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Halogenated sunflower oil as a precursor for synthesis of polysulfide polymer

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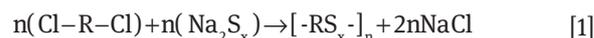
Abstract: Polysulfide polymers usually are prepared by the reaction of different dihalide compounds with disodium polysulfides. In this field, dihalides are expensive and produced from halogenation of organic compounds by different methods with harsh conditions. To overcome this problem, in this work, sunflower oil as polyunsaturated oil was used as precursor to produce polyhalide compound. In this field, double bonds of oil were applied as functional groups to halogenate the sunflower via benzoyl peroxide-catalyzed reaction with hydrochloric acid. Also, Na_2S_3 was synthesized via the reaction between sulfur and sodium hydroxide. Then, halogenated oil was reacted with Na_2S_3 to produce sunflower oil-based polysulfide polymer. Fourier transform infrared spectroscopy (FT-IR) and proton nuclear magnetic resonance (^1H NMR) were used to characterize the structure of sunflower oil and synthesized polysulfide polymer. The content of halogenation was also obtained via energy-dispersive X-ray spectroscopy (EDX). Thermal stability of synthesized polymer was determined by means of thermal gravimetric analysis (TGA) and glass transition temperature was investigated by differential scanning calorimetry (DSC).

Keywords: halogenation; NMR spectra; polysulfides; sunflower oil; synthesis.

1 Introduction

Polysulfide polymers are widely used in different applications such as adhesives and sealants (1–3). They are highly

resistant to solvents and chemicals (4) and used to line fuel tanks. In addition, they are commonly used in building industries due to their excellent weathering resistance properties (5). Polysulfide polymers are commonly produced by the condensation polymerization of short chain dichlorohydrocarbons with aqueous sodium polysulfide (6, 7). During the polycondensation process, polysulfide anions continually interchange with the polysulfide groups to increase the molecular weight of polymer. Equation [1] states the general polycondensation mechanism to produce polysulfide polymers.



where, R denotes the backbone hydrocarbon such as methyl, ethyl, etc.

In recent years, many different types of polysulfide polymers are produced based on different dihalide compounds such as 1,4-dibromo-2-butene (8), styrene dibromide (9), 1,4-bis(chloromethyl)-benzene (10, 11), etc. Also, the effect of dihalide type on the properties of final polysulfide polymer is achieved (12). However, there is no mentionable research work on producing polysulfide polymers based on vegetable oils. Vegetable oils are composed of triglycerides, as contrasted with waxes with lack glycerin in their structure (13). Among various vegetable oils, sunflower oil is one that can be produced easily with proper price to be used in different industries (14). It contains five unsaturated C=C bonds and can be easily functionalized with different electrophile compounds.

In our approach, double bonds of sunflower oil can be used as functional groups to prepare polyhalide compounds which are precursors of polysulfide polymers. To this end, sunflower oil was halogenated via reaction with hydrochloric acid to obtain halogenated oil. Then, halogenated oil was used as precursor and reacted with Na_2S_3 to produce sunflower oil-based polysulfide polymer. Fourier transform infrared spectroscopy (FT-IR) and proton nuclear magnetic resonance (^1H NMR) were used to characterize the structure of sunflower oil, halogenated oil and synthesized polysulfide polymer. Halogenation was further confirmed by means of energy-dispersive X-ray spectroscopy (EDX) and thermophysical properties of polysulfide polymer was investigated by differential

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scanning calorimetry (DSC) and thermal gravimetric analysis (TGA).

2 Experimental section

2.1 Materials

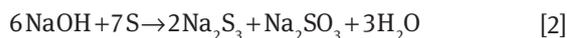
Benzoyl peroxide (BPO, 75%, Merck, Darmstadt, Germany) was purified via recrystallization from methanol prior to use. Sunflower oil was supplied by FRICO, Tehran, Iran. Aqueous hydrochloric acid (HCl, 37%, Mojallali, Tehran, Iran), calcium chloride (CaCl_2 , 97%, Mojallali, Tehran, Iran), sodium hydroxide (NaOH, 97%, Mojallali, Tehran, Iran) and sulfur (S, 99%, Merck, Darmstadt, Germany) was used as received.

