concentration of sulfur diradicals produced from hemolytic bosom of the S_8 to enhance the effective start of the polymerization and effective homopropagation to S_8 /sulfur diradicals and cross-propagation with DIB [11]. Copolymerization was carried out for liquid sulfur at 185 ^{o}C, so comonomers which had been both miscible with melted sulfur and nonvolatile were needed, which enabled from utilization of DIB. Preliminary trial circumstances for such reaction researched copolymerization with comparatively DIB-high contents, S_8 (70 wt%) and DIB (30 wt%), with liquid sulfur warmed to 185 ^{o}C which led to the beginning of ROP. This method was associated with a fast color modify for the medium from yellow-colored to red. At this state liquid of DIB at room temperature was included to the oligomeric sulfur combination at 185 ^{o}C, which after a quite brief combining interval, led to a homogenous yellow-colored solution of low melt viscosity in evaluation for the oligomeric sulfur mixture. Completely vitrification of the medium was noticed through five minutes, after which the reaction mixture was permitted for cooling to a room temperature, leading to the development of a clear red-colored polymeric glass [29].

1.8 Polysulfide Rubber-based Sulfur-rich Composites as Cathode Material for High Energy Lithium/Sulfur Batteries

Han and colleagues were studied and proposed kind of novel sulfur-rich polymer composites as a potential cathode for Li-S batteries which were prepared by vulcanization methods as shown in **Figure 1.9**.

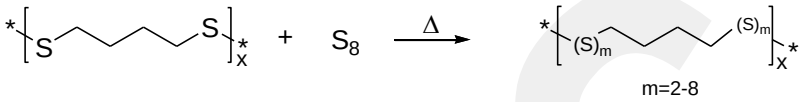


Figure 1.9 Synthetic scheme of polysulfide rubber with sulfur.

The charge-discharge cycle experiments revealed that the sulfur-rich polymer composites with polysulfide rubber to sublimed sulfur (elemental sulfur) ratios of 1:3.68 and 1:6.14 exhibited high initial specific capacities (570 mAh/g and 675 mAh/g respectively) as shown in **Figure 1.10** and good cyclic performances with 87% and 91% capacity retention over 100 cycles. The discharge intermediate could be confined by the polymer chain either through chemical bond or through physical wrapping, thus the decrease of discharge products dissolution and consequently better cycle performance of the battery will be expected. Moreover, the raw material for synthesis of the sulfur-rich polymer composites is commercial available, inexpensive, and the procedure of preparation is simple. Therefore, the sulfur-rich polymer composite materials are promising candidates as cathode material for Li-S batteries [30].

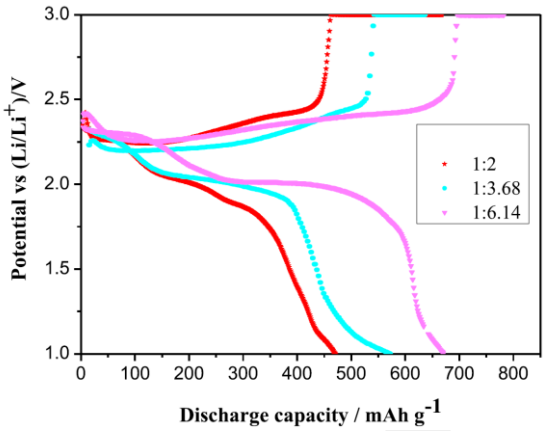


Figure 1.10 Initial charge-discharge information of the sulfur-rich polymer composites with different polysulfide rubber to sublimed sulfur molar ratios [30].

1.9 New Infrared Transmitting Material via Inverse Vulcanization of Elemental Sulfur to Prepare High Refractive Index Polymers

The growth of polymeric components for infra-red (IR) visual applications does not obtained because of difficulties in developing system with completely high refractive index (n) and visible in the IR spectral extent [31].

The planning of great high refractive index polymers (HRIP, where $n \geq 1.7$) has been researched for several optoelectronic device applications, like, organic light emitting diodes, and microlens elements within charge coupled devices and high efficiency complementary image sensors [32].

The synthesis and characterization of a high refractive index (n~1.8) thermoplastic copolymer for IR optics comprising a high feed ratios of S-S bonds (50 -80 wt% sulfur). These copolymer components were produced by a method known as inverse vulcanization. The inverse vulcanization method allowed the features of great sulfur material poly(s-r-DIB) copolymers with tunable copolymer structure, in addition to enhanced processability above elemental sulfur. The improved solubility of the copolymers (compared to elemental sulfur) in organic solvents allowed spin coating of films, which is the first example of thin film handling of a copolymer basic great content of sulfur. These sulfur copolymers were noticed to easily melt into heated 1,2-dichlorobenzen (DCB; above T = 125 ^{o}C). Utilizing this process techniques constant thin

film of controlled width (1 to 60 μm) were obtained for copolymers at compositions of 50–80 wt% S_8.

The maximum refractive index was noticed for components with the greatest sulfur material (80 wt% sulfur) which range from n = 1.865 to 1.845 from 633 to 1554 nm across the visual and near IR spectra. In addition, sulfur copolymers containing small amounts of sulfur (50 wt% sulfur) still maintained great refractive indices of n= 1.765 to 1.745 at the same spectral range. Tunability in the refractive indices of these copolymers has been obtained by management of the copolymer structure as mentioned by the intermediate refractive index data of poly(S-r-DIB) components with 30 and 40 wt% DIB. This look of improving refractive index with greater sulfur feed ratios has been linked to the high polarizability of sulfur electrons, that moved the refractive index to larger values in composition to traditional hydrocarbon polymers as s own in **Figure 1.11**. The great refractive index of these components has been associated with both low visual losses and birefringence from 633 to 1554 nm [33].

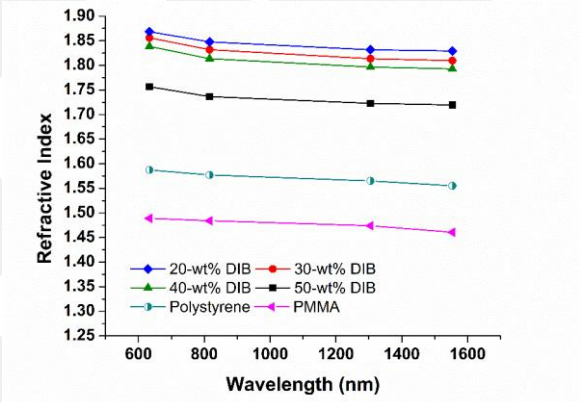


Figure 1.11 Refractive indices versus wavelength of poly(S-r-DIB) copolymer with 200 μm films; the plotted results for the average values of light polarized parallel and perpendicular to the film surface. Calculated refractive indices of polystyrene and polymethylmethacrylate at the same wavelength are shown for comparison [33].

The visual visibility of pol(S-r-DIB) films with 80 wt% sulfur has been examined by using UV-vis-near-IR transmitting spectroscopy over a large visual range (500-300 nm) to measure the effect of sample width on visual transparency. Great visual

visibility (higher than 85% transmission) has been noticed for thin (1 and 10 μm) poly(S-r-DIB) films coated on either glass, or NaCl supporting substrates as shown in **Figure 1.12**. A distinct loss of transmitting was noticed for 10 μm copolymer films on glass higher than 2500 nm, which is linked for consumption from the glass substrate itself, as adapted by minimum absorbance through these wavelengths for 1 μm films throw on NaCl plates [33].

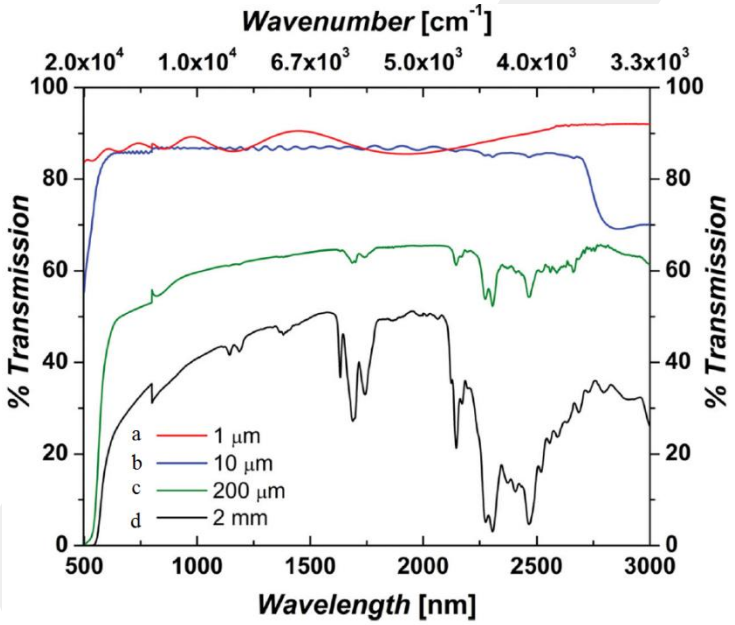


Figure 1.12 UV-vis-near-IR spectra for (80 wt% S_8 and 20 wt% DIB) copolymer films with different thickness (1 μm (a); 10 μm (b); 200 μm (c); 2 mm (d)) [33].

The visual visibility for high thick and free-standing copolymer films (200 μm and 2 mm), as predicted at comparing with thin films, caused by near-IR absorbances from 1500-3000 nm that have been linked to overtone of the C-H vibrations in DIB comonomer units as shown in **Figure 1.13**. On the other hand, the optical transparency of these films might be enhanced by tuning the sulfur feed ratios in the poly(S-r-DIB) copolymers. These films showed low visibility before 600 nm in the red color of the bulk copolymer material. Even so the preservation of great visibility in the obvious (higher than 600 nm) and near-IR spectrum was similar to that of other great refractive

index polymers with the additional advantage of keeping a considerably higher refractive index and lower visual scattering [33].

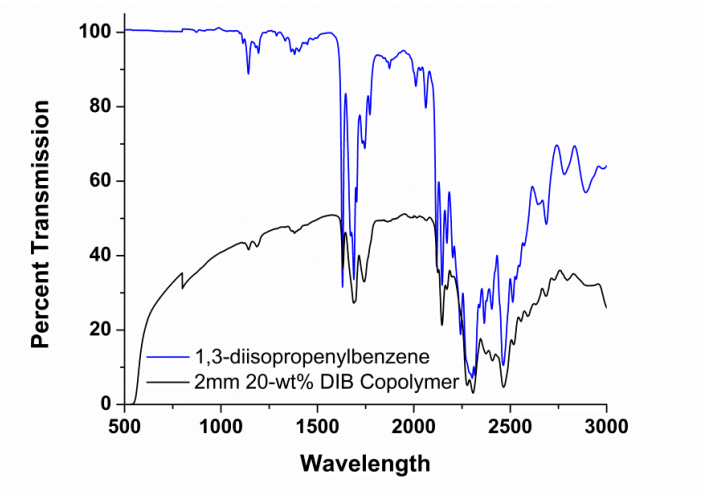


Figure 1.13 Uv-visible/near-infrared transmission spectra comparing a 2 mm thick sample of poly(S-r-DIB) copolymer (20 wt% DIB/80 wt% S_8) copolymer (blue) with 1,3-diisopropenylbenzene (black) [33].

