

Elemental sulfur-based polymeric materials: Synthesis and characterization

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ABSTRACT: New elemental sulfur-based polymeric materials called poly(sulfur-*random*-divinylbenzene) [poly(*S-r*-DVB)] were synthesized by ring opening polymerization via inverse vulcanization technique in the presence of a mixture of *o*-, *m*-, and *p*-divinylbenzene (DVB) as a cross-linker. A clear yellow/orange colored liquid was obtained from the elemental sulfur melted at 160 °C and then by adding various amounts of DVB to this liquid directly via a syringe at 200 °C viscous reddish brown polymeric materials were obtained. The copolymers are soluble in common solvents like tetrahydrofuran, dichloromethane, and chloroform, and they can be coated on any surface as a thin film by a spray coating technique. The characterization of the materials was 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 thermal decomposition temperature. On the other hand, poly(*S-r*-DVB) copolymers exhibited good percent transmittance as 50% T between 1500 and 13,000 nm in electromagnetic radiation spectrum, which makes them good candidates to be amenable use in military and surveillance cameras. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43655.

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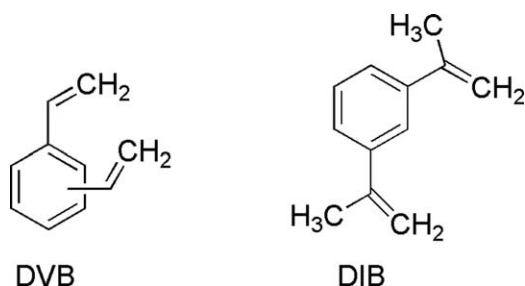
INTRODUCTION

Sulfur-containing polymers have come into considerable attention because of their remarkable properties which make them useful in a wide range of applications. They can be used as ion-exchange membranes,¹ engineering plastics,² high refractive index materials,^{3,4} etc. On the other hand, most of the used elemental sulfur is utilized mostly for the production of sulfuric acid and phosphates as fertilizers.^{5,6} Unfortunately, the existing applications meet a limited demand in industrial area and most of the elemental sulfur is stored above ground about seven million tons annually.^{5,6} The current techniques have a restricted requirement for sulfur and the researchers continue to develop new chemistry and processing techniques to consume the huge amount of sulfur as a novel feedstock.

Under normal circumstances the elemental sulfur melts into an obvious yellow-colored liquid at 120–124 °C. Rings with 8–35 atoms are established and additional warming of the liquid sulfur higher than 159 °C result in polymeric sulfur via ring-opening polymerization.⁷ The diradical way of polymeric sulfur displays a deep-red color and depolymerizes back again to the monomeric ring types when cooled to room temperature.

Stabilizing of the diradical polymeric sulfur with dienes, such as dicyclopentadiene, via copolymerization can be used to prevent the depolymerization. Among these attempts, the sulfur-based composites and copolymers make the elemental sulfur a promising alternative to hydrocarbon-based materials.^{8–22} Unfortunately, these materials either have low level of sulfur content into the ultimate copolymer or form polymeric components with restricted processability and tenability of properties.

Recently, inverse vulcanization technique has been used to get a very high feed ratio of elemental sulfur in the corresponding copolymer.^{5,23–25} 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. In this method, it is well known that elemental sulfur can be polymerized by heating at high temperatures in the presence of 1,3-diisopropylenebenzene (DIB) used as a cross-linker.⁵ Molten elemental sulfur is obtained as a clear yellow liquid at about 160 °C (the floor temperature), and after the addition of DIB the viscosity of the mixture sharply



Scheme 1. Chemical structures of DVB and DIB cross-linkers.

increases within minutes of the reaction at a temperature higher than 185 °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 cross-linkers when the temperature of the reaction is cooled to room temperature. This synthetic approach opened up a new door for the synthesis of new polymeric materials with promising optical and electrochemical properties.

After the pioneering work of Pyun and his colleagues, the polysulfur called poly(sulfur-random-1,3-diisopropenylbenzene) poly(*S-r-DIB*) copolymer obtained via vulcanization methods was used as photoelectrocatalysts for photoelectrochemical water splitting,²⁶ IR optical materials,²⁷ potential cathode materials for Li-S batteries,^{25,28,29} and matrixes for the synthesis of the nanoparticles.^{6,30–32}

Today, except for a few studies, there is a limited usage of elemental sulfur as a feedstock for getting new polymeric materials. Unfortunately, in spite 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. Under the light of this requirement, herein in order to obtain chemically stable and processable polymers with high sulfur feed ratio, a new cross-linker called divinylbenzene (DVB) was used with melted sulfur to get new copolymers via inverse vulcanization method. DVB has a similar chemical structure with DIB without methyl group and is cheaper than DIB.

EXPERIMENTAL

The elemental sulfur sublimed, 99.5% (Acros) was used as received. A mixture of ortho-, meta-, and para-DVB (Merck) as a cross-linker (Scheme 1) was freshly purified by using a column chromatography since the stock solution consists of a mixture of DVB and ethylvinylbenzene. Styrene (Sigma-Aldrich) was used without further purification. Also, the solvents tetrahydrofuran (THF), dimethylformamide (DMF), acetone, dichloromethane, chloroform, dimethylsulfoxide (DMSO), propylene carbonate (PC), sulfuric acid, and 1,2-dichlorobenzene (1,2-DCB) were used as received.

Polymerization of Elemental Sulfur with DVB

S₈ with different mass percentages from 10% to 90% by weight in a test tube equipped with a magnetic stirrer was heated up to 160 °C in a thermostated oil bath until a clear yellow colored molten phase was obtained. Then, freshly 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 up to 200 °C with continuous mixing. By passing time two layers mixed into each other to get a homogeneous solution. After that, the magnetic stirrer bar was removed and the corresponding mixture was heated at 200 °C for 10 min. 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.

