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Synthesis, characterization and application of high sulfur content polymeric materials from fatty acids

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ABSTRACT

A new series of high sulfur content polymers containing various amounts of fatty acids (oleic acid (OA), linoleic acid (LA) and linolenic acid (LnA)) was synthesized via inverse vulcanization method and characterized successfully. In particular, the effect of double bonds and free alkyl chains on polysulfur copolymers has been investigated systematically by using OA with one double bond, LA with two double bonds and LnA with three double bonds. The copolymers with functional carboxylic acid groups are soluble in common organic solvents, processable and electroactive. Also, the usage of the copolymers was tested in the removal of methylene blue and as a cathode material in Li—S battery. Results showed that the polymers can be a potential material for use in dye removal.

1. Introduction

Sulfur is one of the most widespread elements in nature. Although million tons of sulfur was obtained from by-product of petroleum refinery annually [1], its usage areas are very limited: medicine, lamp wicks, fabric bleaching, gunpowder formulation and latex vulcanization in recent years [2]. However, since the amount of sulfur used in the industry is limited, millions of tons of sulfur obtained from petrochemical refineries continue to be stored in megaton blocks open to the environment. The large-scale use of sulfur in the industry and its conversion to high value-added products (such as high-tech polymers) will undoubtedly be an important advance. In addition, the fact that it is possible to obtain elemental sulfur not only from petrochemical refineries but also from geological sources provides a great advantage. At this point, scientists have a clear opportunity to produce new and added value sulfur-based materials.

Development of new synthetic methods necessary to modify or use elemental sulfur to obtain useful materials. Although natural sulfur has been used in the production of various copolymers in the past, difficulties still remain in the preparation of new materials with homogeneous, stable and controllable properties with high sulfur content. In conventional vulcanization, elemental sulfur is used in low amounts to crosslink latex or previously obtained polymers. Thanks to the pioneering work of Pyun and his colleagues, it has been possible to use sulfur much more in the industry [3]. High content (50–95% sulfur by mass) polysulfur copolymers could be obtained by using a small amount of alkene as a co-monomer via a method called inverse vulcanization. One of the advantages of the inverse vulcanization method is that all the reactants (alkene and elemental sulfur) are put into the reaction medium without requiring any solvent or reagent. Therefore, all reactants are converted into products and no material is left unreacted.

Pyun et al. [3] used 1,3-diisopropylbenzene as a crosslinker in the inverse vulcanization method. In polymerization, sulfur was firstly heated up to 185 °C and therefore ring opening polymerization was initiated, and then the crosslinker was added directly to the medium (10–50% by weight) and a vitrification was provided in the reaction medium. The resulting dark red polymeric glassy material has interesting chemical, material and optical properties due to the fact that its backbone is made of polysulfur. For example, the polymers are electroactive and have been used as new generation cathode materials for Li—S batteries [3]. Due to their high sulfur contents, the respective polymers are also potential materials that can be used in night vision,

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thermal imaging and other optical applications due to their high refractive indices and transparency in the middle IR region [4–6]. Also, it has been proven that the high sulfur content polymers are effective in the removal of heavy metal ion pollution [7–9].

Inverse vulcanization method is a very versatile method since a lot of sulfur copolymers can be obtained via using various crosslinkers [10,11]. This practice is an important step for synthesis/production by polymerizing sulfur with renewable vegetable oils such as palm, cottonseed, soy, caster and rapeseed oils in order to use them more effectively [12–22]. These oils are used in the production of the additive material in the industrial production [23]. The use of such vegetable oils as polymer precursors is gaining more attention in academia and industry. Many synthetic routes can be followed to produce such polymers. Vegetable oils are produced on the scale of one million tons per year and they are cheap and non-toxic reagents. It is well-known that the triglycerides and the acids of each vegetable oil are different.

Hoefling et al. [24] and Crockett et al. [7] reported sulfur-containing polymeric materials by using a number of commercial vegetable oils and used them in Li—S batteries as active cathode materials and in palladium, mercury and iron ions treatment. Approximately 80% of global oil and oil production is obtained from vegetable oils and 20% from animal fats. About 25% of the vegetable oil production is derived from soy, followed by palm oil, rapeseed, and sunflower oil [25,26]. Coconut and palm kernel oil contain high levels of saturated fatty acids and are essential for the production of surfactants. High purity fatty acids can be prepared from these vegetable oils after chemical transformations: oleic acid (OA) from sunflower, linoleic acid (LA) from soybean, linolenic acid (LnA) from linseed and ricinoleic acid from castor oil can be obtained in high amounts and purity (Fig. 1). As a result, vegetable oils are expected to play a key role in polymer production from renewable resources in the future [27,28].

Considering the above information, in this study a new series of high sulfur content (1–99% by weight) copolymers will be synthesized using vegetable oils (in the range of 99–1% by weight) via inverse vulcanization technique. The boiling points of fatty acids are very suitable for inverse vulcanization, which is usually carried out at 185 °C, since the boiling point of fatty acids is quite high. Boiling points of OA, LA and LnA are 360, 230 and 230 °C, respectively. In particular, the effect of double bonds and free alkyl chains in polysulfur copolymers will be investigated systematically on the solubility and processability since OA, LA and LnA have one, two and three double bonds, respectively. Also, when compared to triglycerides, these fatty acids have one reactive functional group (carboxylic group, -COOH) and it is possible to functionalize the polysulfur copolymers bearing these groups via post polymerization [29]. For example, carboxylic acid groups can be used to form ether and amide linkages within and/or between chains by using alcohol and amine reactants, respectively. Therefore, we assumed that the modified polysulfur copolymers can represent various properties like higher molecular weight, different optical, electrochemical, and thermal properties, as well as different applications such as sensors. Also, it will be possible to synthesize new polyester and polyamide derivatives containing high amount of sulfur in their structures.

After the characterization (NMR, Raman, FTIR, UV, GPC, SEM, DSC, TGA etc.) of the copolymers, their potential use will be investigated as cathode materials in Li—S batteries and in the dye removal. If aforementioned aims are achieved successfully, it will be possible to use waste sulfur and renewable plant fatty acids in huge amounts for sustainable synthesis/ production in the polymer industry.