2.2 Preparation of halogenated oil

At first, CaCl_2 was used to dry the sunflower oil. In a 200 ml flask BPO (1.0 g, 4.1 mmol) were added to the sunflower oil (100 ml, 104.4 mmol) and mixture was stirred for 10 min at 70°C to activate the radical initiators (15). Then, reactor was placed in an ice-water bath to reduce temperature down to 0°C and HCl vapor was purged into reactor for 5 h. Finally, product was filtered via 0.2 μm -pore size nitrocellulose membrane filters to remove CaCl_2 and dried in vacuum oven at 50°C overnight.

2.3 Preparation of Na_2S_3

NaOH (10.0 g, 311.9 mmol) was dissolved in water (100 ml) and stirred for 10 min at room temperature. Then, sulfur (11.371 g, 363.9 mmol) were added and mixture was stirred for 24 h at room temperature to make a homogeneous orange-colored solution. Obtained solution contains Na_2S_3 as stated via equation [2] (16).



2.4 Preparation of polysulfide polymer

Aqueous solution of Na_2S_3 was heated to 70°C and halogenated oil (20 ml) was added slowly. Mixture was stirred for 24 h at 100°C to obtain dark brown-colored polymer. Product was washed by water to dissolve NaCl salt and subsequently, by HCl to reduce the pH to 5 and convert final groups to $-\text{S}_x\text{H}$ moieties. Finally, synthesized polymer

was dried in vacuum oven at 50°C overnight. The amount of dried polymer was obtained gravimetrically 26.021 g.

2.5 Instrumentation

Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Tensor 27 FT-IR-spectrophotometer (Bruker Corporation, Billerica, MA, USA), within a range of 400–4000 cm^{-1} using a resolution of 4 cm^{-1} . An average of 24 scans has been carried out for each sample. The samples were prepared on a KBr pellet in vacuum desiccators under a pressure of 0.01 torr. ^1H NMR (300 MHz) spectra were recorded on a Bruker Avance 300 spectrometer (Bruker Corporation, Billerica, MA, USA) using deuterated chloroform (CDCl_3) as solvent and tetramethylsilane (TMS) as an internal standard. EDX was carried out on a JSM-6360LV instrument. Thermal gravimetric analysis was carried out with a PL thermo-gravimetric analyzer (TGA 1000, Polymer Laboratories, Shropshire, UK). The thermogram was obtained from ambient temperature to 600°C at a heating rate of 10°C/min. A sample weight of about 10 mg was used for measurement and nitrogen was used as the purging gas at a flow rate of 50 ml/min. Differential scanning Calorimetry was carried out using a DSC instrument (NETZSCH DSC 200 F3, Netzsch Co., Bavaria, Germany). Nitrogen at a rate of 50 ml/min was used as the purging gas. Aluminum pans containing 3 mg of the sample were sealed using the DSC sample press. The sample was heated from -20°C to 180°C at a heating rate of 10°C/min. T_g was obtained as the inflection point of the heat capacity jump.

3 Results and discussion

In the first step, sunflower oil was halogenated to obtain a polyhalide precursor. Then, halogenated oil was reacted with Na_2S_3 to produce polysulfide polymer. Figure 1 shows the FT-IR spectra for the sunflower oil, halogenated oil, and polysulfide polymer. In sunflower oil spectrum, the characteristic peaks at 2930 and 2850 cm^{-1} are related to the asymmetric and symmetric stretching vibration of C-H bonds respectively (17, 18). Also, =C-H bonds show a stretching vibration at 3010 cm^{-1} (19) and an out-of-plane stretching vibration at 915 cm^{-1} (20). Furthermore, vibration peak at 1750 cm^{-1} represents the carbonyl groups of the oil structure (21) and characteristic peaks at 1240 and 1165 cm^{-1} are related to C-O bonds. The stretching vibrations of C=C bonds are observed at 1655 cm^{-1} . Scissoring vibrations and bending vibrations of $-\text{CH}_2-$ at 1465 and 725 cm^{-1} are