1.10 Sulfur Copolymer Nanowires

Photocatalytic water splitting provides a fresh and eco-friendly method to produce fresh and renewable hydrogen [34]. Essentially one of the most difficulties in hydrogen manufacturing is definitely the growth of inexpensive and effective visible-light-driven catalysts with photochemical and photoelectrochemical activity for hydrogen evolution reaction (HER) [35]. In two previous decades, intense interest has become targeted on substance semiconductors as photocatalysts [36, 37]. Lately, substance semiconductors like silicon, selenium, red phosphorus, and boron are already regarded to be an appealing type of photocatalysts and photoelectrocatalysts for solar energy change [38-42]. From these essential elements, silicon was observed to be a very effective photoelectrocatalyst for water splitting hydrogen evolution [43, 44]. These fascinating photoelectrochemical applications of silicon drove researchers to look for another substitute to silicon. Lately, sulfur was getting enhancing attention because of excellent electrochemical capacities and also its variety and ecologically friendly. In this study, α-sulfur had been exposed by Cheng and colleagues as the obvious light efficient

elemental catalyst for photoelectrochemical water splitting and photodegradation of Rhodamine B, showing new possibilities of sulfur as an efficient photoelectrocatalyst for HER [45]. Even so, sulfur used as a catalyst is in the powder state. In comparison to bulk alternatives, nanoscale factors display enhanced actions to photocatalytic and photoelectrochemical HER because of the size-related increase of surface area and effective centers and also the easy migration of photogenerated carriers to the semiconductor surface [46- 48].

The nanosized sulfur is predicted to demonstrate improved photoelectrochemical action than powder sulfur. But, for sulfur, it is challenging to get its nanoscale form because of restricted processability. As thermal ROP of elemental sulfur produce polymeric sulfur with inadequate mechanical properties. Lately, Pyun and colleagues have revealed a facile technique to get ready a higher sulfur material copolymer with tunable thermomechanical properties and similar electrochemical properties to elemental sulfur [49]. Moreover, the doping of g-C_3N_4 with S varieties is efficient to reduce the bandgap and enhance the photocatalytic activity of carbon materials [50]. Consequently, the nanoscale sulfur copolymer with great sulfur feed ratios may be extremely effective for HER.

The manufacturing of the poly(S-*r*-DIB) copolymer nanowires employing anodic aluminum oxide membranes as template as shown in **Figure 1.14**, illustrate for the first time that the sulfur copolymer nanowires were visible-light active for photoelectroncatalytic HER through water splitting with efficiency of the photochemical properties of elemental sulfur. The sulfur copolymers were produced by a revealed copolymerized technique known as inverse vulcanization by Pyun and colleagues. Then, anodic aluminum oxide membranes were used as templates for the preparing copolymer nanowires with 80 wt%, 70 wt% and 50 wt% sulfur content, respectively [51].

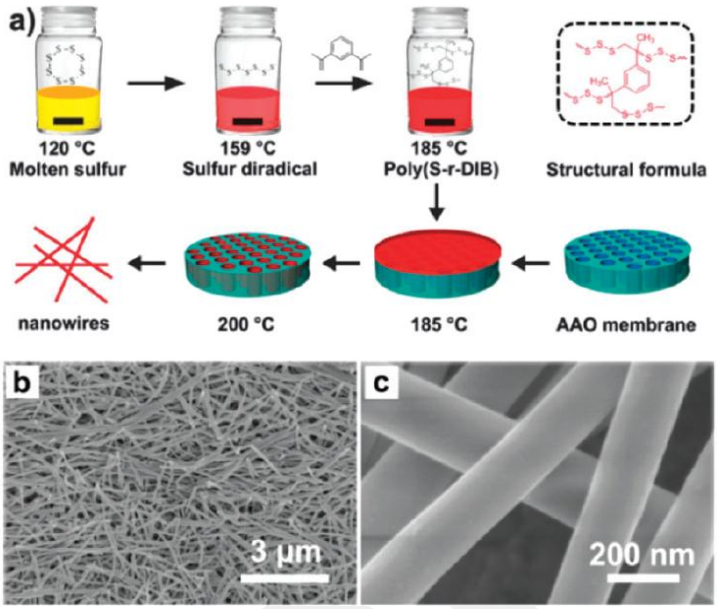


Figure 1.14 (a) Scheme shows synthesis procedure of the poly(S-r-DIB) Copolymers and copolymer nanowires. (b) and (c) SEM images of the sulfur copolymer nanowires created by using anodic aluminum oxide membranes as templates [51].

To enhance the using of elemental sulfur, increase the chemical properties of the sulfur copolymer and also development of an inexpensive and efficient photocatalyst, the photoelectrocatalytic hydrogen creation of the sulfur copolymer nanowires was examined within noticeable visual light illumination. UV was dissipate reflectance spectra as shown in **Figure 1.15(a)** which revealed that the spectrum of sulfur copolymer nanowires shifted to longer wavelengths with stronger absorption capability compared to the spectrum of α-sulfur crystal powder, showing a decrease in the band gap of sulfur upon incorporation into the copolymer with DIB. As shown in **Figure 1.15(b)**, the photocurrent produced from sulfur copolymer nanowires increased extremely with exterior bias voltage and gets to ~6.7 μA cm^{-2} at 0.8 V compared to saturated calomel reference electrode (SCE), which matches to hydrogen evolution on the Pt electrode [51].

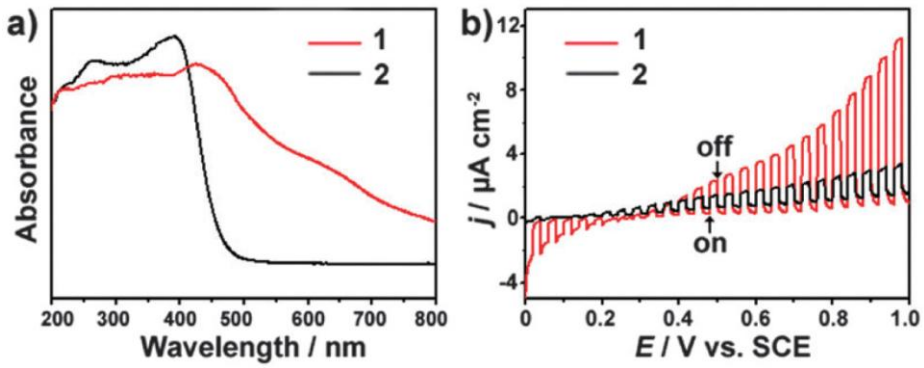


Figure 1.15 (a) UV/Vis spectra of dissipate reflectance and (b) photocurrent transients of the applied potential for sulfur copolymer nanowires photoanode (1) and sulfur powders (2) repeated on–off cycles of visible-light illumination (λ> 420 nm) in 0.2 M Na_2SO_4, respectively [51].

1.11 Elemental Sulfur as a Reactive Medium for Gold Nanoparticles and Nanocomposite Materials

Chung and co-workers survey for the first time the employment of elemental sulfur as a novel feedstock for the production of AuNPs and for in situ cross-linking of these colloidal dispersions to produce vulcanized nanocomposites as shown in **Figure 1.16**, by the immediate dissoluble of organometallic Au^I complexes in molten sulfur with the production of specific, spread metal AuNPs. Moreover, to improve the mechanical properties of these disperses, reaction of the elemental sulfur with divinylbenzene (DVB) provided cross-linked nanocomposites with AuNP impurities.

The general way of the preparing of Au nanoparticles and nanocomposites was the immediate dissolving of organometallic complexes and vinylic monomers into molten sulfur devoid of require for added organic solvents. Nonpolar complexes like gold(I) triphenylphosphine chloride ($ClAu^IPPh_3$) and gold(I) chlorocarbonyl ($ClAu^ICO$) were observed being dissolved in molten sulfur at temperature ranges higher than 120 ^oC and were at first utilized for the synthesis of AuNPs [52]. But in their research they did not show the general procedure for polymerization of monomer sulfur with cross-linker DVB.

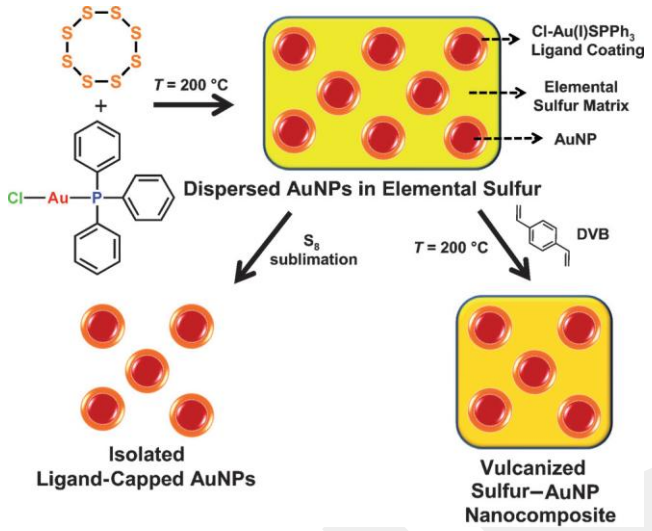


Figure 1.16 Synthesis of isolated Ligand-Capped AuNPs by using molten sulfur and vulcanized Sulfur-AuNP to form cross-linked nanocomposites [52].

1.12 Copolymerization of Elemental Sulfur with Cyclic (Arylene Disulfide) Oligomers

In the process of copolymerization, the cyclic(arylene disulfide) oligomers had been produced by oxidative coupling of aromatic dithiols with oxygen in the presence of coperranine catalyst. The cyclic(arylene disulfide) oligomers follow melting ROP and produce high molecular weight liner poly(arylene disulfide)s.

Poly(arylene sulfide)s, were produced from the reaction of cyclic(arylene disulfide) oligomers with diiodo- or dibromoaromatic substances. As a continuous method the free radical copolymerization of elemental sulfur with cyclic(arylene disulfide) oligomers produce high molecular weight liner poly(arylene sulfane)s with high sulfur contents as shown in **Figure 1.17** [53].

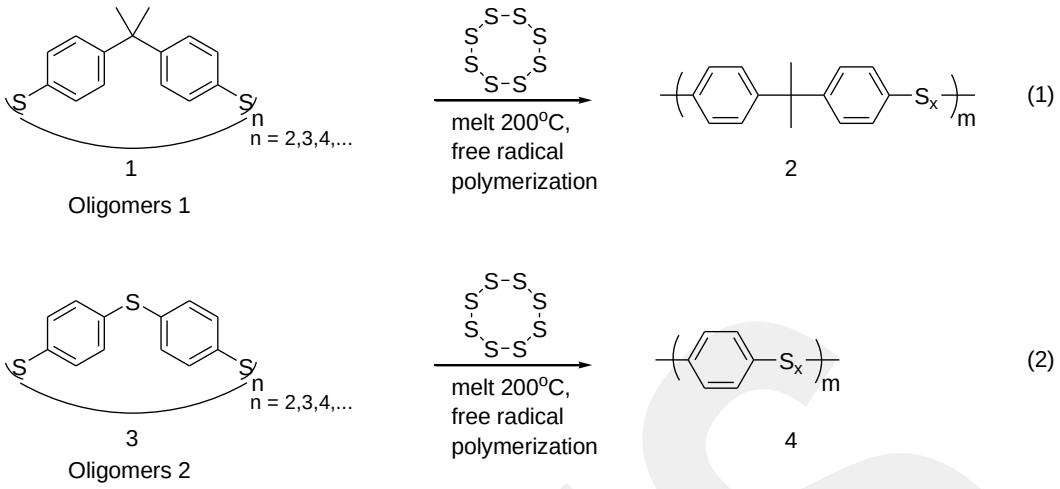


Figure 1.17 The chemical reactions for producing polydisulfides [53].