Characterization

¹H NMR spectra of obtained polymers were recorded on a Bruker Spectrospin Avance DPX-400 Spectrometer with CDCl₃ and chemical shifts were given relative to tetramethylsilane as the internal standard. Chemical shifts are reported in terms of ppm and that of CDCl₃ is 7.26 ppm. FTIR spectra were recorded on Nicolet 510 FTIR with attenuated total reflectance. Raman spectra were monitored by using a Helix Jobin Yvon, HR-800 Raman Spectrometer. Molecular weight measurements were performed via Shimadzu LC-20A/Prominence Gel Permeation Chromatography (GPC) according to polystyrene standards. Micrographs were collected at 30 kV and all other operating information is given in the related figures. Scanning electron microscope (SEM) analysis was monitored by using

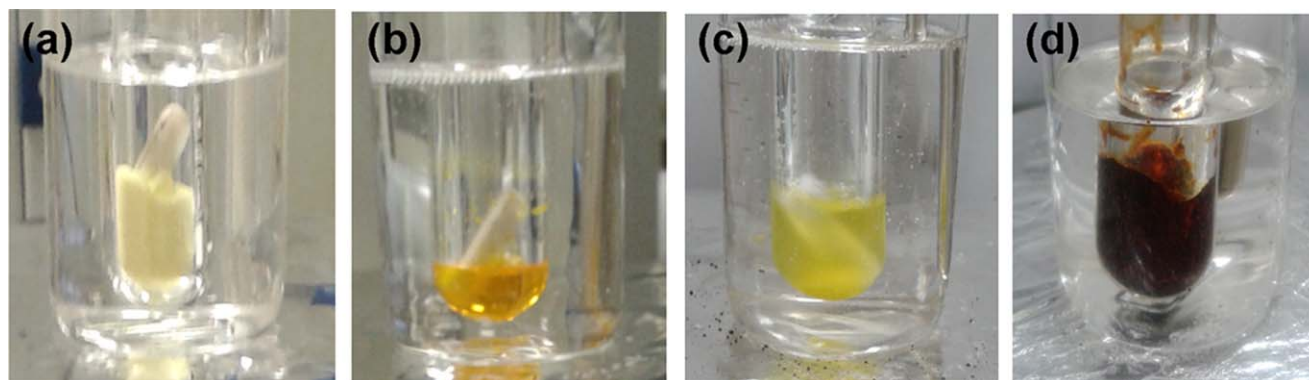
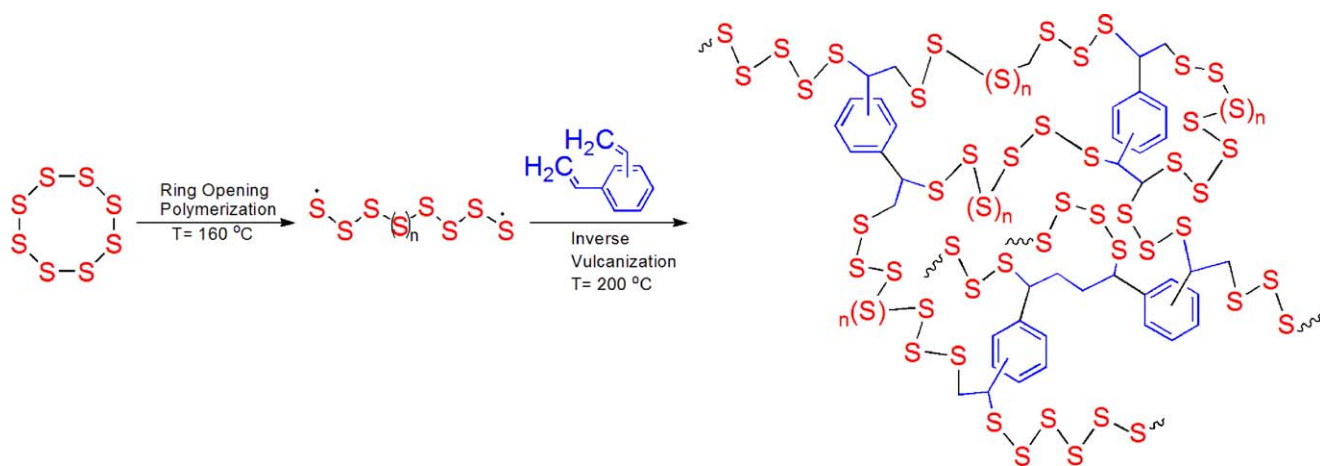


Figure 1. Polymerization of elemental sulfur with DVB: (a) elemental sulfur at room temperature, (b) molten sulfur at 160 °C, (c) molten sulfur with DVB at 160 °C, and (d) poly(*S-r-DVB*) after 10 min by heating at 200 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 2. Copolymerization of elemental sulfur (S_8) with DVB. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Quanta 200 FEG Model. Energy-dispersive X-ray (EDS) analysis was performed by using environmental scanning electron microscope (ESEM) FEI QUANTA 200 F. Samples were coated with

Au/Pd with a thickness of 10 nm by using precision etching coating system (PECS): GATAN Model 682. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA)