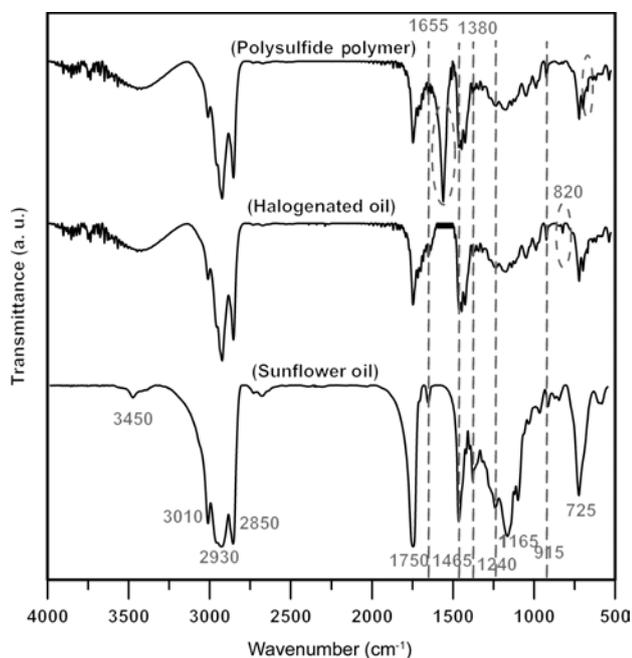


Figure 1: FTIR spectra for the sunflower oil, halogenated oil, and polysulfide polymer.

obvious and bending vibrations of -CH in -CH₃ groups are shown at 1380 cm⁻¹. The characteristic peak at 3450 cm⁻¹ is related to the water molecules absorbed by sample or

KBr powder (22). After halogenation, some of C=C bands are converted to C-Cl bands; thus, no significant change is expected in FT-IR spectra just only characterization peak related to C-Cl. With this regard, a new characteristic peak at 820 cm⁻¹ related to C-Cl bonds appears (23). The weakness of this peak is due to low Cl content of halogenated oil. In polysulfide polymer, the stretching vibration corresponding to C-S bond appears at 690 cm⁻¹ (24). In addition, peak around 1560 cm⁻¹ may correspond to the C-S stretching vibration (25). It is noteworthy that after polymerization, peak at 820 cm⁻¹ disappears due to reaction of halogenated oil with Na₂S₃.

¹H NMR analysis was carried out in CDCl₃ for sunflower oil (Figure 2), halogenated oil (Figure 3) and polysulfide polymer (Figure 4). The characteristic signals of sunflower oil are as follow as depicted in Figure 1: δ((CH₂)_nCH₃, a, 9H)=0.86–0.91 ppm, δ((CH₂)_n, b, 54H)=1.25–1.31 ppm, δ(CH=CHCH₂(CH₂)_n, c, 12H)=2.00–2.08 ppm, δ(CH=CHCH₂CH=CH, d, 4H)=2.75–2.79 ppm, δ(COOCH₂(CH₂)_n, e, 6H)=2.28–2.33 ppm, δ(CH=CH, f, f', 10H)=5.32–5.40 ppm, δ(CH₂-OCO and CH-OCO, g, g', 5H)=4.15–4.29 ppm. These signals are similar to ones reported by other researchers (26). Signals at 0.00 ppm, 1.61 ppm and 7.28 ppm are related to the TMS, water and CDCl₃, respectively. After halogenation process and obtaining halogenated oil, no significant change may occur in ¹H NMR spectrum except than reduction and increment of protons related to CH=CH