1.12.1 Melt Copolymerization of Cyclic Disulfide Oligomers 1 with Elemental Sulfur

Melt polymerization of cyclic disulfide oligomers 1 with sulfur produce polymers with higher sulfur content, the polymerization processes were done for one equivalent of cyclic disulfide oligomers 1 at 150 ^{o}C and 200 ^{o}C. Higher temperature anticipated to produce polymers with lower molecular weight and more complicated.

Inclusion of free sulfur led to melting points much lower; this way aperient melts copolymerization reaction at 150 ^{o}C. After the addition of sulfur, high molecular weight polysulfans created in 15 min with only little quantity of cyclic oligomers remaining. These polysulfance are highly dissolved in $CHCl_3$ when four equivalents or less of sulfur was added [53].

The copolymerization reaction happens significantly quicker at 200 ^{o}C and produces polysulfanes with nearly the same molecular weights resulted at 150 ^{o}C [53].

1.12.2 Melt Copolymerization of Cyclic Disulfide Oligomers 3 with Elemental Sulfur

Melt copolymerization of cyclic disulfide oligomers 3 form polysulfanes dissolvable in common organic solvents at room temperature, so no molecular weight details were obtained. One diverse characteristic of these cyclic oligomers is that they

contain a thioether linkage, which is also reactive with sulfur and can form many sulfur linkage, so the producing polymers are poly(phenylene sulfur)s [53].

The polymerization process was carried out at 200 ^{o}C, that is the perfect temperature for melt ROP and melt copolymerization of cyclic disulfide oligomers, the reaction time for copolymerization is 2 h. T_g of polysulfanes 4 with different numbers of sulfur linkage shown in **Table 1.1**, which clarifies that when the sulfur content increases the T_g decreases. The existence of the phenylene group produces the higher T_g for polysulfanes compound with polysulfur [53].

Table 1.1 Properties of Polysulfanes 4 Resulted from Melt Copolymerization Reactions [53].

No	Sulfur Linkage (X)	T_g (^{o}C)	T_d (^{o}C)
1	2[a]	84	459
2	3	50	342
3	4	38	303
4	5	22	280
5	6	21	285
6	7	12	249

1.13 Aim of This Work

Today, except for few studies, there is a limited usage of elemental sulfur as a feedstock for getting new polymeric materials. Unfortunately, inspite of its interesting futures, the lack of suitable polymerization methods to get polymers with a very high sulfur feed ratio hindered the development of polysulfur based polymers. Therefore, in order to obtain chemically stable and processable polymers with high sulfur feed ratio, a new crosslinker called divinylbenzene (DVB) will be used with melted sulfur to get new copolymers via inverse vulcanization method. Prepared copolymer will be characterized via fourier transform infrared (FTIR), nuclear magnetic resonance (NMR), gel permeation chromatography (GPC), Raman, thermal gravimetric analysis (TGA),

differential scanning calorimetry (DSC) and scanning electron microscope (SEM) techniques and also their properties will be compared with their analogues.

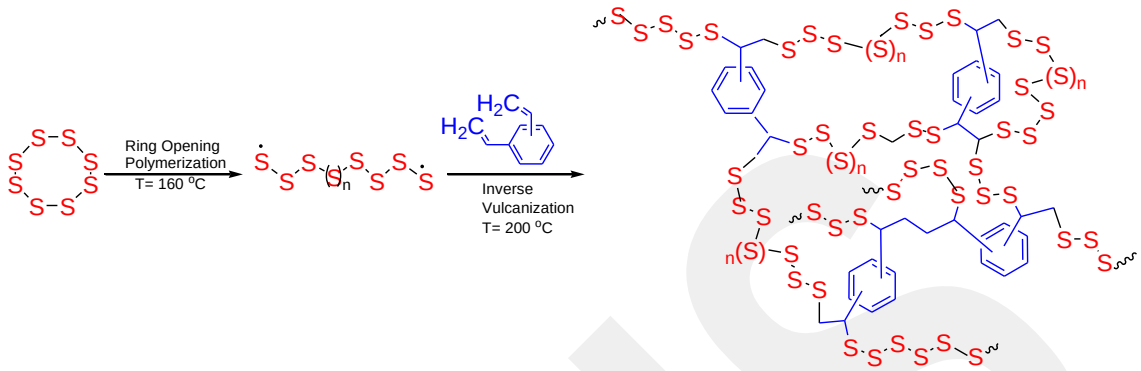


Figure 1.18 Scheme of the copolymerization of elemental sulfur (S_8) with DVB.

CHAPTER 2
EXPERIMENTAL

2.1 Materials

The elemental sulfur sublimed, 99.5% (Acros) was used as received. A mixture of ortho-, meta-, and para-divinylbenzene (DVB) (Merck) as a crosslinker was freshly purified by using a column chromatography since the stock solution consists of a mixture of DVB and ethylvinylbenzene. Methacryl-POSS Cage mixture (Hybrid Plastics), pentaerythritol tetraacrylate (Aldrich), 1,6-hexanediol dimethacrylate (Aldrich), 1,4-butandiol divinyl ether (Aldrich), 1,4-cyclohexanedimethanol divinyl ether, mixture of isomers (Aldrich), tri(ethylene glycol) divinyl ether (Aldrich), styrene (Sigma-Aldrich) and oleic acid (Merck) were used without further purification. Also, The solvents tetraheydrofuran (THF), dimethylformamide (DMF), acetone, dichloromethane, chloroform, dimethylsulfoxide (DMSO), propylene carbonate (PC), sulfuric acid and 1,2-dichlorobenzene (1,2-DCB) were used as received.

2.2 Polymerization of Elemental Sulfur with DVB

S_8 with different mass percentages from 10% to 90% by weight in a test tube equipped with a magnetic stirrer was heated up to 160 ^oC in a thermostated oil bath until a clear yellow colored molten phase was obtained. Then, fresh purified DVB with different mass percentages from 90% to 10% was directly added to molten sulfur medium via a syringe and the temperature starts to increase gradually to 200 ^oC with continuous mixing. By passing time two layers mixed into each other to give a homogeneous solution. After that, the magnetic stirrer bar was removed and the corresponding mixture was heated at this temperature (200 ^oC) for 8-10 minutes. During polymerization process the color of the viscous product changed severely from clear yellow to dark brown, depending on the amount of DVB in the mixture. Finally, the reaction was cooled gradually to room temperature.

2.3 Polymerization of Elemental Sulfur with Various Crosslinkers

S_8 with 50% mass percentage by weight in a test tube equipped with a magnetic stirrer was heated up to 160 ^oC in a thermostated oil bath until a clear yellow colored molten phase was obtained. Then, the related crosslinker with 50% mass was directly added to molten sulfur medium via a syringe and the temperature started to increase gradually to 200 ^oC with continuous mixing. After 10 min, the magnetic stirrer bar was removed and the corresponding mixture was heated at this temperature (200 ^oC) for additional 8-10 min. During polymerization process the color of the viscous product changed severely depending on the used crosslinkers in the mixture. Finally, the reaction was cooled gradually to room temperature.

2.4 Characterization

In order to measure the IR transmittance of the copolymers, they were coated on substrates via a spray casting technique (Deluxe Professional Airbrush by Aztek A4709). Photographs of the polymer films were taken by using a Canon (PowerShot A75) digital camera. ^1H NMR spectra of obtained polymers were recorded on a Bruker Spectrospin Avance DPX-400 Spectrometer with $CDCl_3$ and chemical shifts were given relative to tetramethylsilane as the internal standard. Chemical shifts are reported in terms of ppm and that of $CDCl_3$ is 7.26 ppm. FTIR spectra were recorded on Nicolet 510 FTIR with attenuated total reflectance. Raman spectra were monitored by using a Helb Jobin Yvon, HR-800 Raman Spectrometer. Molecular weight measurements was performed via Schimadzu LC-20A/Prominence GPC according to polystyrene standarts. Scanning electron microscope (SEM) analysis was monitored by using Quanta 200 FEG Model, Bilkent University Location: UNAM-M03. TGA analysis performed via Q500 Model and DSC device Model 204-F1.

CHAPTER 3
RESULTS AND DISCUSSIONS

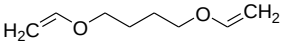
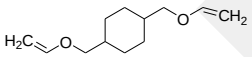
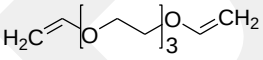
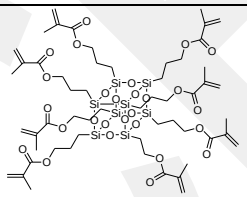
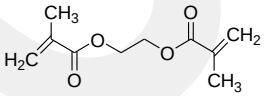
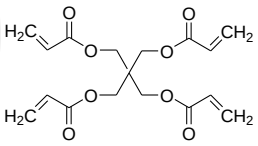
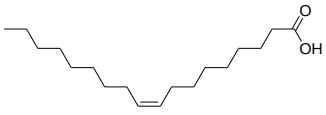
3.1 Copolymerization of Elemental Sulfur with Various Crosslinkers

It is well-known that elemental sulfur can be polymerized by heating at high temperatures in the presence of diisopropylenebenzene (DIB) used as a crosslinker [29]. Molten elemental sulfur is obtained as a clear yellow liquid at about 160 ^{o}C (the floor temperature), and after the addition of DIB the viscosity of the mixture sharply increases within minutes of the reaction at a temperature higher than185 ^{o}C. Then, a glassy and red transparent polymeric material is obtained. The presence of DIB prevents the depolymerization of obtained copolymer since pure polysulfur obtained by melted elemental sulfur depolymerizes gradually in the absence of crosslinkers when the temperature of the reaction is cooled to room temperature.

This pioneering study showed that the amount of elemental sulfur used in copolymerization can be increased by using efficient crosslinkers instead of DIB. Under the light of above information, a number of different crosslinkers bearing various vinylic groups was used to get new sulfur based copolymers in the present study. Therefore, the amount of crosslinkers can be decreased by using the crosslinkers having more than two vinylic groups when compared to DIB. In order to achieve this aim, a new series of the vinylic compounds as shown in **Table 3.1** was used to examine their crosslinker ability during the copolymerization of elemental sulfur.

It must be noticed that the used crosslinker must have high boiling point and must be miscible with molten sulfur during polymerization. Unfortunately, as seen in **Table 3.1** the compounds of methacryl POSS cage mixture, 1,6-hexanediol dimethacrylate and pentaerythritol tetraacrylate are not miscible with molten sulfur and therefore the copolymerization was not carried out successfully.

Table 3.1 Copolymerization of elemental sulfur with various compounds contain different numbers of vinylic groups.