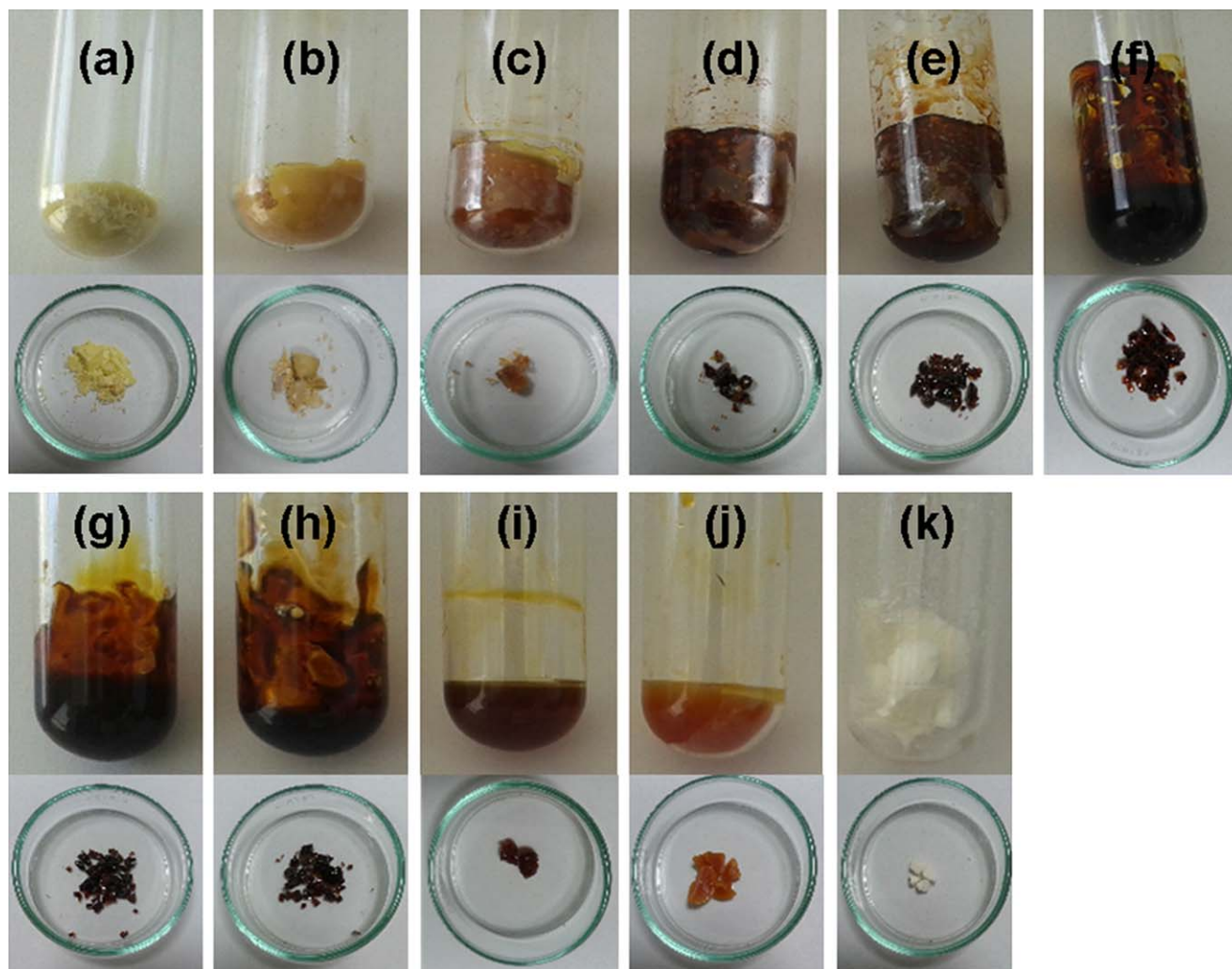


Figure 2. The pictures of (a) elemental sulfur and poly(S-r-DVB) with (b) 10 wt % DVB, (c) 20 wt % DVB, (d) 30 wt % DVB, (e) 40 wt % DVB, (f) 50 wt % DVB, (g) 60 wt % DVB, (h) 70 wt % DVB, (i) 80 wt % DVB, (j) 90 wt % DVB, and (k) polydivinylbenzene (PDVB). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

were performed via Q500 Model and DSC device Model 204-F1. In order to measure the IR transmittance of the copolymers, they were coated on substrates via a spray coating technique (Deluxe Professional Airbrush by Aztek A4709).

RESULTS AND DISCUSSION

First of all, the copolymerization of elemental sulfur was performed in the presence of styrene as a cross-linker. The comonomers are miscible at 200 °C and a sharp increase in the viscosity of the mixture was obtained at the end of heating about 10 min. 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.

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

Aforementioned results showed that a mixture of ortho-, meta-, and para-DVB can be an appropriate cross-linker to get sulfur-based copolymers. Therefore, the mixture of DVB was purified freshly by using a column chromatography and then added to molten elemental sulfur at 160 °C. The mixture was heated to 200 °C and a homogeneous mixture was formed. At the end of heating for 10 min, chemically stable copolymers were obtained and they did not change their color over a period of several months under ambient conditions. 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, the copolymerization procedure can be summarized like that: first of all, the elemental sulfur was melted at 160 °C and therefore ring opening polymerization of the S₈ was promoted and a clear yellow/orange colored liquid was obtained. Then, DVB was added directly to the molten sulfur via a syringe and continue to further mixing at 200 °C for 10 min to get a viscous reddish brown polymeric material called poly (sulfur-random-DVB) [poly(S-r-DVB)] (see Figure 1 and Scheme 2).