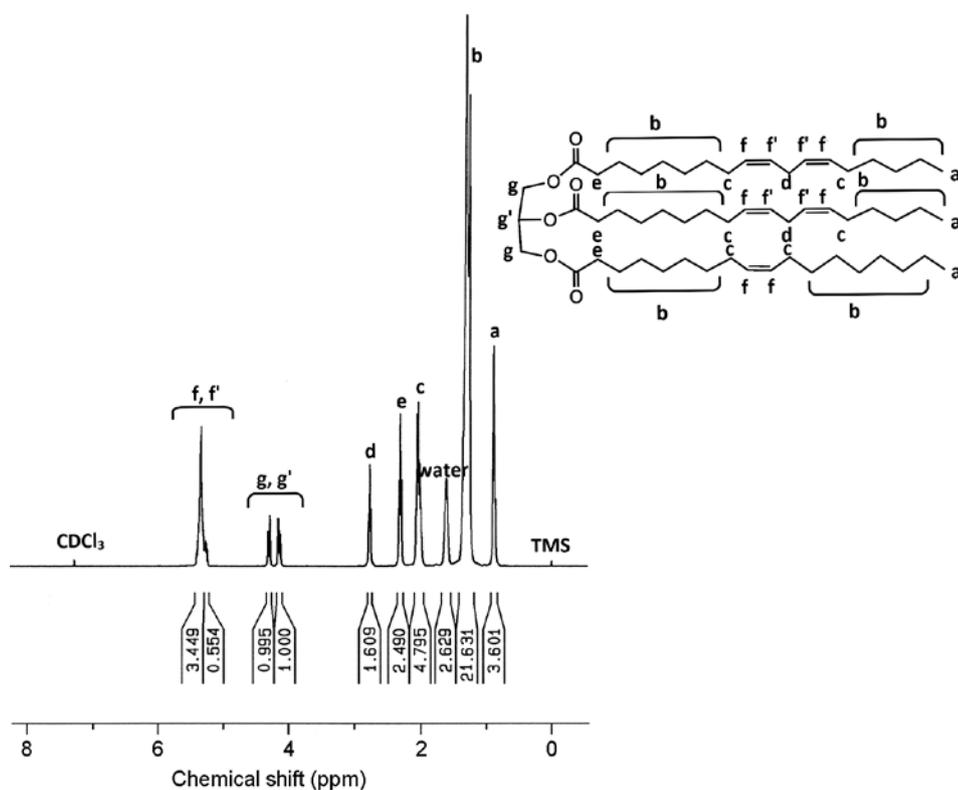


Figure 2: ¹H NMR result for sunflower oil.