Crosslinker	Chemical Structure	Freshly Prepared Copolymers	After One Month
1,4-butanediol divinyl ether, $C_8H_{14}O_2$ bp = 62 – 64 ^oC			
1,4-cyclohexane dimethanol divinyl ether, $C_{12}H_{20}O_2$ bp = 126 ^oC			
Tri(ethylene glycol) divinyl ether, $_{10}H_{18}O_4$ bp = 120 – 126 ^oC			
Methacryl POSS cage mixture $(C_7H_{11}O_2)_n(SiO_{1.5})_n$ n = 8,10,12, T_d = 386 ^oC			
1,6-hexanediol dimethacrylate, $C_{14}H_{22}O_4$ bp = 98 - 100 ^oC			
Pentaerythritol tetraacrylate, $C_{17}H_{20}O_8$ bp = 450.3 ^oC			
Oleic acid, $C_{18}H_{22}O_2$ bp = 360 ^oC			

On the other hand, the compounds of 1,4-butanediol divinyl ether, 1,4-cyclohexanedimethanol divinyl ether and tri(ethylene glycol) divinyl ether having lower boiling point were used with molten sulfur to get flexible copolymers due to the presence of etheric bridge in the crosslinkers. Unfortunately, the homogeneous copolymers were not obtained since whether the crosslinkers are not miscible or volatile. The obtained polymers were depolymerized by cooling the reaction to room temperature.

Also, oleic acid was used as a crosslinker to get carboxylic acid functionalized copolymer which can be used as a sensor in chemistry and biochemistry areas. Unlike the previous attempts, although the oleic acid has higher boiling temperature, is nonvolatile and miscible with molten sulfur, when the polymerization was completed, the obtained polymers started to change its color from dark reddish brown to a mixture of dark brown and orange and by passing time the product was turned into orange color.

3.2 Copolymerization of Elemental Sulfur with DivinylBenzene (DVB)

Under the light of these unsuccessful attempts, copolymerization was carried out by using a mixture of divinyl benzene (DVB) as a crosslinker which has similar chemical structure with DIB without methyl group and is cheaper than DIB as shown in **Figure 3.1**.

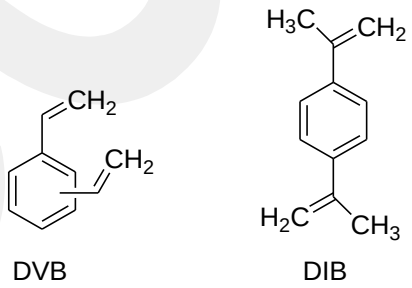


Figure 3.1 Scheme of the chemical structures of DVB and DIB

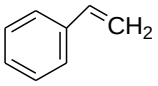
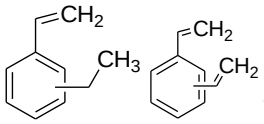
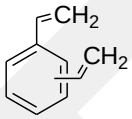
First of all, the copolymerization of elemental sulfur was performed in the presence of styrene as a crosslinker. The comonomers are miscible at 200 ^{o}C and a sharp increase in the viscosity of the mixture was obtained at the end of heating about 10 minutes. When the polymerization was completed, a rubbery like material was obtained. Unfortunately, after cooling to room temperature, depolymerization started and sulfur was appeared at the bottom as an orange solid separated from styrene **Table 3.2**.

After this control experiment, a mixture of ethylvinylbenzene and DVB was used and due to the presence of DVB a copolymer was obtained as a dark reddish brown material and unlike styrene experiment, depolymerization occured gradually. The color of the material changed to light orange color and to orange by passing time (after one month) **Table 3.2**.

Aforementioned results showed that pure DVB can be an appropriate crosslinker to get sulfur based copolymers. Therefore, a mixture of ortho-, meta-, and para-DVB was purified freshly and then added to molten elemental sulfur at 160 ^{o}C. The mixture was heated to 200 ^{o}C and a homogeneous mixture was formed. At the end of heating at about 10 minutes chemically stable copolymers were obtained and they did not change their color over a period of several months under normal circumstances **Table 3.2**. By the inspiration of the results, the copolymers with different amount of sulfur and DVB were obtained and their physical and chemical properties were investigated.

As a result, first of all, the elemental sulfur was melted at 160 ^{o}C and therefore ROP of the S_8 was promoted and a clear yellow/orange colored liquid was obtained. Then, DVB was added directly via a syringe and continue to further mixing at 200 ^{o}C for 10 minutes to get a viscous reddish brown polymeric material called poly (sulfur-*random*-divinylbenzene) (poly(S-*r*-DVB)) (see **Figure 3.2** and **Figure 3.3**).

Table 3.2 Copolymerization of elemental sulfur with styrene, mixture of divinylbenzene and ethylvinylbenzene, and divinylbenzene.

Crosslinker	Chemical Structure	Freshly Prepared Copolymers	After One Month	After Two Months
Styrene C_8H_8 bp = 145 ^oC				
A mixture of DVB and ethylvinylbenzene				
DVB $C_{10}H_{10}$ bp = 195 ^oC				

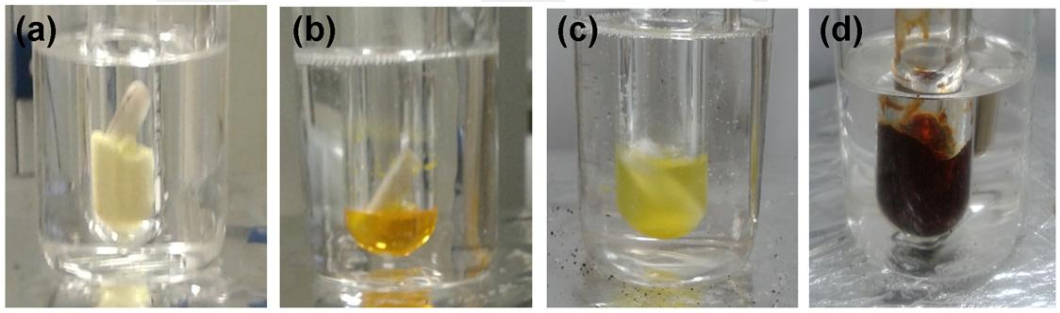


Figure 3.2 Polymerization of elemental sulfur with divinylbenzene: (a) elemental sulfur at room temperature, (b) molten sulfur at 160 ^oC, (c) molten sulfur with DVB at 200 ^oC and (d) poly(S-*r*-DVB) after 10 min by heating at 200 ^oC.

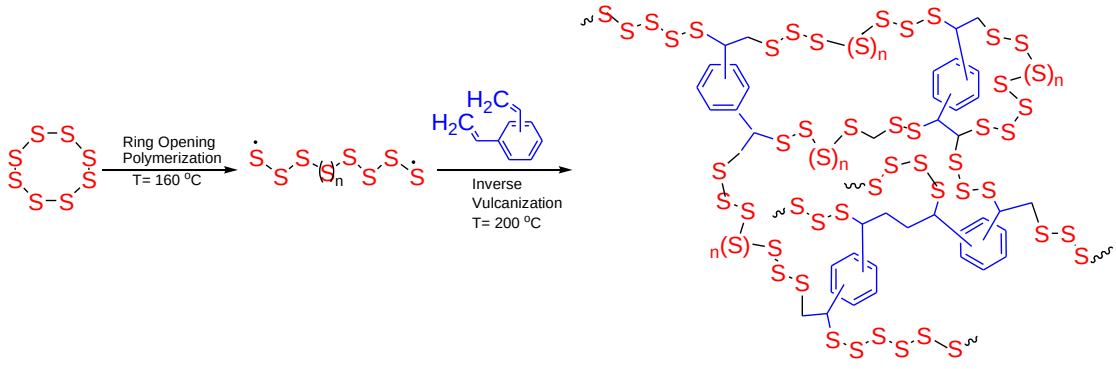


Figure 3.3 Scheme of the copolymerization of S_8 with DVB.

The suitable polymerization temperature of elemental sulfur with DVB had been studied, where the copolymerization procedure was repeated at different temperature like 185 °C, 190 °C, 200 °C, 210 °C and 220 °C for the same monomer feed ratio of elemental sulfur and DVB (50:50 by wt) in order to determine the suitable temperature for the copolymerization. As shown in **Figure 3.4**, 200 °C was selected as a suitable copolymerization temperature. It can be easily seen that the polymerization performed at 185 °C and 190 °C did not result in a homogenous polymeric material and the products did not have uniform colors: a thin layer of sulfur was appeared as yellow color when the product mixture was cooled to room temperature. On the other hand, at higher temperatures than 200 °C, homogeneous polymeric products were obtained and they persisted their colors by passing time but these temperatures are very close to the beginning of the decomposition temperature of the copolymers based on elemental sulfur and DIB [29]. Therefore, 200 °C was chosen and used for further studies. The colors of end products are changed from yellow to reddish brown depending on the amount of elemental sulfur and DVB crosslinker as shown in **Figure 3.5**.

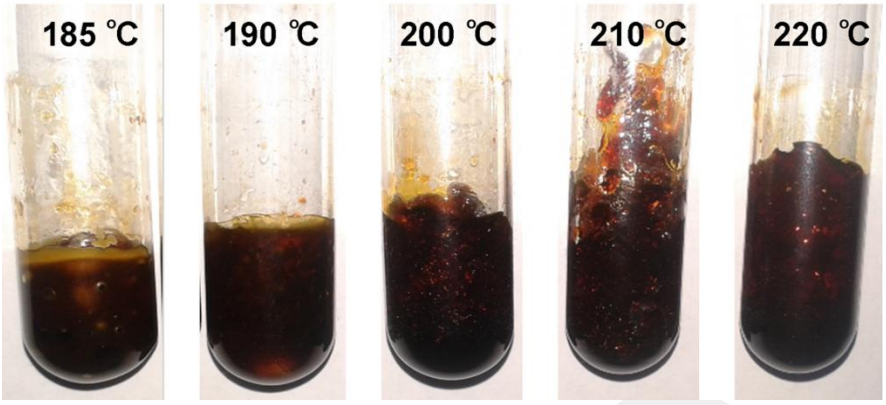


Figure 3.4 Polymerization of elemental sulfur with 50 wt% of DVB at different temperatures.