The suitable polymerization temperature of elemental sulfur with DVB had been studied, where the copolymerization procedure was repeated at different temperatures 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 weight) in order to determine the suitable temperature for the copolymerization. Two hundred °C was selected as a suitable copolymerization temperature. The polymerization performed at 185 °C and 190 °C did not result in a homogenous polymeric material and the products did not have a uniform color: 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 over 200 °C, homogeneous polymeric products were obtained and they persisted their colors by passing time but

Table 1. The Solubility of the Copolymers in Organic Solvents

Solvents	Polymers										
	Poly(S-r-DVB) with 10 wt % DVB	Poly(S-r-DVB) with 20 wt % DVB	Poly(S-r-DVB) with 30 wt % DVB	Poly(S-r-DVB) with 40 wt % DVB	Poly(S-r-DVB) with 50 wt % DVB	Poly(S-r-DVB) with 60 wt % DVB	Poly(S-r-DVB) with 70 wt % DVB	Poly(S-r-DVB) with 80 wt % DVB	Poly(S-r-DVB) with 90 wt % DVB	Polysulfur	
THF	is	is	is	ss	s	s	s	s	is	is	
DMF	is	is	is	is	ss	ss	is	is	is	is	
Acetone	is	is	is	is	is	is	is	is	is	is	
CH ₂ Cl ₂	is	is	is	ss	s	s	is	is	is	is	
CHCl ₃	is	is	ss	ss	s	s	s	s	is	is	
DMSO	is	is	is	is	is	is	is	is	is	is	
PC	is	is	is	is	is	is	is	is	is	is	
conc. H ₂ SO ₄	s	is	is	ss	s	s	s	s	s	is	
1,2-DCB	s	is	s	s	s	s	s	s	s	is	

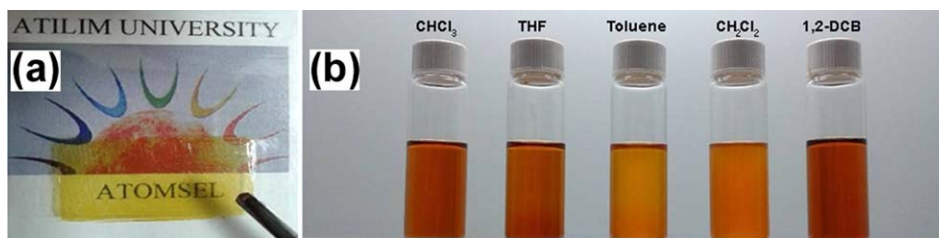


Figure 3. Digital photographs of poly(*S-r*-DVB) with 50 wt % DVB (a) film and (b) dissolved in CHCl_3 , THF, toluene, CH_2Cl_2 , and 1,2-DCB. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

these temperatures are very close to the beginning of the decomposition temperature of the copolymers based on elemental sulfur.⁵ Therefore, a temperature of 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 cross-linker as shown in Figure 2.

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 I represented the solubility of the copolymers in various organic solvents. As shown in Table I 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-dichlorobenzene (1,2-DCB), etc. and they have brown solution (see Figure 3). 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.

It is possible to use NMR spectroscopic technique to investigate the chemical structure of soluble copolymers. As shown in Figure 4, ^1H NMR spectrum of poly(*S-r*-DVB) with 50 wt % DVB confirmed the presence of cross-linkers in/between the polymer chains. For example, the broad peaks between 6.8 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 and 1.0 ppm. On the other hand, the presence of a broad peak centered at 4.3 ppm confirmed the hydrogens in $-\text{CH}_2-\text{S}-$ covalent bonds.⁵ It can be easily concluded that the obtained polymers