2. Experimental

Elemental sulfur (Acros, 99.5%), oleic acid, (OA, Hiegel De), linoleic acid (LA, Tokyo *Chemical* Industry), linolenic acid (LnA, Tokyo *Chemical* Industry), the solvents (Sigma-Aldrich) (hexane, acetone, chloroform, dichloromethane (DCM), dimethylsulfoxide (DMSO), dimethylformamide (DMF), ethyl acetate, tetrahydrofuran (THF), toluene, ethanol and benzene), methylene blue (MB) dye (Sigma Aldrich), titanium dioxide nanoparticles (Degussa P25)), lithium foil (Sigma-Aldrich, 99.9%), conductive carbon (Super-P, Timcal), polyethylene binder (Avg. Mw ~4000 g/mol, Sigma-Aldrich), polypropylene separator (Celgard), conductive carbon coated aluminum foil current collector (MTI), and the conventional 1 M LiTFSI (lithium bis(trifluoromethane)sulfonimide) in DOL:DME (1,3-dioxolane: dimethoxyethane) 1:1 vol. electrolyte with 1% *w*/w $LiNO_3$ as additive were used as received. CR2032 coin cell cases (MTI) were soxhlet extracted using ethanol, dried in oven and stored in an Argon filled glove box.

Attenuated Total Reflectance (ATR) unit with Thermo Scientific Nicolet iS10FTIR spectrometer device was used for Fourier transform infrared (FTIR) spectra. Nuclear Magnetic Resonance (NMR) spectra of the polymers were recorded by a Bruker DPX-400 Spectrometer in DMSO or d-$CHCl_3$. Tetramethylsilane is used as an internal standard to interpret the chemical shifts in ^1H and ^{13}C NMR spectra. Gel Permation Chromatography(GPC) measurements were performed using Malvern-Omnisec system coupled with Viscotek T6000M column and T6000M guard column at 35 °C. All copolymer samples are fully soluble in THF solvent. Measurement data were collected with using polystyrene standarts. A mobile phase of THF was used with a flow rate of 1 mL/min. GPC data was analyzed using universal calibration in the range of 1.2×10^3–6.0×10^6. The QUANTA 400F Field Emission device was used for scanning electron microscopy (SEM) images of the polymers. TA Instruments SDT 650 Simultane and Perkin Elmer Diamond devices were used for thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) measurements of the polymers, respectively. For TGA measurements, the samples were heated up to 800 °C using a 10 °C/min heating rate and for DSC measurements, the samples were firstly cooled to −50 °C and waited for 5 min at this temperature, and then heated to 200 °C at 10 °C/min heating rate.

The copolymers were put in a test tube as approximately 10 mg in 1 mL of solvent for the solubility tests. Test tubes were shaken for 24 h. After waiting 1 h without shaking to see whether or not there is a precipitate in the test tubes, the solubility properties of the polymers were determined.

Shimadzu UV-1800 UV–Vis Spectrophotometer was used to figure out the percent degradation of MB dye solution after irradiation. ATLAS Solar Simulator equipped with metal halide lamp operated at 150 W was used as the light source for the photocatalytic processes.

All the battery related chemicals and materials were stored and manipulations were performed in an Innovative Technology IL-2GB Inert Lab Two Glove Box under 99.9% dry argon atmosphere with oxygen and moisture level below 1 ppm. Battery cycling was done on MTI 8 channel battery analyzer at a rate of C/10 from 1.7 to 2.6 V.

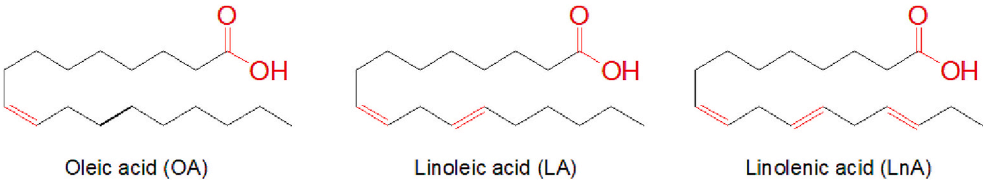

Fig. 1. Chemical structures of some fatty acids derived from vegetable oils.

2.1. *Synthesis of Poly(sulfur-random-fatty acid) (Poly(S-r-FA)) Copolymers with 50% Sulfur by Weight*

Elemental sulfur (2.0 g) was heated up to 165 °C and then 2.0 g of liquid OA (or LA or LnA) was added to the molten sulfur and the resulting heterogeneous mixture was left to stir at 1000 rpm for 1.0–1.5 h. The color of the reaction changed from yellow to dark brown during mixing. After 1.5 h, the reaction temperature was increased up to 185 °C to complete the polymerization. Then, the reaction was stopped and cooled up to room temperature slowly (see Supporting Information, Fig. S1).

2.2. *Photocatalytic applications*

Photocatalytic activity of all materials was tested by using the ATLAS solar simulator as a light source. MB dye was chosen as a model compound for textile-based wastewater. For photocatalytic degradation of MB under solar light, 40 mg of polymer in the powder form was dispersed in 10 mL of MB solution which is 2.0×10^{-5} M. Then 500 μL of ethanol was added to the mixture to reduce the surface tension and increase the dispersion of copolymer in the MB solution. After that mixture was irradiated for 10, 30, 60, and 120 min. At each time 2 mL portion of the mixture was isolated by centrifugation and degradation of MB was followed with UV–Vis measurements by using the Shimadzu UV-1800 UV–Vis Spectrophotometer. The percent degradation of the MB was calculated from the reduction in absorbance value.

2.3. *Fabrication of coin cells and battery testing*

The synthesized polysulfur copolymers as cathode active materials were combined with conductive carbon and polyethylene in a mass ratio of 75:20:5, respectively, in chloroform and vigorously mixed using a teflon coated magnetic bar in a screw-top glass vessel to obtain a slurry [3]. The slurry was evenly spread on a carbon coated aluminum foil using a micrometer adjustable film applicator with a wet film thickness of around 100 μm and dried in air. The cathode samples were cut using an MTI disc cutter before being dried at 70 °C under a high vacuum until a constant weight was reached and stored in the glove box. The cathodes were assembled into CR2032 coin cells with a polypropylene separator and a lithium foil anode using the conventional 1 M LiTFSI in DOL:DME 1:1 vol. with 1% *w*/w $LiNO_3$ as the battery electrolyte. Battery cycling was done at a rate of C/10 from 1.7 to 2.6 V.