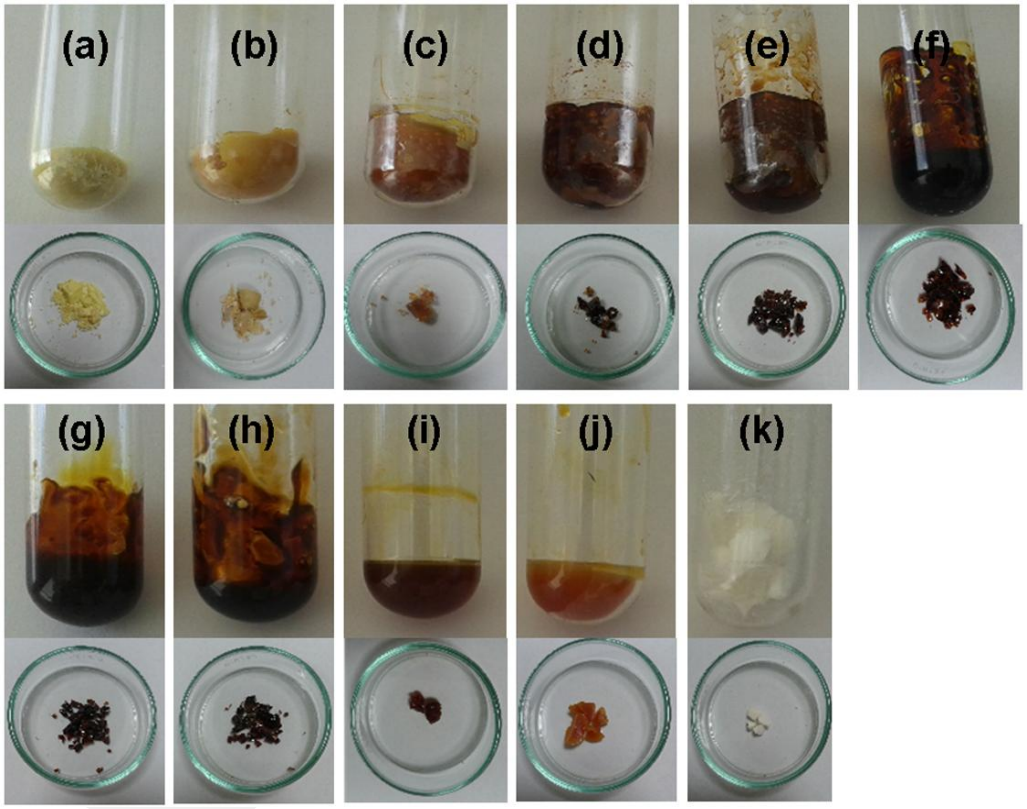


Figure 3.5 The pictures of (a) elemental sulfur, poly(S-*r*-DVB) with (b) 10 wt % DVB, (c) 20 wt % DVB, (d) 30 wt % DVB, (e) 40 wt % DVB, (f) 50 wt % DVB, (g) 60 wt % DVB, (h) 70 wt % DVB, (i) 80 wt % DVB, (j) 90 wt % DVB and (k) PDVB.

3.3 Solubility of Poly(S-*r*-DVB)

Solubility is an important parameter since the structural characterization of these copolymers bearing various amounts of DVB could be performed by using NMR, GPC, UV-vis techniques, etc. **Table 3.3** represented the solubility of the copolymers in various organic solvents. As shown in **Table 3.3** the copolymers containing high amount of S-S repeating units have limited solubility. If the ratio of DVB equals to or smaller than elemental sulfur, the related copolymers have high solubility in common solvents like THF, dichloromethane, chloroform, 1,2-DCB, etc. and they have brown solution (see **Figure 3.6**). Also, the related soluble copolymers can be coated on any surfaces and obtained in the film forms. On the other hand, the copolymers are not soluble in water.

Table 3.3 The solubility of the copolymers in organic solvents. is: insoluble, ss: slightly soluble and s: soluble.

Solvents	**Polymers**										
	PDVB	**Poly(S-*r*-DVB) with 10wt%DVB**	**Poly(S-*r*-DVB) with 20wt%DVB**	**Poly(S-*r*-DVB) with 30wt%DVB**	**Poly(S-*r*-DVB) with 40wt%DVB**	**Poly(S-*r*-DVB) with 50wt%DVB**	**Poly(S-*r*-DVB) with 60wt%DVB**	**Poly(S-*r*-DVB) with 70wt%DVB**	**Poly(S-*r*-DVB) with 80wt%DVB**	**Poly(S-*r*-DVB) with 90wt%DVB**	**Polysulfur**
THF	is	is	İs	is	ss	s	s	s	s	İs	is
DMF	is	is	İs	is	is	ss	ss	is	is	İs	is
Acetone	is	is	İs	is	is	is	is	is	is	İs	is
CH_2Cl_2	is	is	İs	is	ss	s	s	is	is	İs	is
$CHCl_3$	is	is	İs	ss	ss	s	s	s	s	İs	is
DMSO	is	is	İs	is	is	is	is	is	is	İs	is
PC	is	is	İs	is	is	is	is	is	is	İs	is
Conc. H_2SO_4	s	is	İs	is	ss	s	s	s	s	S	is
1,2-DCB	s	is	İs	s	s	s	s	s	s	S	is

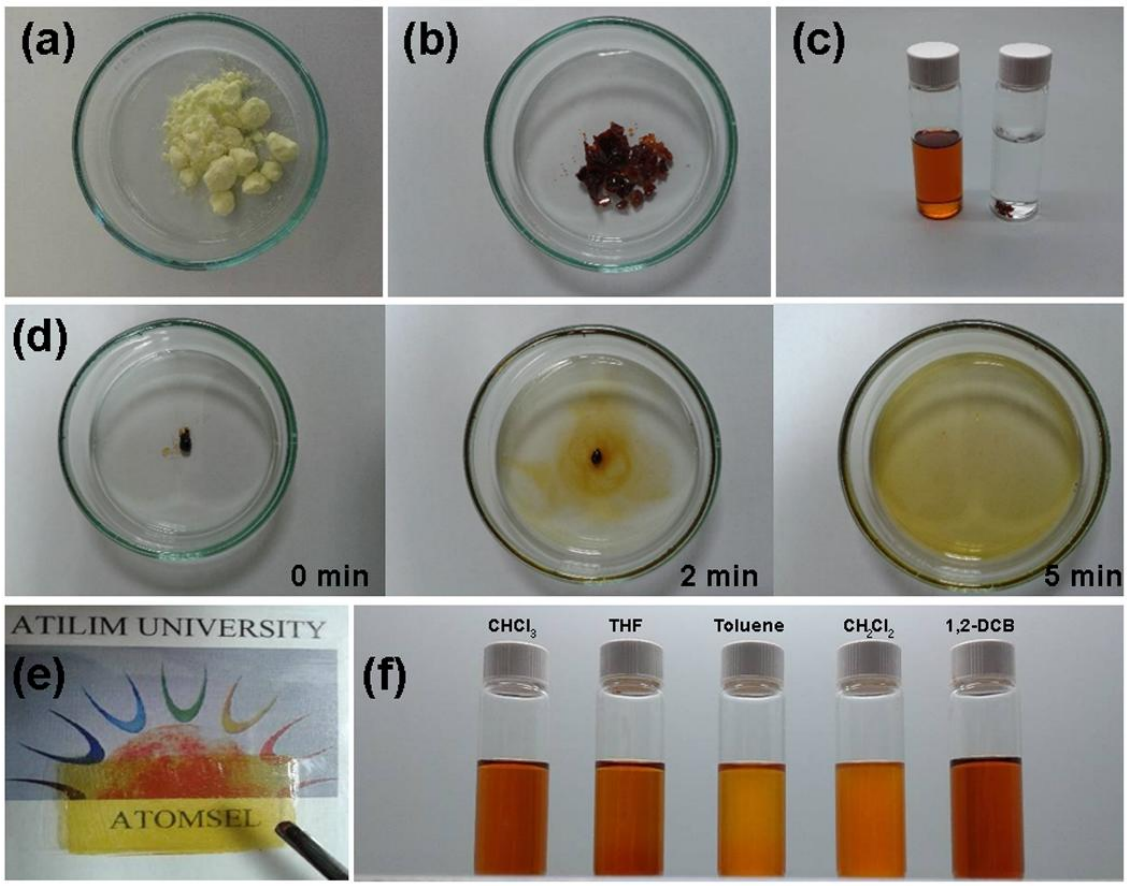


Figure 3.6 Digital photographs of (a) sulfur, (b) poly(S-*r*-DVB) with 50 wt% DVB, (c) poly(S-*r*-DVB) with 50 wt% DVB in $CHCl_3$ (left) and in water at room temperature (right) (d) solubility of 10 mg poly(S-*r*-DVB) with 50 wt% DVB in $CHCl_3$ in 5 min, (e) film of $CHCl_3$, (f) poly(S-*r*-DVB) with 50 wt% DVB dissolved in $CHCl_3$, THF, toluene, CH_2Cl_2 and 1,2-DCB.

3.4 Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR)

It is possible to use NMR spectroscopic technique to investigate the chemical structure of soluble copolymers. As shown in **Figure 3.7**, ^{1}H NMR spectrum of poly(S-*r*-DVB) with 50 wt% DVB confirmed the presence of crosslinkers in/between the polymer chains. For example, the broad peaks between 6.8 ppm and 7.8 ppm can be attributed to the aromatic hydrogens while the peaks ascribed to the aliphatic hydrogens can be seen between 3.5 ppm and 1.0 ppm. On the other hand, the presence of a broad peak centered at 4.3 ppm confirmed the hydrogens in -CH_2-S- covalent bonds [29]. It can be easily concluded that the obtained polymers are the copolymers bearing S-S repeating units and DVB based crosslinkers.

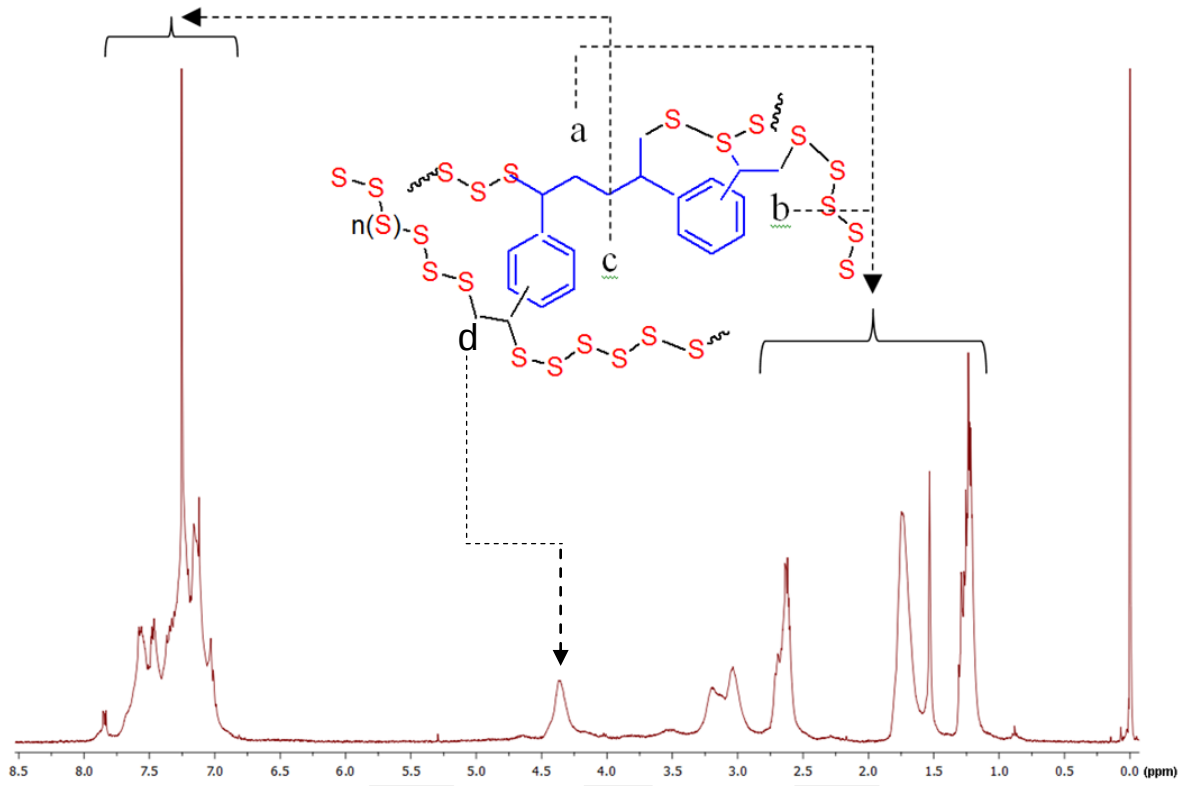


Figure 3.7 ^{1}H NMR spectrum of poly(S-*r*-DVB) with 50 wt% DVB in $CDCl_3$.