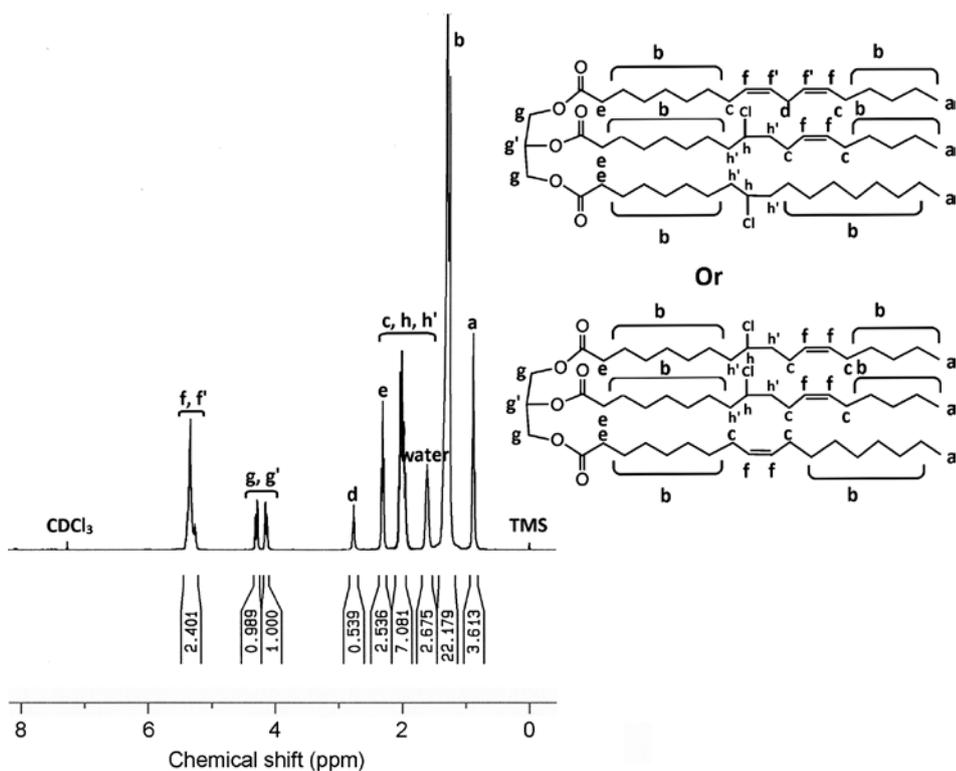


Figure 3: ^1H NMR result for the halogenated oil.

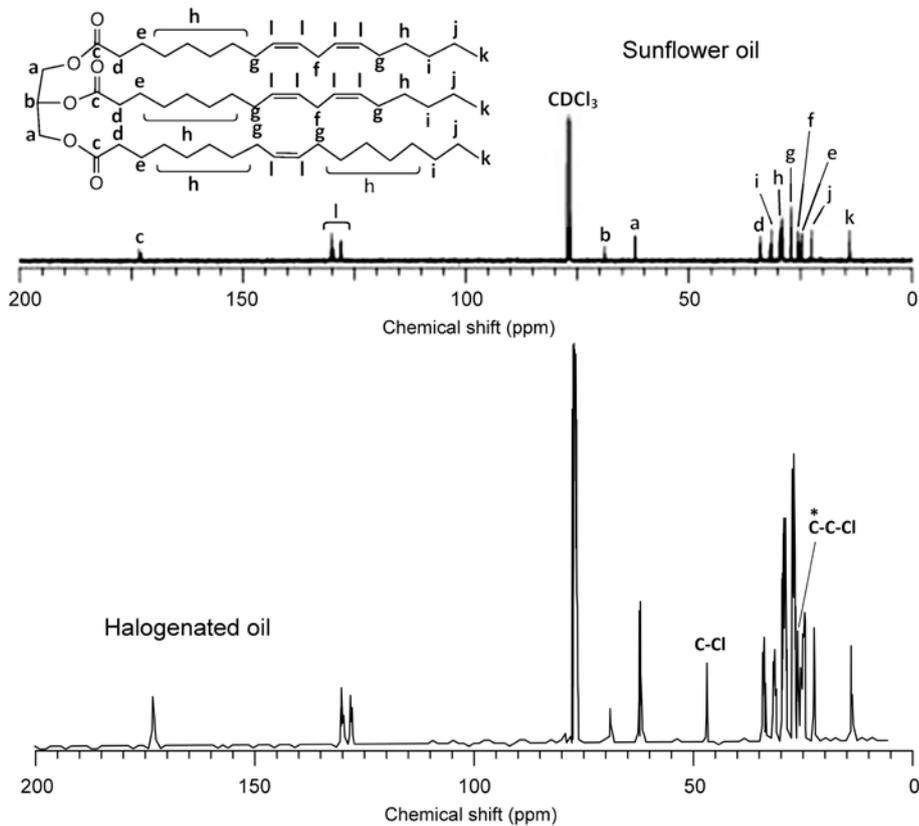
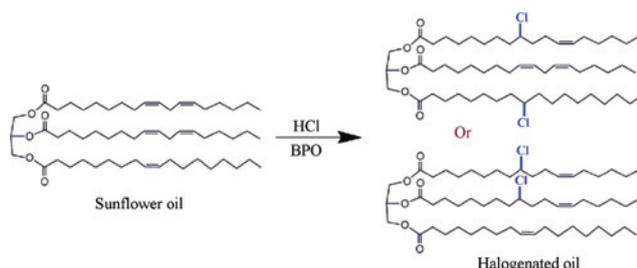