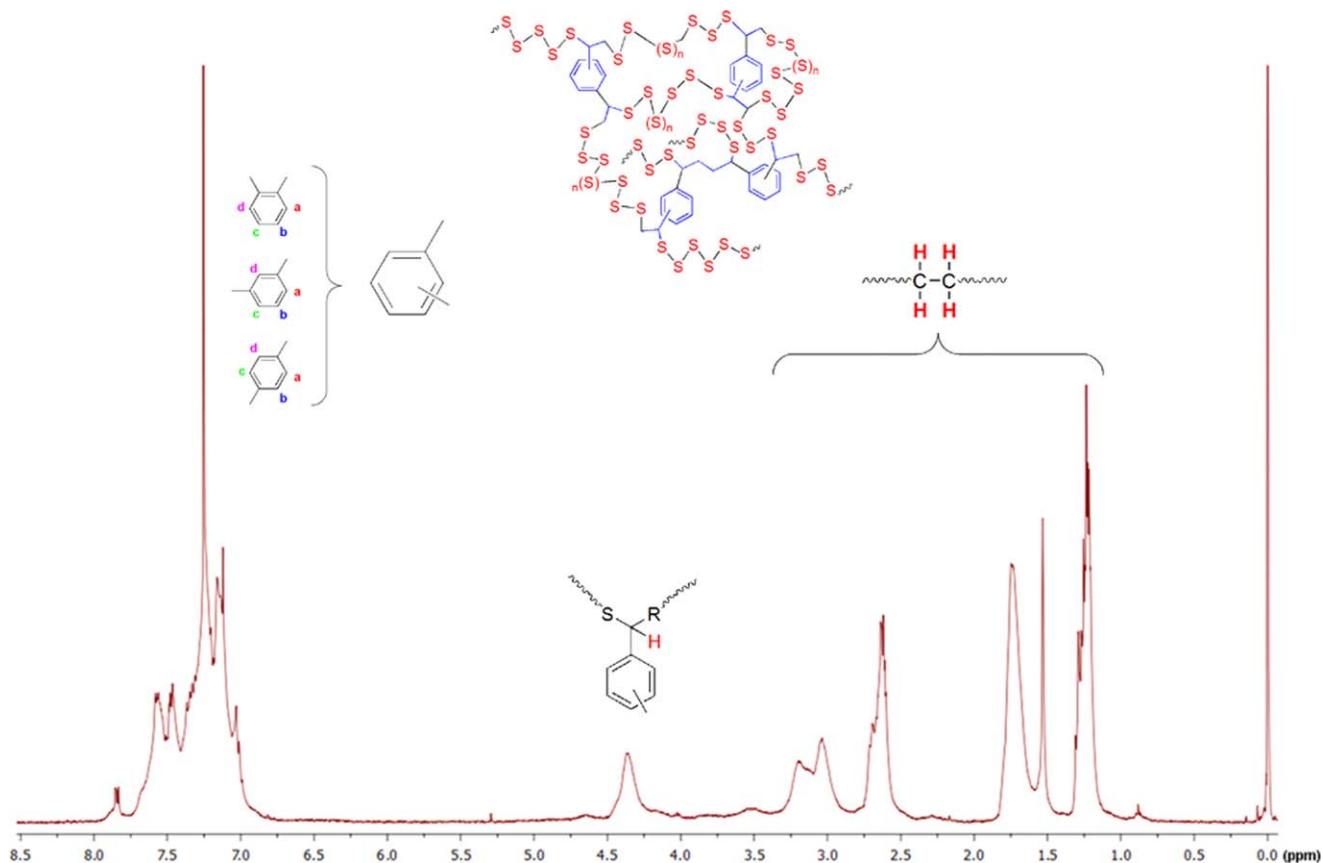


Figure 4. ^1H NMR spectrum of poly(*S-r*-DVB) with 50 wt % DVB in CDCl_3 . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

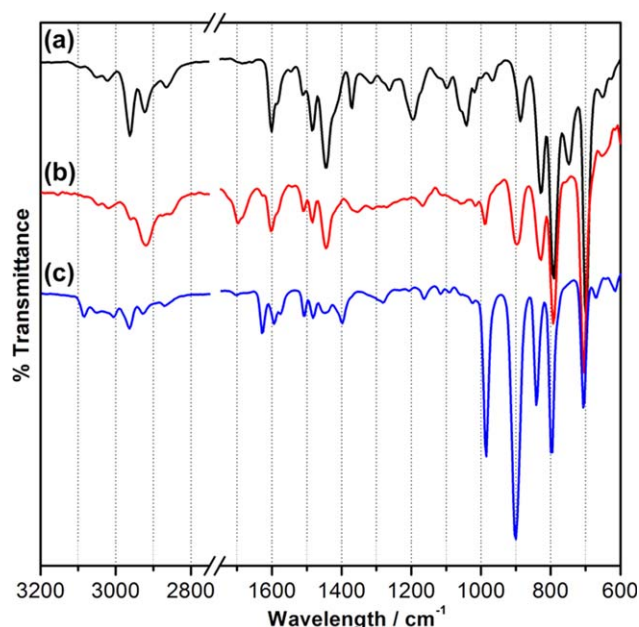


Figure 5. FTIR spectra of (a) poly(*S-r*-DVB) with 50 wt % DVB, (b) PDVB, and (c) DVB. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

are the copolymers bearing S-S repeating units and DVB-based cross-linkers.

FT-IR spectrum of poly(*S-r*-DVB) with 50 wt % DVB was compared those of PDVB and DVB as shown in Figure 5. First of all, the spectrum of poly(*S-r*-DVB) looks like that of PDVB, as expected. Except for PDVB, the band appeared at around 2950 cm^{-1} can be ascribed to the methylene stretching in $-\text{CH}-\text{CH}_2-$ and $-\text{S}-\text{CH}_2-$ units in poly(*S-r*-DVB). In addition, the formation of the C-S chemical bond in the copolymer can be confirmed by the peaks attributed to the C-S stretching observed at 705 , 1015 , and 1042 cm^{-1} .^{26,28} Also, the band at 900 cm^{-1} attributed to the $\text{C}=\text{CH}_2$ vinyl stretching has lost its intensity when compared to DVB, which confirmed the disappearance of vinylic groups during copolymerization.

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 II, GPC results showed that the copolymers have low weight-averaged molecular weight with high polydis-

Table II. GPC Results of Poly(*S-r*-DVB) Copolymers

Copolymers	M_w	M_n	$\text{PDI} = M_w/M_n$
Poly(<i>S-r</i> -DVB) with 50 wt % DVB	6300	2301	2.74
Poly(<i>S-r</i> -DVB) with 60 wt % DVB	4383	2165	2.02
Poly(<i>S-r</i> -DVB) with 70 wt % DVB	7393	3579	2.07
Poly(<i>S-r</i> -DVB) with 80 wt % DVB	19,420	4320	4.50