3.5 Fourier Transform Infrared Spectroscopy (FTIR)

FT-IR spectrum of poly(S-*r*-DVB) with 50 wt% DVB was compared those of PDVB and DVB as shown in **(Figure 3.8)**. First of all, as expected, the spectrum of poly(S-*r*-DVB) looks like that of PDVB. Except for PDVB, the band appeared at around 2950 cm^{-1} can be ascribed to the methylene stretching in -CH-CH_2- and -S–CH_2- units in poly(S-*r*-DVB). Also, the band at 900 cm^{-1} attributed to the C═CH_2 vinyl stretching is lost its intensity when compared to DVB, which confirmed the disappearance of vinylic groups during copolymerization.

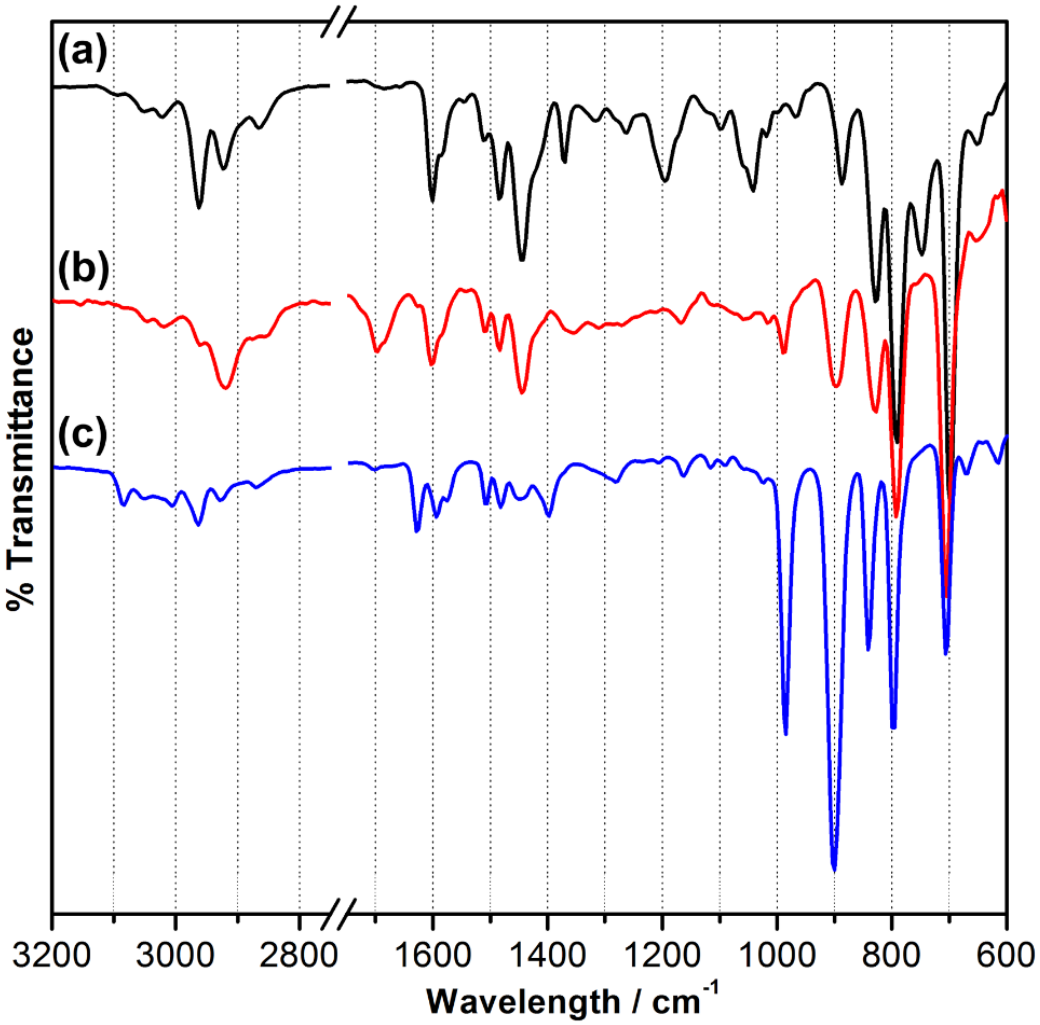


Figure 3.8 FTIR spectra of (a) poly(S-*r*-DVB) with 50 wt % DVB, (b) PDVB and (c) DVB.

3.6 Gel Permeation Chromatography (GPC)

Gel permeation chromatography (GPC) analysis calibrated against polystyrene standards was performed in $CHCl_3$ solution of the poly(S-*r*-DVB) copolymers with different wt% DVB. As shown in **Table 3.4**, GPC results showed that the copolymers have low weight-averaged molecular weight with high polydispersity index (PDI). When compared to its poly(S-*r*-DIB) copolymer derivatives [29], the poly(S-*r*-DVB) copolymers with 50-80wt% DVB have higher molecular weights with PDI between 2.02 and 4.50. The low noticeable molar mass and high polydispersity of this copolymer was linked to both branching through DVB units and prevalent termination by intramolecular coupling of sulfur radical branches to

create more stable S-S bonded “loops”, which a suggested procedure for covered up depolymerization as a consequence of DVB copolymerization [29].

Table 3.4 GPC Results of poly(S-*r*-DVB) copolymers.

Copolymers	**M_w**	**M_n**	**PDI=M_w/M_n**
Poly(S-*r*-DVB) with 50 wt % DVB	6300	2301	2.74
Poly(S-*r*-DVB) with 60 wt % DVB	4383	2165	2.02
Poly(S-*r*-DVB) with 70 wt % DVB	19420	4320	4.50
Poly(S-*r*-DVB) with 80 wt % DVB	7393	3579	2.07

3.7 Raman Spectroscopy

The comparison of Raman spectra of elemental sulfur, PDVB and poly(S-r-DVB) copolymers with different wt% DVB confirmed the copolymerization of elemental sulfur and DVB. As shown in **(Figure 3.9)**, S-S vibrational stretches at 239- 483 cm^{-1} started to lost their intensities and new peaks attributed to the aromatic stretches at 1050 and 1625 cm^{-1} appeared and started to intensify by an increase in the amount of DVB in the copolymer. On the other hand, the Raman spectrum of poly(S-r-DVB) with 80wt% DVB looks like that of PDVB as expected.

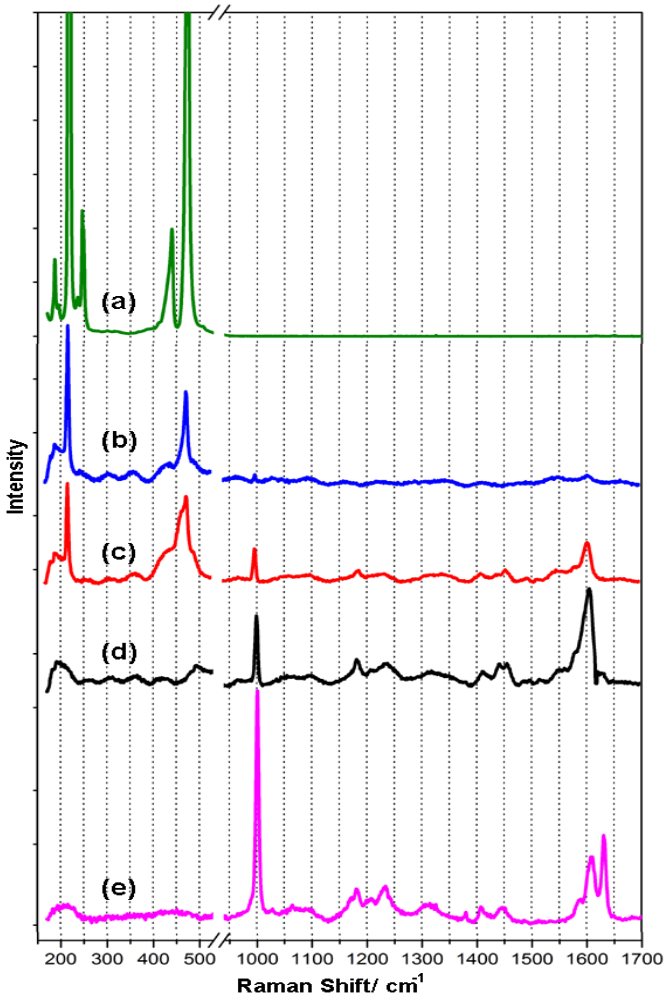


Figure 3.9 Raman spectra of (a) elemental sulfur, (b) poly(S-*r*-DVB) with 20 wt % DVB, (c) poly(S-*r*-DVB) with 40 wt % DVB, (d) poly(S-*r*-DVB) with 80 wt % DVB and (e) PDVB.

3.8 Scanning Electron Microscope (SEM)

The scanning electron microscope (SEM) was conducted to produce the images of the polymer samples (**Figure 3.10** and **Figure 3.11**). The copolymers showed different morphologies depending on the amount of DVB used in copolymerization. For example, as shown in (**Figure 3.11 (e)-(f)**), the PDVB has a smooth surface and by increasing the amount of elemental sulfur up to 50 wt% in copolymerization, new and uniform morphologies were formed, which are absolutely different from that of PDVB. On the other hand, the weight percent of elemental sulfur was increased up to 80%, elemental sulfur started to appear on the surface of the samples, indicating the formation of two phases. Under the light of this information, it can be easily

concluded that the poly(S-*r*-DVB) copolymers containing 50 wt% or less elemental sulfur exhibited the combination of elemental sulfur and DVB uniformly.