Figure 4: ^{13}C NMR results for sunflower oil and halogenated oil.

before and after it participates in reaction. After halogenation, the area under curve related to $\text{CH}=\text{CH}$ indicates functional groups that do not participate in reaction. According to Figure 3 (^1H NMR of halogenated oil), six protons still exist in structure and conclusively, two $\text{C}=\text{C}$ have participated in halogenation. Also, chemical shift related to $\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}$ shows how many $\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}$ still exists in structure. According to results, 4 proton reduced to only 1.3 proton, i.e. a random-wise halogenation was occurred and mechanism of reaction may be illustrated as Scheme 1. Briefly, the characteristic signals are as follow: $\delta((\text{CH}_2)_n\text{CH}_3, \text{a}, 9\text{H})=0.86\text{--}0.91$ ppm, $\delta((\text{CH}_2)_n, \text{b}, (54\times 0.33+56\times 0.67)\text{H}=55.3\text{H})=1.25\text{--}1.31$ ppm, $\delta(\text{CH}=\text{CHCH}_2(\text{CH}_2)_n, \text{c}, (12\times 0.33+8\times 0.67)\text{H}=9.3\text{H}; \text{CHCl}, \text{h}, 2\text{H}; \text{CHClCH}_2, \text{h}', 8\text{H}; \text{total H}=19.3)=2.00\text{--}2.06$ ppm, $\delta(\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}, \text{d}, (2\times 0.67)\text{H}=1.3\text{H})=2.76\text{--}2.77$ ppm, $\delta(\text{COOCH}_2(\text{CH}_2)_n, \text{e}, 6\text{H})=2.29\text{--}2.33$ ppm, $\delta(\text{CH}=\text{CH}, \text{f}, \text{f}', 6\text{H})=5.32\text{--}5.39$ ppm, $\delta(\text{CH}_2\text{-OCO and CH-OCO}, \text{g}, \text{g}', 5\text{H})=4.15\text{--}4.29$ ppm. According to results, a good correlation appears between random-wise halogenation and ^1H NMR results. Based on these results, the efficiency of halogenation is obtained equal to nearly 40%. It means that in oil structure, two $\text{C}=\text{C}$ bond are converted to halogenated bonds and can be used as halogenated monomer to produce polysulfide polymer.

Figure 4 shows ^{13}C NMR spectrum of sunflower oil and halogenated oil. The aliphatic carbons resonate in the range of 14–34 ppm. The terminal methyl carbons is found at $\delta=14.00\text{--}14.03$ ppm. CH_2 carbons beside the terminal carbon appear at $\delta=22.55\text{--}22.65$ ppm whereas chemical shift at $\delta=24.81$ ppm is related to the acrylic methylene carbons with respect to carbonyl group. $\text{C}=\text{C}-\text{C}=\text{C}$ carbon is observed at $\delta=25.60$ ppm and carbons beside the double bonds appear at $\delta=27.15$ ppm. $-\text{CH}_2$ carbons in fatty acid central chains is shown at $\delta=29.08\text{--}29.73$ ppm except carbons named *i* that are located at $\delta=31.50$ ppm. Chemical shift at $\delta=34.00$ ppm is attributed to carbons beside carbonyl groups. Signals at 62.08 ppm and 68.91 ppm are assigned to the glyceryl CH_2 and CH carbon atoms. Signals



Scheme 1: Random-wise mechanism of halogenation reaction of sunflower oil. Scheme is prepared based on addition mechanism reported by Kharasch et al. (15).

at 127.89–130.19 ppm are assigned to the vinyl carbon atoms and the signals at 172.75–173.16 ppm are related to the carbonyl ($\text{C}=\text{O}$) carbon atoms of the ester functionalities (27). After halogenation process, two new signals appear in ^{13}C NMR spectrum of halogenated oil. The signal at 26.22 ppm is ascribed to the carbons beside the halogenated carbon atom and signal at 46.91 is attributed to the halogenated carbon atoms. These two new signals obviously approve the success of halogenation process.