3. Results and discussion

During the inverse vulcanization, some difficulties were observed like phase difference and incomplete polymerization. In order to overcome these problems, the effect of stirring rate and temperature on polymerization was investigated. It was observed that stirring rate and polymerization temperature must be at least or higher than 1000 rpm and 185 °C, respectively (Fig. S2). Also, after the polymerization, the product must retain its homogeneity and color stability at room temperature. Thermally unstable polymeric products lost their colors and yellow color starts to appear partially in the polymer sample. The poly (S-r-OA)-50 wt% S obtained at 1000 rpm and 185 °C retained its homogeneity and color stability even after months (Fig. S3). After deciding the optimum conditions for the inverse vulcanization, the polysulfur copolymers bearing various amount of elemental sulfur and fatty acids were obtained. Fig. 2 represents the pictures of various poly(S-*r*-OA) copolymers obtained via inverse vulcanization technique. Poly(S-r-OA) copolymers can be obtained in solid form when the elemental sulfur was used more than 80% by weight.

In order to confirm the structure of poly(S-*r*-OA) copolymers (Fig. 3), ^{1}H NMR spectra of OA and the polysulfur copolymers were compared. As seen in Fig. 4, while the protons of double bond appear at 5.35 ppm, aliphatic protons can be observed as multiple signals between 0.5 and 3.0 ppm. A broad signal centered at 11.34 ppm confirms the presence of carboxylic acid group in OA structure.

In order to confirm the polymerization, the protons of double bond must disappear in the spectrum of the copolymer. When compared to the spectrum of OA, there is no any signal at 5.35 ppm, confirming the use of double bond in polymerization, and a new signal group was observed

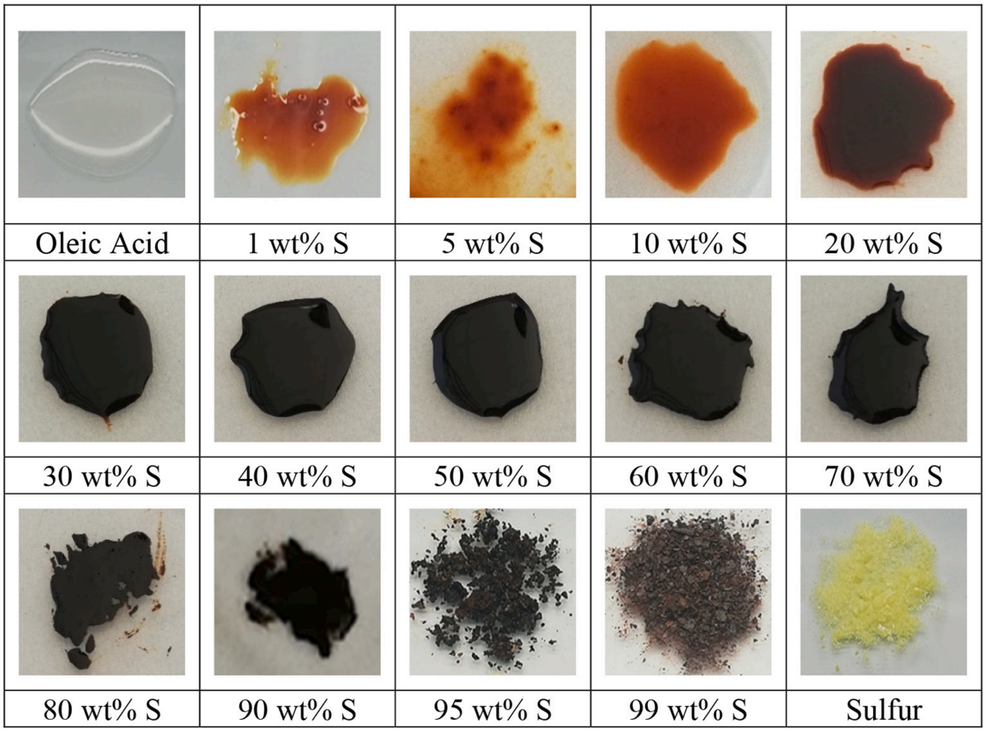

Fig. 2. Pictures of poly(S-*r*-OA) copolymers with various amount of S by weight obtained at 1000 rpm and 185 °C under atmospheric pressure.

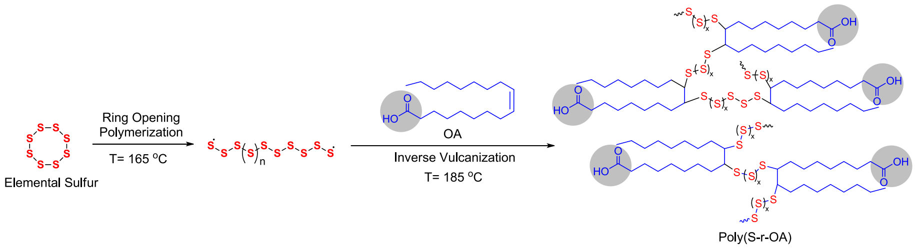

Fig. 3. Reaction pathway for the synthesis of poly(S-*r*-OA) copolymer.