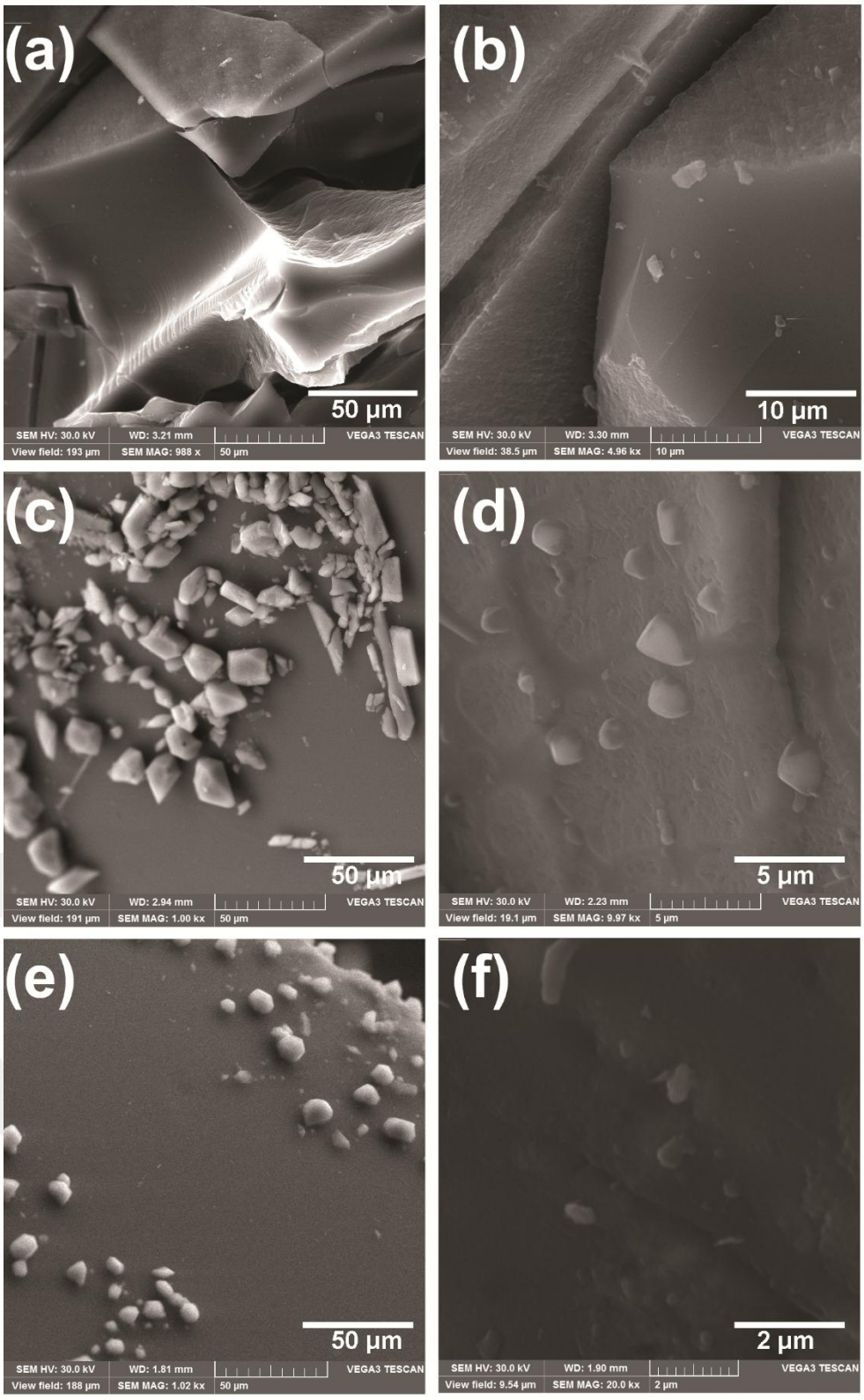


Figure 3.10 SEM images of (a)-(b) elemental sulfur, (c)-(d) poly(S-*r*-DVB) with 20wt% DVB, (e)-(f) poly(S-*r*-DVB) with 40wt% DVB at different magnifications.

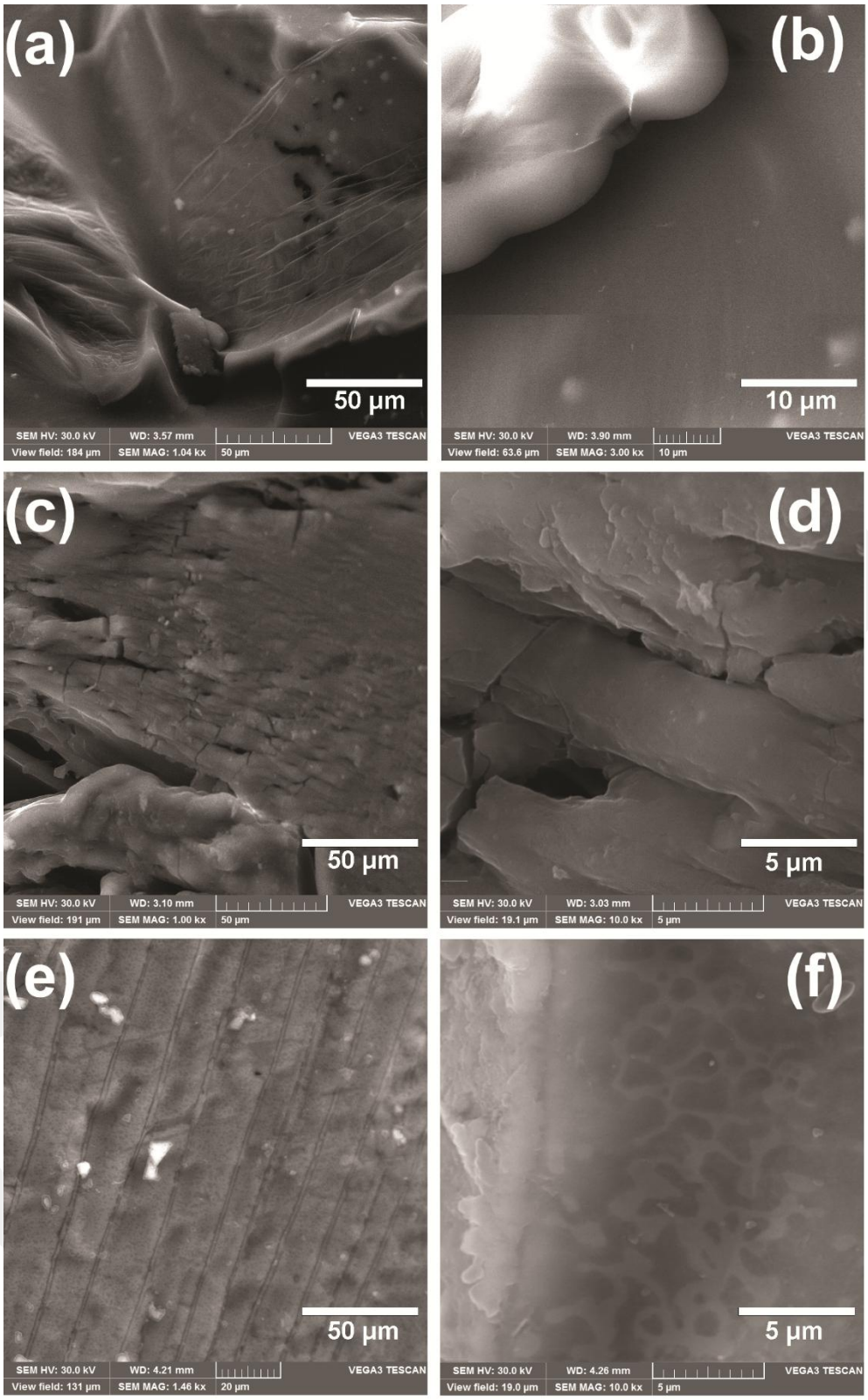


Figure 3.11 SEM images of (a)-(b) poly(S-*r*-DVB) with 50 wt% DVB, (c)-(d) poly(S-*r*-DVB) with 80wt% DVB and (e)-(f) PDVB at different magnifications.

3.9 Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

Thermal stability of elemental sulfur, PDVB and poly(S-*r*-DVB) copolymers was investigated by TGA. As seen in **Figure 3.12**, the elemental sulfur starts to lose its weight at around 180 ^{o}C due to partial sublimation or decomposition, whereas the starting decomposition temperature is around 400 ^{o}C for PDVB. By increasing the amount of DVB in poly(S-*r*-DVB) copolymers the decomposition temperature shifted to higher temperatures. Also, unlike PDVB, after heating up to 600 ^{o}C, the amount of substance remained in the sample holder increased up to 30% by increasing DVB amount in the samples, indicating the formation of copolymers with a robust structure.

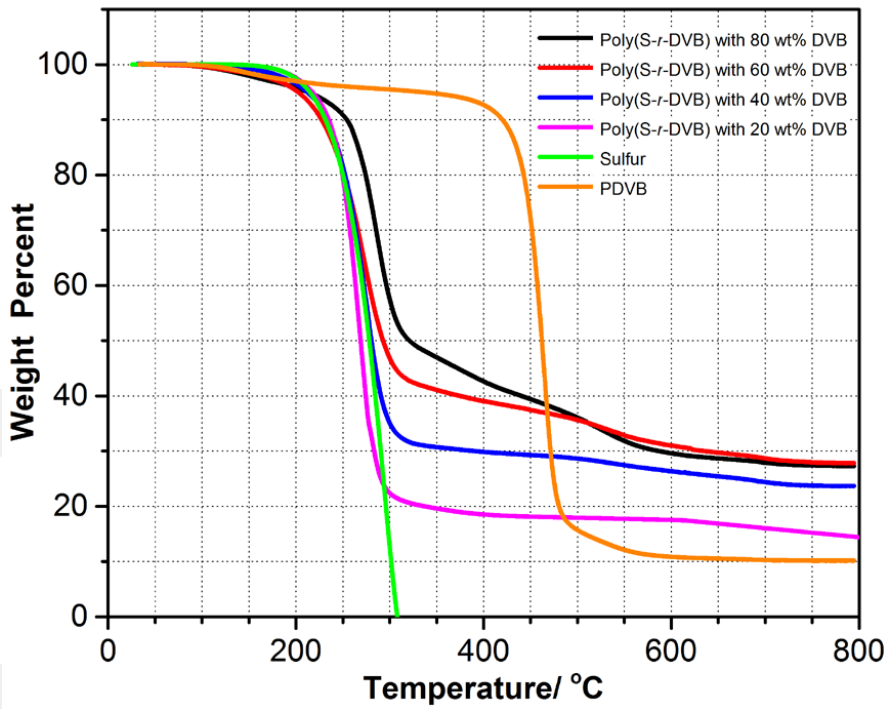


Figure 3.12 TGA of elemental sulfur, PDVB and poly(S-*r*-DVB) copolymers.

DSC studies were carried out up to 150 ^{o}C and a single melting transition (T_m) for the monoclinic phase of sulfur was observed for commercially available sulfur at about 119 ^{o}C in **Figure 3.13(a)**. On the other hand, no melting transition were observed for poly(S-*r*-DVB) copolymers synthesized with 20 wt% more than 20wt% of DVB, which verified these copolymers to be amorphous materials (**Figure**

3.13(b)-(c)). Additionally the glass transition temperature (T_g) of these polymers increased when the wt% of DVB increased.