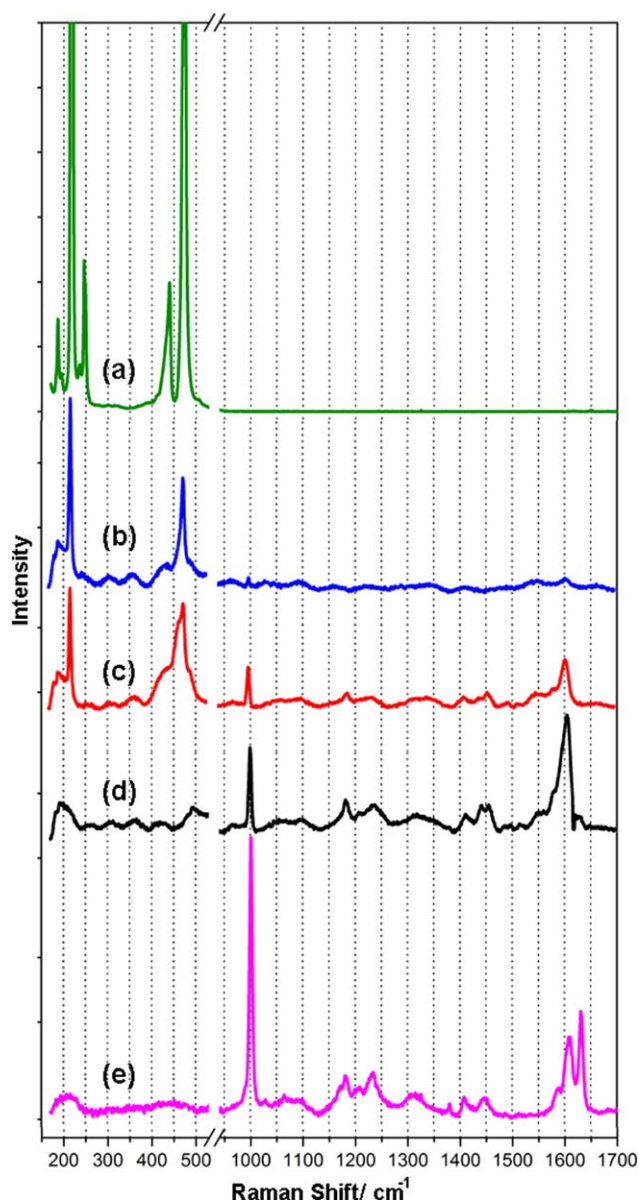


Figure 6. Raman spectra of (a) elemental sulfur, (b) poly(*S-r*-DVB) with 20 wt % DVB, (c) poly(*S-r*-DVB) with 40 wt % DVB, (d) poly(*S-r*-DVB) with 80 wt % DVB, and (e) PDVB. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

persity index (PDI). When compared to its poly(*S-r*-DIB) copolymer derivatives,⁵ the poly(*S-r*-DVB) copolymers with 50–80 wt % DVB have higher molecular weights with PDI between 2.02 and 4.50. The low 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”.⁵

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 6, S-S vibrational stretches at $239\text{--}483\text{ cm}^{-1}$ started to lose their intensities and new peaks attributed to the

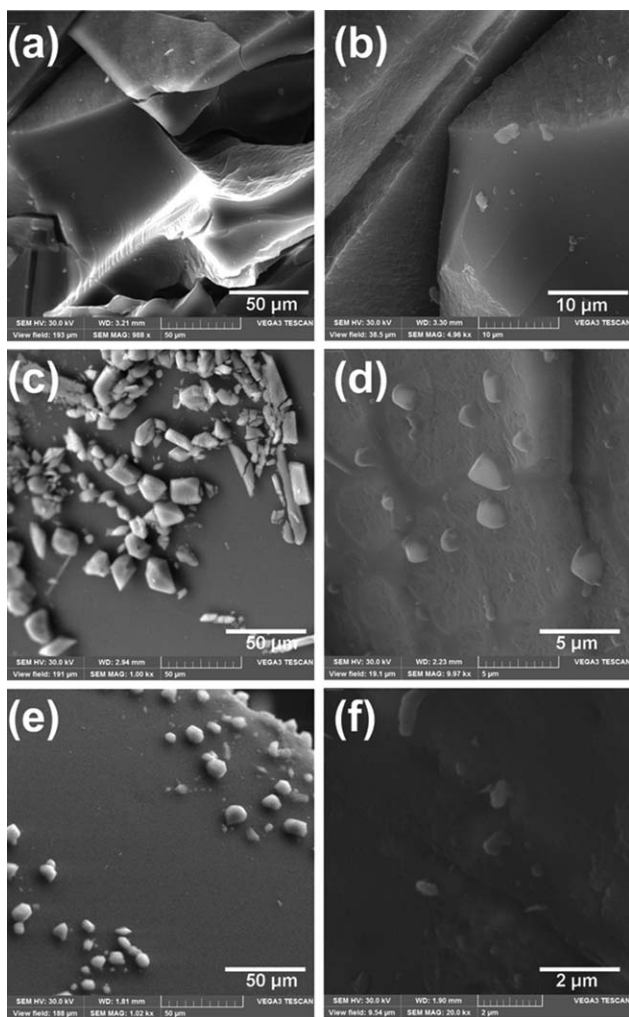


Figure 7. SEM images of (a,b) elemental sulfur, (c,d) poly(S-*r*-DVB) with 20 wt % DVB, (e,f) poly(S-*r*-DVB) with 40 wt % DVB at different magnifications.

aromatic stretches at 1001 and 1625 cm^{-1} appeared and started to intensify by an increase in the amount of DVB in the copolymer. As expected, the Raman spectra of PDVB and poly(S-*r*-DVB) with 80 wt % DVB are quite different in terms of peak intensity and Raman shift wavenumber. In the spectrum of the PDVB, the peak at 1001 cm^{-1} lost its intensity and the double peak between 1590 and 1650 cm^{-1} become a broad single band centered at 1605 cm^{-1} in the spectrum of poly(S-*r*-DVB) with 80 wt % DVB. Also, the peak appeared at 492 cm^{-1} confirmed the presence of sulfur in the poly(S-*r*-DVB) with 80 wt % DVB.

The scanning electron microscope (SEM) was conducted to produce the images of the polymer samples (Figures 7 and 8). The copolymers showed different morphologies depending on the amount of DVB used in copolymerization. For example, as shown in Figure 8(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. Also, the EDS spectra of the copolymers confirmed that elemental sulfur and DVB were on the top of poly(S-*r*-DVB) samples (Figure 9).