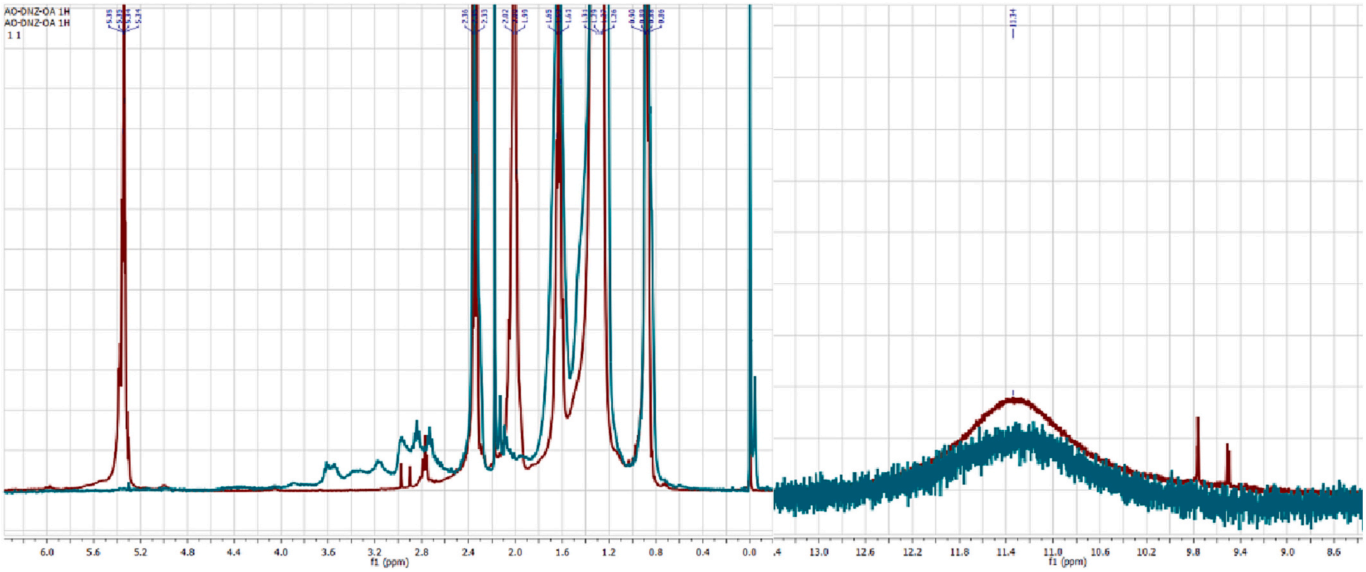

Fig. 4. ^{1}H NMR spectra of OA (red) and the poly(S-r-OA)- 50 wt% S copolymer (green) in d-CHCl$_3$ (a) between 00 and 6.0 ppm and (b) between 8.6 and 13.0 ppm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

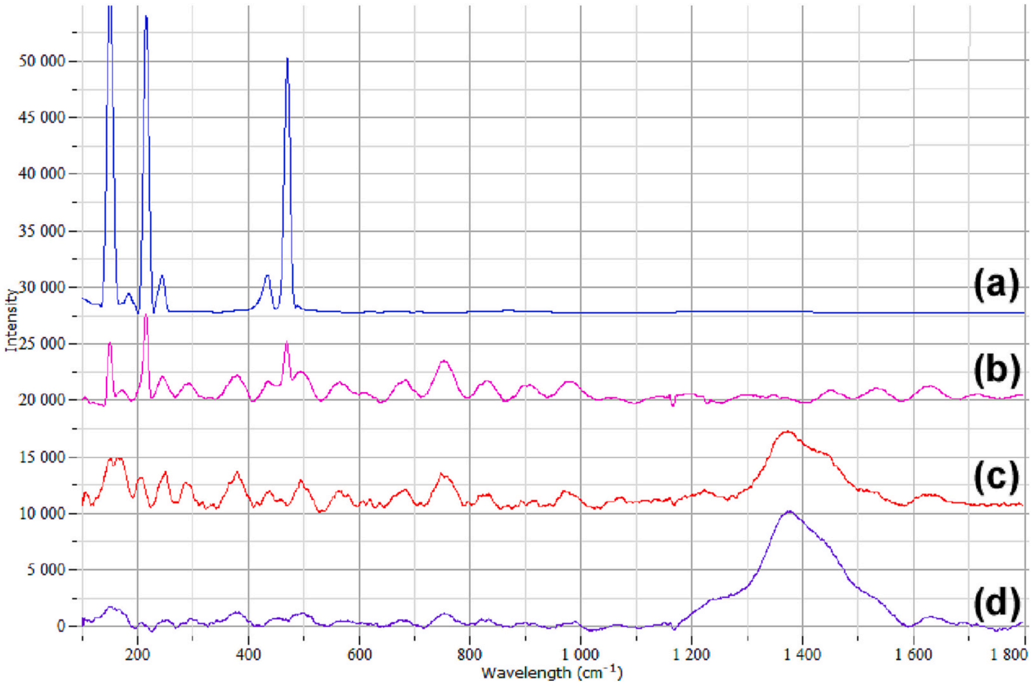

Fig. 5. Raman spectra of (a) elemental sulfur, (b) poly(S-*r*-OA)- 70 wt% S, (c) poly(S-*r*-OA)- 30 wt% S and (d) OA.

between 2.5 and 4.0 ppm, which can be attributed to -CH-S- units in the polymer structure. In OA, the signals of the protons (2.00 ppm) of the –CH_2- groups attached to the double bond will need to be replaced, since the double bonds will disappear during polymerization and therefore the -CH_2- protons were affected by this change and shifted to the higher area. On the other hand, the presence of carboxylic acid group appeared at 11.34 ppm confirms that the copolymers have reactive functional groups, which can be used to get new linkages like ester and amide via post polymerization in order to give new properties to the polysulfur copolymers.

In order to test the reaction efficiency between elemental sulfur and fatty acids during polymerization, ^{1}H NMR spectra of the copolymers were compared (see Fig. S4 and Fig. S5). As seen in figures, while all copolymers have reactive carboxylic acid groups in their structures, the copolymers bearing less than 30% OA by weight show the double bond protons at 5.35 ppm and the intensity of the peaks decreases as a function of used amount of OA. On the other hand, the poly(S-r-OA)- 30 wt% OA does not represent any peak at 5.35 ppm, representing all double bonds used in polymerization. It can be concluded that in order to get the polysulfur copolymers without double bond in their structures, the inverse vulcanization method must be performed by using at least 30% of OA by weight.

Raman spectra of elemental sulfur and the copolymers which contain different amounts of fatty acid are given in Fig. 5. The main signals located at 150–475 cm^{-1} in the spectrum of elemental sulfur can be attributed to the vibrational stretching signals of the S—S bond (Fig. 5(a)) [30]. When the amount of sulfur decreases these signals lost their intensity (Fig. 5(b)) and disappeared (Fig. 5(c)) due to the interaction with OA and weak Raman scattering from the S—S bond. When the weight percentage of OA in the copolymer increased, the Raman signal started to appear and the intensity of the signal attributed to C—C bond vibrations at 1392 cm^{-1} began to increase (Fig. 5(c) and 5(d)) [31]. This observation supports the fatty acid-elemental sulfur interaction.

FTIR analysis is an efficient method to determine the functional groups like carboxylic acid and vinylic groups present in the polymer structure. As shown in Fig. 6(a), while the bands between 2954 and 2852 cm^{-1} are attributed to the alkyl groups, the band at 1701 cm^{-1} is ascribed to the carbonyl groups (C=O) in the structure of OA. Also, OH group (O—H stretching) can be seen between 2500 and 3500 cm^{-1} as a broad band. The bands at 3007 cm^{-1} (C—H stretching) and 722 cm^{-1} (C—H out of plane bending mode) are ascribed to the double bond [22]. When compared to OA spectrum, the band at 3007 cm^{-1} disappears and the band intensity of peak at 722 cm^{-1} decreases, confirming the reaction of double bonds during polymerization. Also, a new band at 665 cm^{-1} appears due to the formation of C—S bond (stretching) in the polymer spectrum (Fig. 6(b)) [22]. In addition, new characteristic peaks appeared at 839 and 794 cm^{-1} can be attributed to the rocking vibrations of C—H bonds in the vicinity of C—S bonds, supporting the formation of C—S bonds between elemental sulfur and oleic acid. The similar bahavior was observed previously published works [13,32–34].