Also, Figure 5 shows the ^1H NMR spectrum of polysulfide polymer. The characteristic signals of synthesized polymer are as follow: $\delta((\text{CH}_2)_n\text{CH}_3, \text{a}, 9\text{H})=0.86\text{--}0.89$ ppm, $\delta((\text{CH}_2)_n, \text{b}, 55.3\text{H})=1.25\text{--}1.31$ ppm, $\delta(\text{CH}=\text{CHCH}_2(\text{CH}_2)_n, \text{c}, (12\times 0.33+8\times 0.67)\text{H}=9.3\text{H}; \text{CHS}_x, \text{h}, 2\text{H}; \text{CHS}_x\text{CH}_2, \text{h}', 8\text{H}; \text{total H}=19.3)=2.00\text{--}2.08$ ppm, $\delta(\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}, \text{d}, 1.3\text{H})=2.75\text{--}2.79$ ppm, $\delta(\text{COOCH}_2(\text{CH}_2)_n, \text{e}, 6\text{H})=2.29\text{--}2.33$ ppm, $\delta(\text{CH}=\text{CH}, \text{f}, \text{f}', 6\text{H})=5.29\text{--}5.39$ ppm, $\delta(\text{CH}_2\text{-OCO and CH-OCO}, \text{g}, \text{g}', 5\text{H})=4.15\text{--}4.29$ ppm. However, there are two weak signals at 2.42 and 2.54 ascribed to the $-\text{S}-\text{SH}$ and $-\text{S}-\text{S}-\text{SH}$ protons respectively (28). So, the total number of thiolic protons is obtained equal to 0.4. The peak area ratio of CH_3 protons to thiolic protons (1:22.5) corresponds to a molecular weight of 8800 g/mol for the synthesized polysulfide polymer.

EDX analysis was employed to investigate the relative elemental percentage. As shown in Table 1, sunflower oil shows just O and C as expected from its structure. After halogenation, some carbon atoms become halogenated and Cl content increased to around