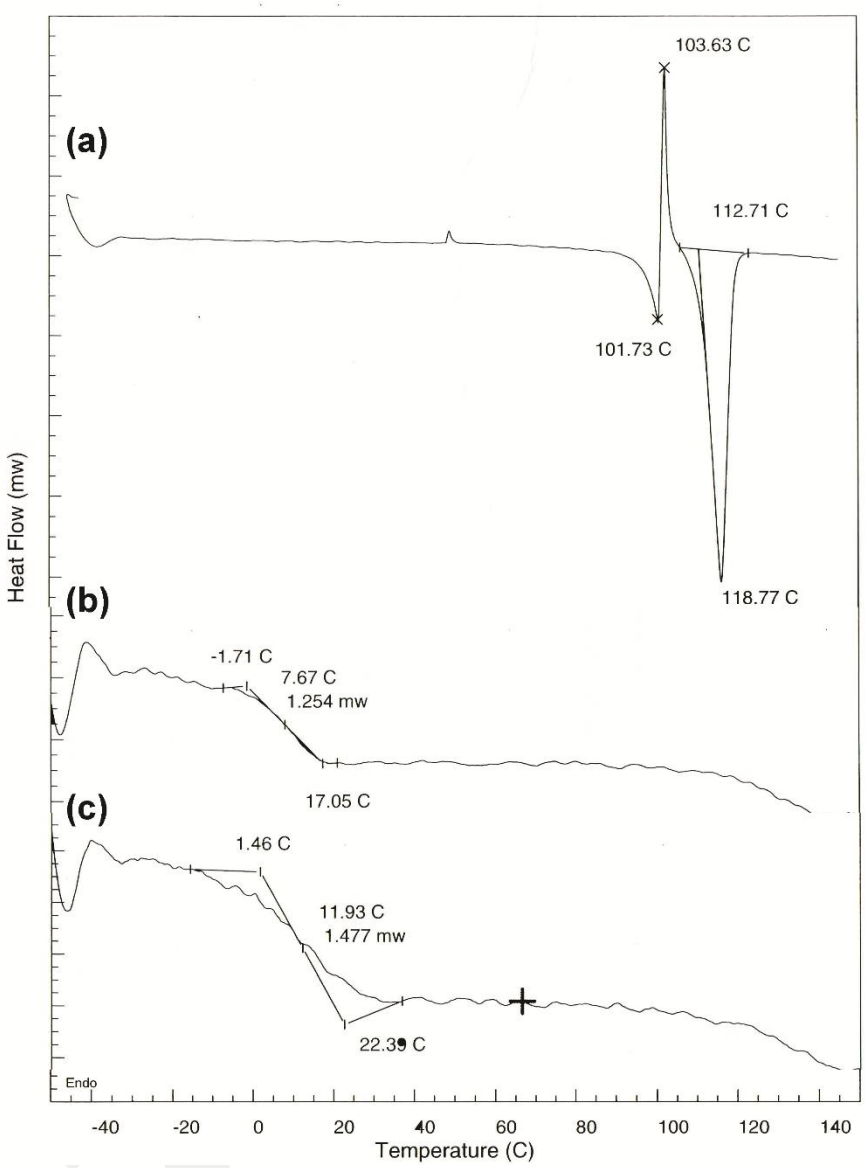


Figure 3.13 DSC thermograms of (a) elemental sulfur, (b) poly(S-*r*-DVB) with 20 wt% DVB and (c) poly(S-*r*-DVB) with 40 wt% DVB.

3.10 IR-Transmittance

IR-transmittance materials, which detect radiation in the infrared range of 0.9 to 14 micrometer in the electromagnetic spectrum, can be thought as advanced materials in infrared imaging science such as thermal imaging and thermal video. It well known that all objects with a temperature above zero absolute emit infrared radiation and therefore thermography makes any object to see. Also, it is possible to

see variations in temperature and thus warm objects can be seen well against cooler objects. Due to these properties, IR-transmittance materials are promising materials in military and surveillance cameras. Germanium and silicon are examples of IR transmittance materials.

In order to investigate the percent transmittance of poly(S-*r*-DVB) copolymers, they were coated as tin films on germanium and silicon substrate (see **Figure 3.14**) to compare their percent transmittance. As shown in **Figure 3.15**, both samples exhibited the similar percent transmittance of 55%T. Also, the similar behavior was observed when silicon was used instead of germanium as shown in **Figure 3.16**.

After these promising results, in future work, a thick film of pure poly(S-*r*-DVB) with 60 wt% DVB will be prepared and by comparing with germanium and silicon substrates the usability of poly(S-*r*-DVB) copolymers can be tested in the applications of thermal imaging and thermal video.

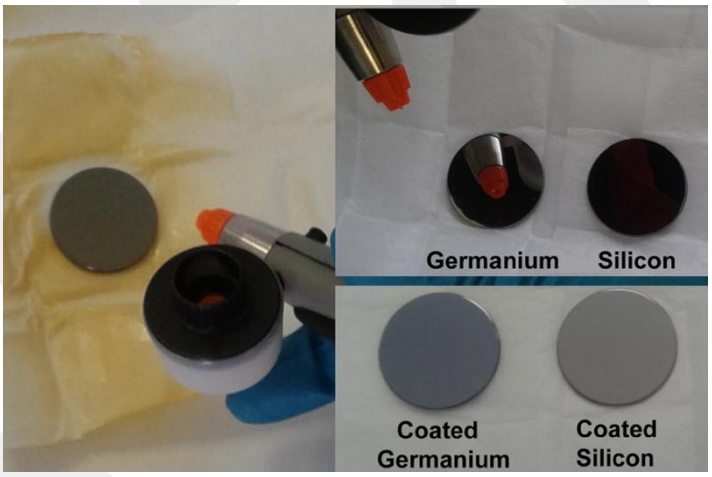


Figure 3.14 The coating of germanium and silicon with poly(S-*r*-DVB) with 60 wt% DVB dissolved in $CHCl_3$ via a spray coating method.

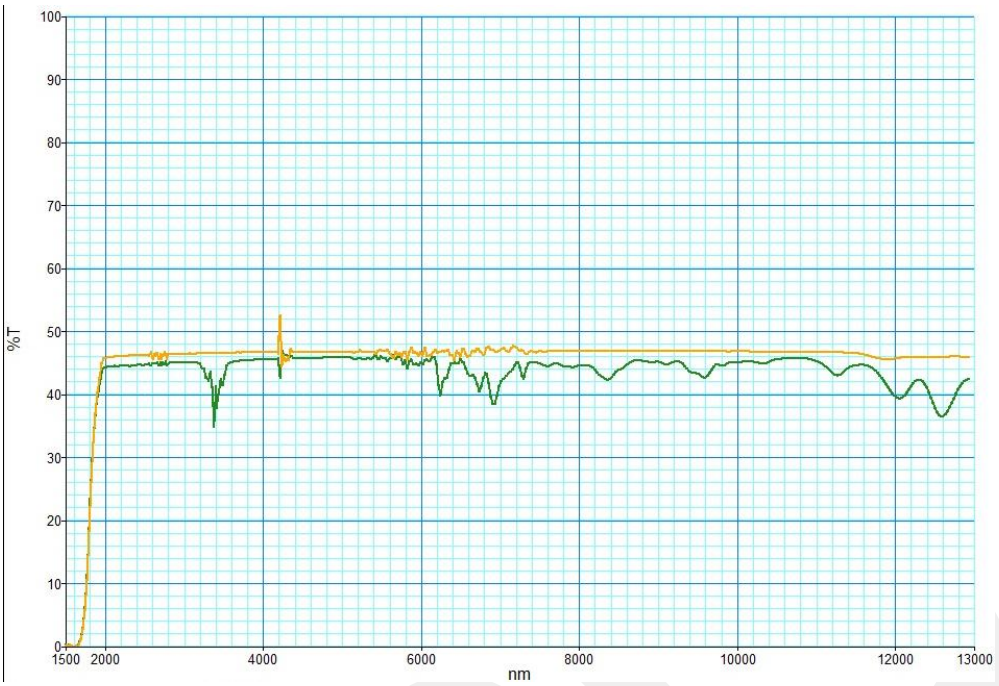


Figure 3.15 The comparison of percent transmittance between Germanium substrate (orange line) and coated substrate with poly(S-*r*-DVB) with 60 wt% DVB (green line).

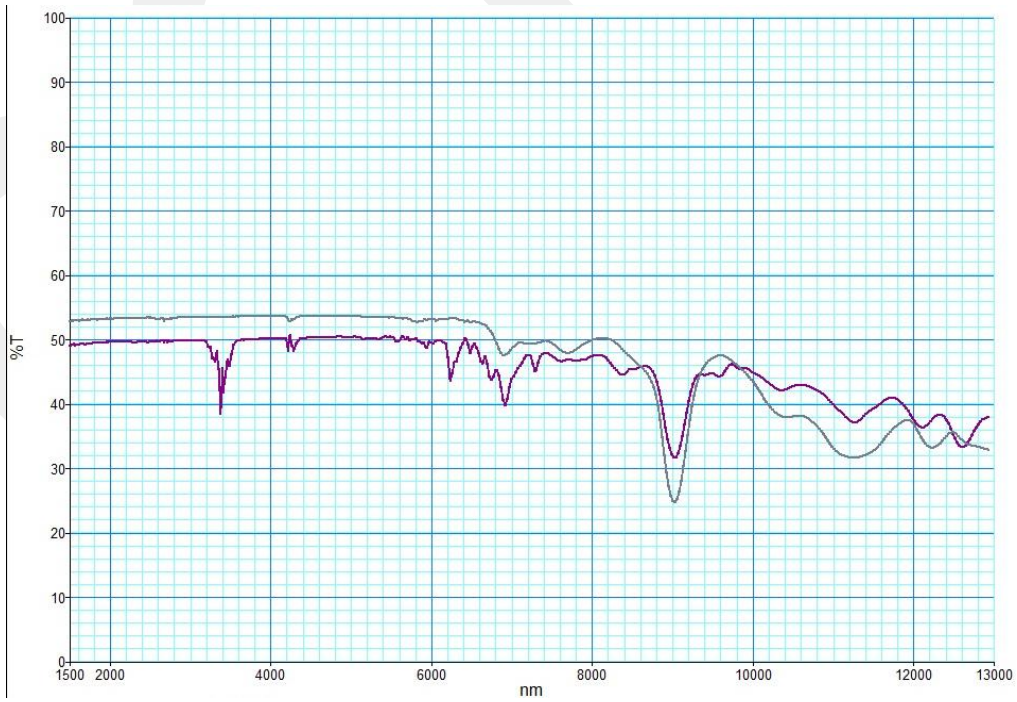


Figure 3.16 The comparison of percent transmittance between silicon substrate (purple line) and coated substrate with poly(S-*r*-DVB) with 60 wt% DVB (grey line).

CHAPTER 4
CONCLUSIONS

In this study, a number of new elemental sulfur based polymeric materials called poly(sulfur-*random*-divinylbenzene) (poly(S-*r*-DVB)) were synthesized chemically by using a ring opening polymerization method in the presence of a mixture of o-, m- and p-diviniylbenzene (DVB) as a crosslinker.

The related copolymers containing various amount of DVB crosslinkers are soluble in common solvents like tetrahydrofuran, dichloromethane and chloroform, and they can be coated on any surface as thin film. The amount of DVB crosslinker in the copolymer determined the solubility of the obtained materials.

The characterization of the materials were performed by using nuclear magnetic resonance, fourier transform infrared and Raman spectroscopies. They confirmed the formation of new covalent bond between carbon and sulfur atoms. The morphological properties were monitored via scanning electron microscope technique, which showed that a homogeneous and uniform copolymer could be obtained by using 50 wt% or more than 50 wt% DVB. Thermal analysis showed that an increase in the amount of DVB in the copolymers resulted in an increase in the thermal decomposition temperature and amorphous materials could be formed, which was confirmed by DSC thermograms.

On the other hand, poly(S-*r*-DVB) copolymers exhibited 50 %T of percent transmittance at a range of 1500 to 13000 nm in electromagnetic radiation spectrum, which can make them alternative candidates to be amenable use in military and surveillance cameras.

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