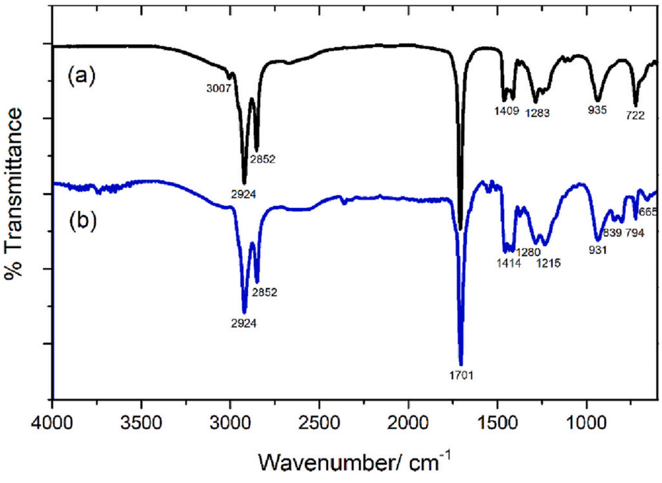

Fig. 6. FTIR spectra of (a) OA and (b) poly(S-*r*-OA)- 50 wt% S copolymer.

After the confirmation of polymer structure, the solubility of polymers was tested in various organic solvents (Table S1). The poly(S-*r*-OA) copolymers bearing various amount of OA are insoluble in hexane and water but soluble in other solvents like acetone, chloroform, dichloromethane, DMSO, THF, toluene, ethanol and ethyl acetate. All the solutions are in brown tones and can be coated on the glass surface as a film and the solid polymer was reshaped if it were heated (Fig. S6).

3.1. Synthesis of Poly(Sulfur-random-Linoleic Acid) (Poly(S-r-LA)) and Poly(Sulfur-random-Linolenic Acid) (Poly(S-r-LnA))

After the sulfur-based copolymers successfully obtained with OA (one double bond), the same polymerization conditions were applied for linoleic acid (LA, two double bonds) and linolenic acid (LnA, three double bonds) since they have similar structure with OA except for double bond numbers. Thus, it will be possible to see the effect of double bonds on the properties of polymeric products. The copolymers bearing 80 wt% S will be synthesized since poly(S-*r*-OA)- 80 wt% S looks like a waxy substance at room temperature and therefore the effect of double bond on polymer appearance can be seen easily. When the number of double bonds in fatty acid increases, solidity of the corresponding polymer increases (Fig. S7).

When compared to poly(S-*r*-OA)- 80 wt% S, the copolymers poly(S-*r*-LA)- 80 wt% S and poly(S-*r*-LnA)- 80 wt% S look like more rigid and solid form due to the presence of more double bonds in the structures of LA and LnA, which causes more crosslinking in the polymer structure. On the other hand, except for the appearance of the polymers, the solubility of the copolymers also confirms the effect of double bonds on the crosslink polymer structure. As expected, the copolymers obtained from LA and LnA will be more crosslinked compared to OA derivative. Therefore, poly(S-*r*-LA) and poly(S-*r*-LnA) derivatives will be less soluble when compared to poly(S-*r*-OA) derivative (see Table S2). For example, while poly(S-*r*-OA)- 80 wt% S and – 90 wt% S copolymers are soluble in acetone, MeOH, NMP, DMSO, etc., poly(S-*r*-LA) and poly(S-*r*-LnA) derivatives are partially soluble.

When compared to poly(S-*r*-OA), poly(S-*r*-LA) and poly(S-*r*-LnA) copolymers represent a similar behavior (see Figs. S8-S9). The aliphatic (2924 and 2955 cm^{-1} for LA; 2931 ve 2852 cm^{-1} for LnA), carboxyl (1701 cm^{-1}) and hydroxyl groups (between 2500 and 3500 cm^{-1}) retain in the spectra of the copolymers. On the other hand, in the spectra of poly(S-*r*-LA) and poly(S-*r*-LnA) copolymers, the bands at 3011 cm^{-1} (C—H stretching) and 723 or 715 cm^{-1} (C—H out of plane bending mode) ascribed to the double bonds disappear, confirming that double bonds enter the reaction during polymerization [22]. In addition, the rocking vibrations of C—H bonds in the vicinity of C—S were confirmed by the fingerprint peak at 799 and 794 cm^{-1} [13,32–34]. When the FTIR spectra of polysulfur copolymers prepared with the same weight sulfur content are compared, it is seen that the copolymers obtained by using all three fatty acids have similar structures (see Fig. S10).

Whether the double bonds in OA reacted or not was examined by NMR analysis and it was shown that the double bonds were used completely in the copolymers containing 30% or more sulfur by weight. A similar study should be done for LA and LnA based copolymers. The signal of the protons (5.32 ppm) ascribed to the double bonds disappeared completely in the spectrum of poly(S-*r*-LA)- 50 wt% S. Also, the protons of carboxylic acid groups can be observed as a broad signal centered at 12.00 ppm. In addition, the formation of -S-CH- groups can be observed as a new signal group between 2.5 and 3.6 ppm. When compared to poly(S-*r*-LA)- 50 wt% S, a similar behavior was observed for the spectrum of poly(S-*r*-LnA)- 50 wt% S copolymer (see Figs. S11-S14).