Thermal stability of elemental sulfur, PDVB and poly(S-*r*-DVB) copolymers was investigated by TGA. As seen in Figure 10, the elemental sulfur started to lose its weight at around 180°C because of the partial sublimation or decomposition, whereas the starting decomposition temperature is around 400°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°C , the amount of substance remained in the sample holder increased up to 30% by increasing DVB amount in the

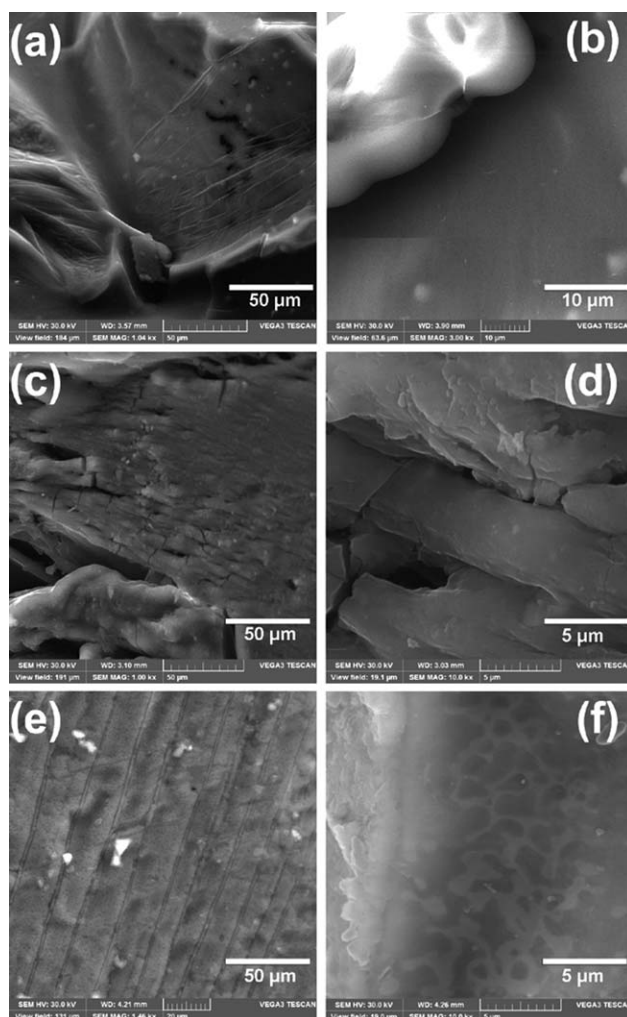


Figure 8. SEM images of (a,b) poly(S-*r*-DVB) with 50 wt % DVB, (c,d) poly(S-*r*-DVB) with 80 wt % DVB and (e,f) PDVB at different magnifications.

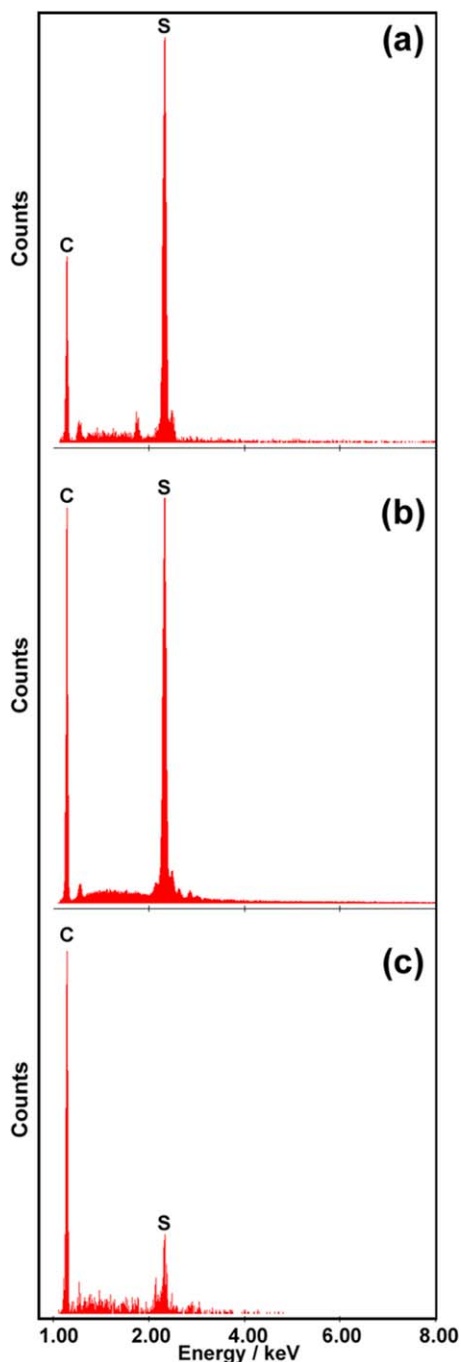


Figure 9. The EDS spectra of (a) poly(S-*r*-DVB) with 20 wt % DVB, (b) poly(S-*r*-DVB) with 50 wt % DVB, and (c) poly(S-*r*-DVB) with 80 wt % DVB. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

samples, indicating the formation of copolymers with a robust structure.

DSC studies were carried out up to 150 °C and a single melting transition (T_m) for the monoclinic phase of sulfur was observed for commercially available sulfur at about 119 °C in Figure 11(a). On the other hand, no melting transition was observed for poly(S-*r*-DVB) copolymers synthesized with 20 wt % more than 20 wt % of DVB, which verified these copolymers to be

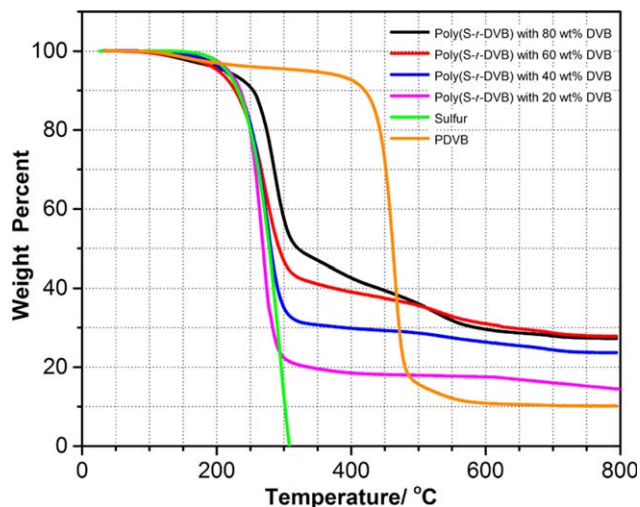


Figure 10. TGA of elemental sulfur, PDVB and poly(S-*r*-DVB) copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

amorphous materials [Figure 11(b,c)]. Additionally the glass transition temperature (T_g) of these polymers increased when the wt % of DVB increased.