In order to investigate the effect of type of fatty acids on morphological properties of polysulfur copolymers, SEM images of poly(S-*r*-FA)-

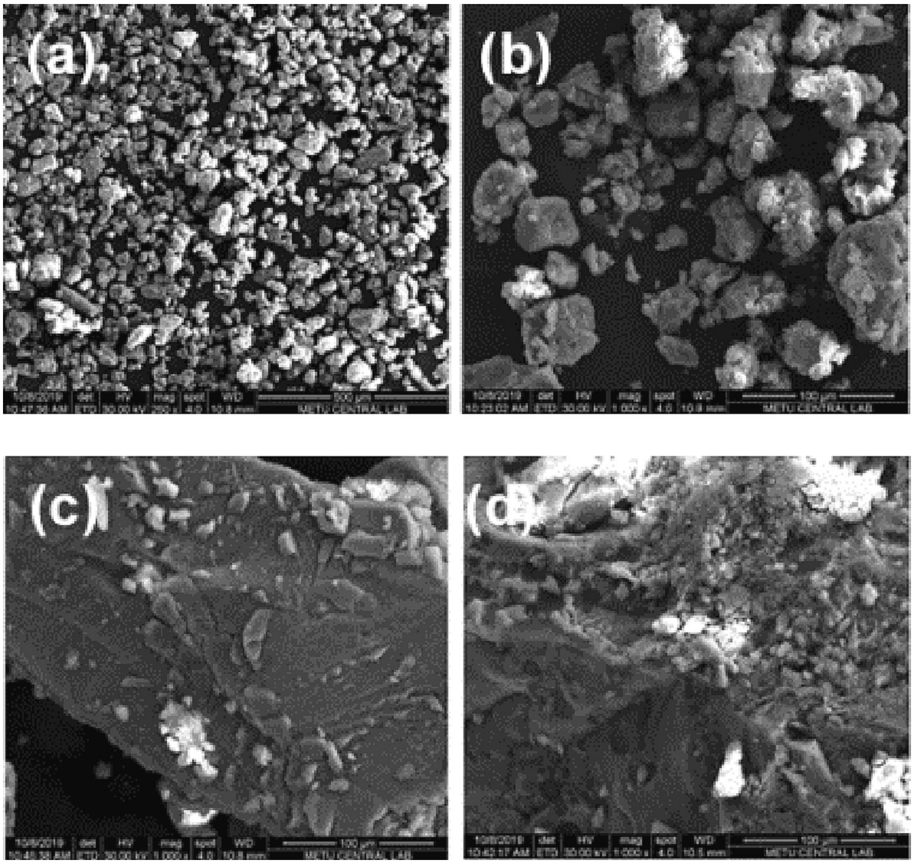

Fig. 7. SEM images of (a) elemental sulfur, (b) poly(S-*r*-OA)- 90 wt% S, (c) poly(S-*r*-LA)- 90 wt% S, and (d) poly(S-*r*-LnA)- 90 wt% S.

90 wt% S copolymers were compared. As shown in Fig. 7, when compared to elemental sulfur, all copolymers represent somewhat difference in their morphological structures due to the presence of high amount of sulfur in their polymer structures.

3.2. Gel Permeation Chromatography Analysis of Poly(S-r-FA) Polymers

The molecular weight of the copolymers was analyzed by gel permeation chromatograpy (Table 1 and Fig. S15-S21). As can be understood from the GPC data, the copolymers showed low molecular weights like previously reported polysulfur copolymers [3,7,13]. When the sulfur content of OA, LA and LnA based polysulfur copolymers increases, the molecular weights of the copolymers also tend to increase. For example, the molecular weights of the copolymers are 3451, 10,505 and 23,659 g/mol for poly(S-r-OA) copolymers of 50, 70 and 90wt%S, respectively. Also, the samples exhibited the very narrow dispersity in a range of 1.06 and 1.62. These results can be attributed to a polymer backbone with a few branches containing high-order sulfur chains. During inverse vulcanization, all the double bonds in fatty acids being consumed and contrary to expectation (hyperbranched structure) [24] less branched copolymers with long alkyl units were obtained.

Table 1
GPC results of poly(S-r-FA) polymers obtained at 1000 rpm and 185 °C under atmospheric pressure.

Polymer	M_w (g/mol)	M_n (g/mol)	PDI (M_w/M_n)
Poly(S-*r*-OA)- 50 wt% S	3451	2949	1.17
Poly(S-*r*-OA)- 70 wt% S	10,505	9741	1.08
Poly(S-*r*-OA)- 90 wt% S	36,778	22,641	1.62
Poly(S-*r*-LA)- 50 wt% S	3964	3400	1.17
Poly(S-*r*-LA)- 70 wt% S	6816	6423	1.06
Poly(S-*r*-LnA)- 50 wt% S	4783	4027	1.19
Poly(S-*r*-LnA)- 70 wt% S	7521	6506	1.16

3.3. Thermal Analysis of Poly(S-r-FA) Polymers

When thermal gravimetric analysis (TGAs) of polysulfur copolymers were examined, it was observed that they displayed a different behavior than sulfur. Sulfur begins to decompose at approximately 220 °C (5% loss in mass) and when it reaches 300 °C, the whole sample is spoiled. As seen in Fig. 8, when sulfur is taken as the reference point, poly(S-*r*-FA)-90%wt S copolymers started to decompose at a much higher temperature than sulfur at 210 °C and unlike sulfur, it was able to preserve approximately 42–62% of their weights at 300 °C. These copolymers

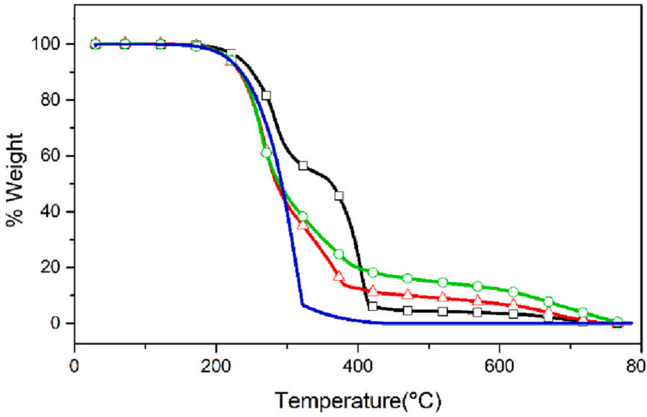

Fig. 8. TGA thermograms of poly (S-r-OA)- 90 wt% S polymer (square), poly (S-r-LA)- 90 wt% S polymer (triangle), poly (S-r-LnA)- 90 wt% S polymer (circle), elemental sulfur (solid line).

were completely decomposed approximately at 800 °C.

As a result of TGA analysis, it is thought that the samples are thermally stable up to about 200 °C, and the differential scanning calorimetry (DSC) analyzes are performed between −50 °C and 200 °C considering the molten or waxy state of the samples at room temperature, and the glass transition temperatures (T_g) and melting temperature (T_m) of the samples are tried to be obtained. As can be seen in Fig. 9, it was observed that each sample showed a characteristic peak at around −39 °C, ascribed to the T_g of polymeric segments [21]. Also, the polysulfur copolymer samples gave an endothermic signal at approximately 116 °C, and this was attributed to the long polysulfur chains in the copolymer structure [35].

3.4. Removal of Methylene Blue by using Poly(S-r-FA) Polymers

For the dye removal application initially, 90, 95, and 99 wt% S contents were tried and the highest efficiency was obtained with 99 wt % S content. So, poly(S-*r*-OA)-90 wt% S, poly(S-*r*-LA)-90 wt% S and poly (S-*r*-LnA)-90 wt% S were chosen and their photocatalytic activities were tested in the degradation of methylene blue under solar light. Since the first usage of TiO_2 in water photolysis as a photoanode [36], it has been the most used semiconductor in photocatalytic applications in environmental remediation and solar energy conversion due to its chemical and physical properties like non-toxicity, stability and high activity [37,38]. For this reason, pure TiO_2 is used as a reference material and the catalytic activity of TiO_2 nanoparticles was tested under solar light for comparison.

Initially adsorption behavior of polymers was investigated. For this, 40 mg of the copolymer was mixed with 10 mL of methylene blue in a dark environment. 17% reduction in MB concentration was obtained at the end of 120 min of stirring in the dark. The percentage of self-degradation of the dye was also determined by directly exposing 10 mL of MB at 1.0 absorbance to the solar simulator in a polymer-free environment and 7% self-degradation was detected in MB solution exposed to solar light.

In all photocatalytic measurements, 40 mg polymer was mixed with 2.0×10^{-5} M MB solution (1.0 A) and exposed to solar light under stirring conditions. After a certain time, a 2 mL portion of the MB solution was taken from the reaction mixture. After isolation of the solid catalyst, UV–Vis measurement was performed, and percent degradation was calculated by following the absorption peak located at 665 nm. The sample UV–Vis spectra and the comparison of the percent degradation of poly(S-r-OA)-90wt%S, poly(S-r-LA)-90wt%S, poly(S-r-LnA)-90wt%S and TiO_2 nanoparticles are given in Fig. 10.

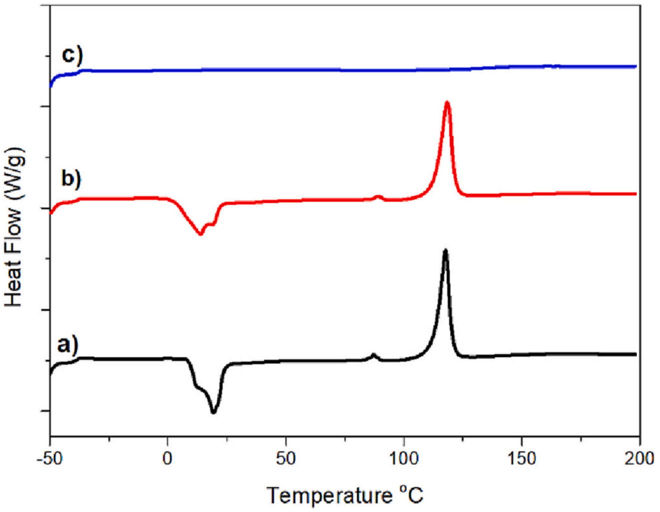

Fig. 9. DSC thermograms of a) poly(S-r-OA)- 90 wt% S, b) poly(S-r-LA)- 90 wt % S, and c) poly (S-r-LnA)- 90 wt% S.

From the results given above, 78% degradation of MB was achieved by TiO_2 nanoparticles after 120 min exposure to solar light. In the case of poly(S-r-OA)-90wt%S, 76% degradation of MB was achieved under the same conditions. For poly(S-r-LA)-90wt%S and poly(S-r-LnA)-90wt%S 68% and 64% degradation of MB under solar light were achieved respectively. As can be seen from the results, comparable photocatalytic activities were observed with the use of poly(S-r-FA)-90 wt% S with TiO_2 nanoparticles. When the prices of prepared polymers and titanium nanoparticles are compared, it is seen that polymers are much cheaper, so poly(S-r-OA)-90wt%S can be a good candidate for environmental remediation applications.

3.5. Electrochemical characterization of polysulfur copolymers as cathode active materials

High sulfur content (90%, 95% and 99%) poly(S-*r*-OA), poly(S-*r*-LA) and poly(S-*r*-LnA) copolymers were investigated in order to evaluate the potential performances of them as cathode active materials in Li—S batteries. Although a relatively higher ratio of a binder was employed to ensure a strong adhesion of electrode materials to the current collector, it seemed to not prevent the pulverization of the poly(S-*r*-LA) and poly (S-*r*-LnA) based cathode (Fig. S22). No further attempts were done for the optimization and the electrochemical characterizations were continued with the corresponding poly(S-*r*-OA) copolymers.

There have been some physical and chemical methods for the preparation of elemental sulfur based cathodes for lithum-sulfur batteries, improving the overall cycling performance of such systems [39]. However, a cathode system using elemental sulfur was prepared under the same conditions for the comparison, and charge-discharge and coulombic efficiency data are given in Fig. S23(a). Although elemental sulfur has a relatively high theoretical capacity of 1675 $mAhg^{-1}$, it suffers from the reactivity of discharge intermediates, the shuttle effect, the volume effect, etc. These shortcomings limits the long-term performance of the system [39]. The initial discharge capacity value of 740 $mAhg^{-1}$ was therefore followed by a steep decrease to around 200 $mAhg^{-1}$ just after 20 cycles and completed the 100th cycle at this level as expected (Fig. 11).

The charge-discharge and coulombic efficiency data for poly(S-*r*-OA) copolymers with 90, 95 and 99 wt% S content are also given in Fig. S23 (b-d). Both poly(S-r-OA)-90 wt% S and poly(S-r-OA)-99 wt% S showed initial discharge capacity values of around 600 $mAhg^{-1}$, but they showed better capacity values of around 250 and 350 $mAhg^{-1}$, respectively, at the end of the 100th cycle when compared to pure sulfur. Poly (S-*r*-OA)- 95 wt% S with an initial discharge capacity value of 1370 $mAhg^{-1}$ and the highest discharge capacity value of around 700 $mAhg^{-1}$ at the end. Although the poly(S-*r*-OA)- 90 wt% S copolymer with higher amount of OA (i.e. statistically highest degree of cross-linking ratio) was expected to prevent the dissolution of soluble sulfur intermediates formed during the charge-discharge process more than the others, poly (S-*r*-OA)- 95 wt% S appeared to be the optimum composition for use as cathode active material in lithium-sulfur batteries.