IR-transmittance materials, which detect radiation in the infra-red range of 0.9–14 μm in the electromagnetic spectrum, can be

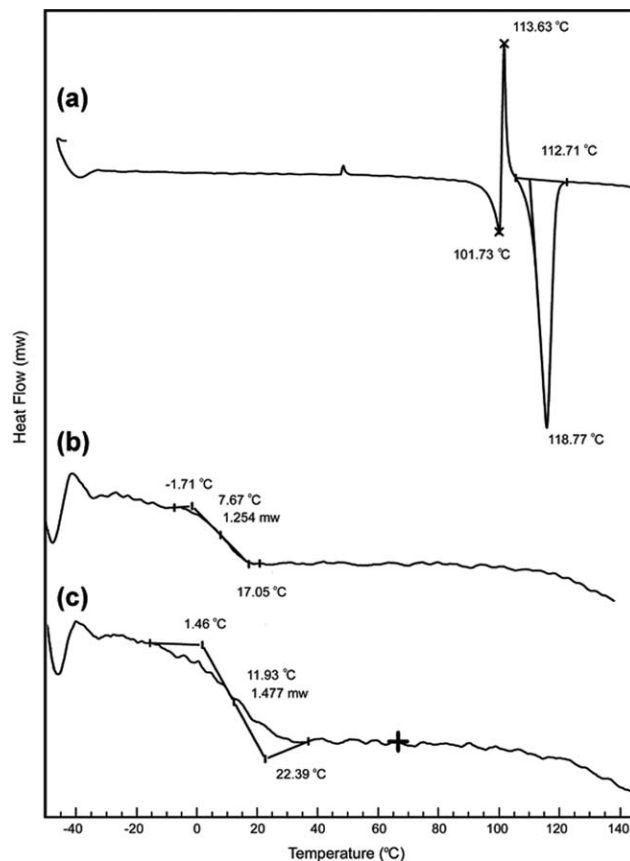


Figure 11. DSC thermograms of (a) elemental sulfur, (b) poly(S-*r*-DVB) with 20 wt % DVB, and (c) poly(S-*r*-DVB) with 40 wt % DVB.

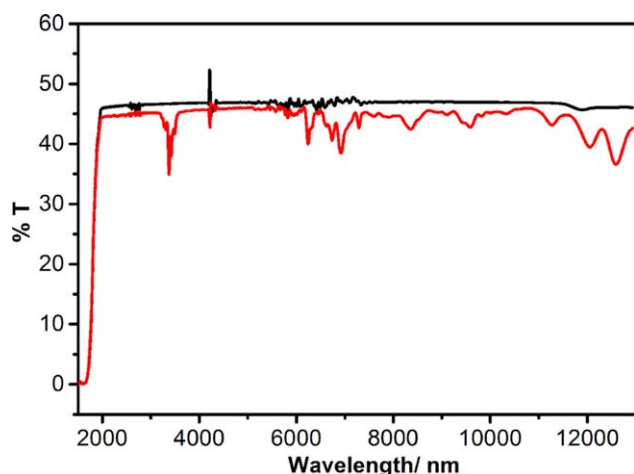


Figure 12. The comparison of percent transmittance between Germanium substrate (black line) and coated substrate with poly(*S-r*-DVB) with 60 wt % DVB (red line). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

thought as advanced materials in infrared imaging science such as thermal imaging and thermal video. It is well known that all objects with a temperature above the absolute 0 K 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. Because of 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 thin films on germanium and silicon substrate to compare their percent transmittance. As shown in Figure 12, 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 13.

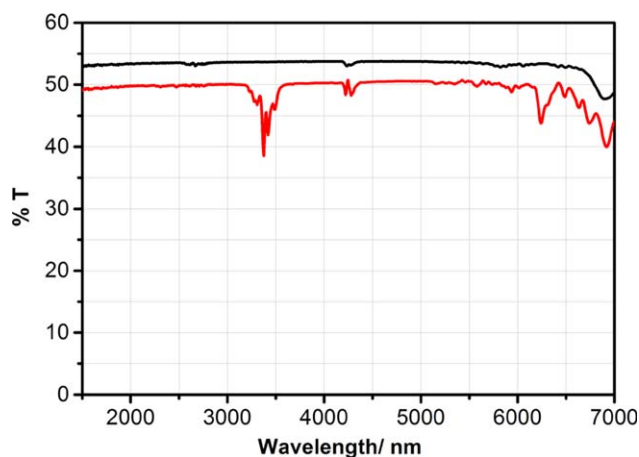


Figure 13. The comparison of percent transmittance between silicon substrate (black line) and coated substrate with poly(*S-r*-DVB) with 60 wt % DVB (red line). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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.

CONCLUSIONS

In this study, a number of new soluble and processable elemental sulfur-based polymeric materials called 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*-divinylbenzene (DVB) as a cross-linker. Homogeneous and uniform copolymers could be obtained by using 50 wt % or more than 50 wt % DVB. An increase in the amount of DVB in the copolymers resulted in an increase in the thermal decomposition temperature. Also, poly(*S-r*-DVB) copolymers exhibited 50% T of percent transmittance at a range of 1500–13,000 nm in electromagnetic radiation spectrum, which can make them alternative candidates to be amenable use in military and surveillance cameras.

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