The goal of inverse vulcanization in this case is to allow elemental sulfur modification in the form of a processable polymeric structure that retains the chemical stability and electrochemical activity of an elemental sulfur cathode. The results here demonstrate that these copolymers exhibit comparable electrochemical properties to elemental sulfur and could serve as the active material in Li—S batteries. Poly(S-r-OA)- 95 wt% S with an initial discharge capacity value over 1000 $mAhg^{-1}$ and high capacity retention (around 700 $mAhg^{-1}$ at 100 cycles at C/10 discharge rate). These results were in accordance with a study concerning a similar cathode system prepared via direct copolymerization of elemental sulfur with vinylic monomers, where the copolymer exhibited 1100 $mAhg^{-1}$ of an initial specific discharge and 823 $mAhg^{-1}$ capacity retention values after 100 cycles [3].

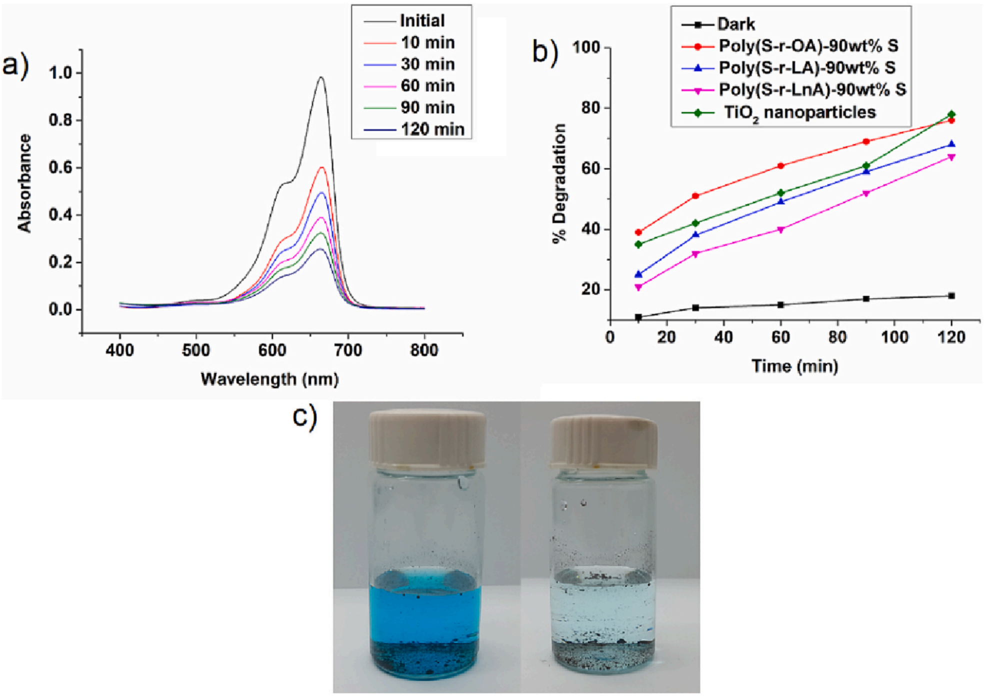

Fig. 10. a) Sample UV–Vis spectra, b) Comparison of the catalytic activities of the poly(S-r-OA)-90wt%S, poly(S-r-LA)-90wt%S, poly(S-r-LnA)-90 wt% S, and TiO2 nanoparticles used for MB degradation under solar light, c) picture of the MB dye befor and after degradation.

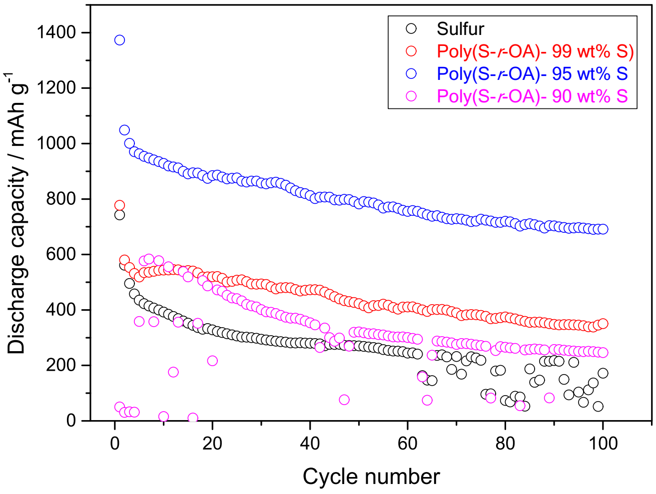

Fig. 11. The discharge capacity comparison of sulfur, poly(S-r-OA) copolymers with 90, 95 and 99 wt% S at C/10 discharge rate.

4. Conclusion

In this study, poly(S-*r*-FA) copolymers were obtained in various amount of elemental sulfur and fatty acids (oleic acid (OA), linoleic acid (LA) and linolenic acid (LnA)) via inverse vulcanization technique. It is clearly shown that when the sulfur amount increases, the corresponding copolymers become more solid. Also, an increase in the double bond number in fatty acid increases the solidity and decreases the solubility of the related polymers. Successfully obtained thermally stable poly(S-r-FA) copolymers represent a good sensitivity for the removal of MB dye from aqueous solutions and the photocatalytic activity of the copolymers can be improved by using them together with magnetic and TiO$_2$ nanoparticles in composites. After some improvements, poly(S-r-OA) copolymers can be considered as a candidate for use in lithium-sulfur batteries. On the other hand, after inverse vulcanization, carboxylic acid groups of fatty acids remain unaltered in the polysulfur copolymers. In future work, by using these functional groups, the copolymers can be modified via post polymerization and therefore the polymers bearing unique properties such as higher molecular weight, different optical, electrochemical, and thermal properties can be obtained. Also, these modified copolymers like polyester and polyamide derivatives can be used in various applications. Work to synthesize of modified polysulfur copolymers is currently underway in our laboratories.

Author contributions

CRediT authorship contribution statement.

CRediT authorship contribution statement

Hasan Berk: Writing – original draft, Investigation. **Murat Kaya:** Writing – original draft, Investigation, Supervision, Funding acquisition. **Mert Topcuoglu:** Writing – original draft, Investigation. **Nazli Turkten:** Writing – original draft, Investigation. **Yunus Karatas:** Writing – original draft, Investigation, Supervision. **Atilla Cihaner:** Conceptualization, Methodology, Investigation, Writing – original draft, Writing – review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.reactfunctpolym.2023.105581.

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