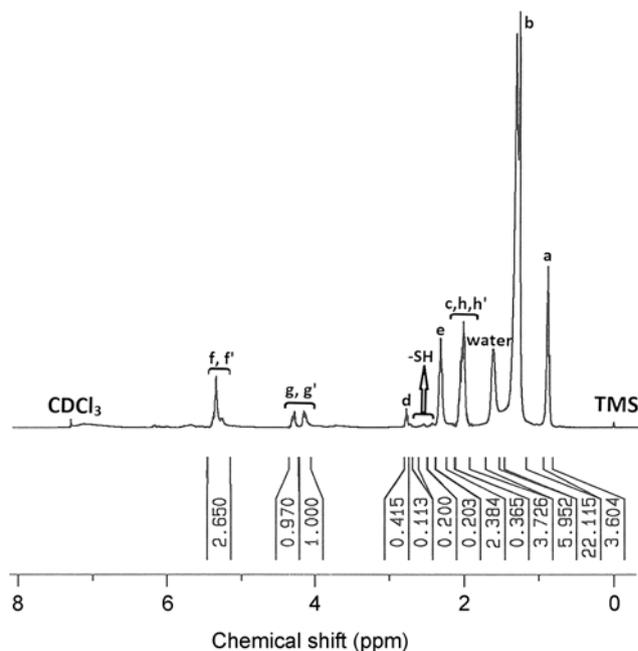


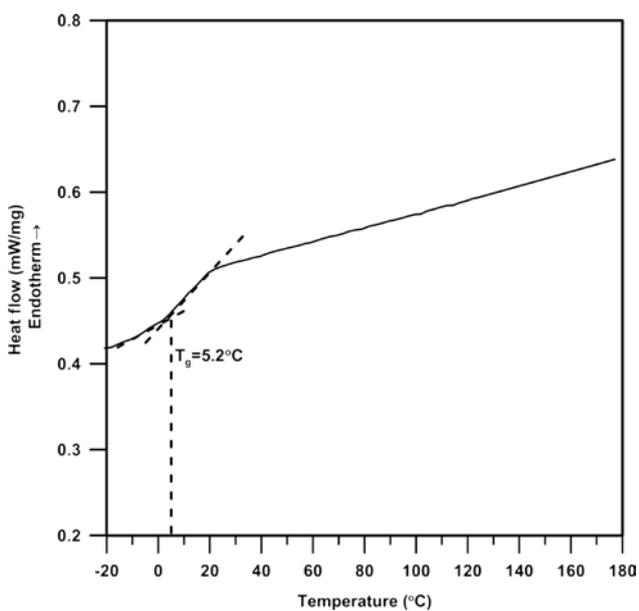
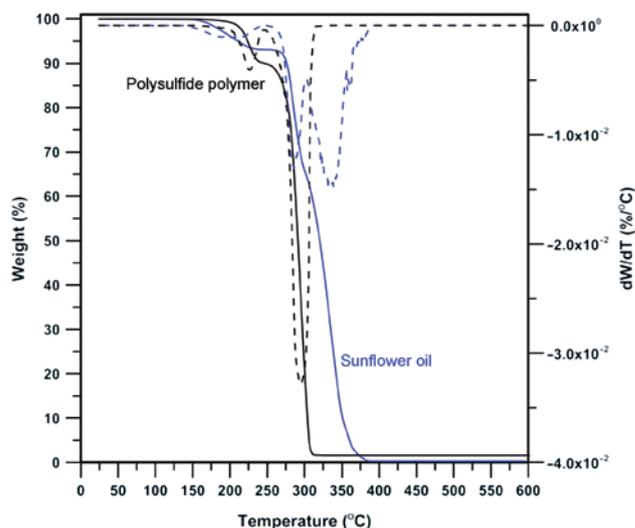
Figure 5: ^1H NMR result for the synthesized polysulfide polymer.

Table 1: Results of EDX of different compounds.

| Sample | wt.% | | | | | |
|---------------------|-------|-------|------|-----|------|-----|
| | C | O | Cl | Ca | S | Na |
| Sunflower oil | 70.07 | 29.93 | – | – | – | – |
| Halogenated oil | 55.4 | 25.2 | 17.1 | 2.3 | – | – |
| Polysulfide polymer | 52.9 | 23.1 | 1.3 | 0.5 | 21.4 | 0.8 |

17 wt.% that means halogenation was performed successfully. Also, a little Ca content is originated from presence of CaCl_2 as residue in halogenated oil. It is clearly observed that after polymerization process, the content of Cl significantly decreased to 1.3 wt.% due to reaction of this functional groups with Na_2S_3 . Also, 21.4 wt.% of S confirms the success of polymerization and shows that sulfur atoms exist in polymer structure. A little amount of Na was related to residue of NaCl salt as side product of polymerization process.

The Thermophysical properties of the synthesized polysulfide polymer were studied by DSC and TGA techniques. Glass transition temperature (T_g) of synthesized polymer was obtained to be 5.2°C that indicates the product is in rubbery state in room temperature. Also, no distinct peak related to the melting could be observed that shows synthesized polymer has amorphous structure (Figure 6). TGA and DTG results of sunflower oil and synthesized polymer are shown in Figure 7. According to the results, sunflower oil shows three thermal decomposition steps with no residue remaining at 600°C .

**Figure 6:** DSC pattern of synthesized polysulfide polymer.**Figure 7:** TGA and DTG thermogram of sunflower oil and synthesized polysulfide polymer.

These three decomposition stages are related to the decomposition of oxygen-containing groups between 150 and 230°C , and unsaturated and saturated fatty acids between 250 and 380°C (29). However, polysulfide polymer shows two stages of degradation. First stage of degradation is related to the decomposition of oxygen-containing moieties (19) of oil structure which takes between 190 and 240°C with $T_{d,max}$ of 228°C . The main stage of degradation is ascribed to random chain scission (30) that initiates at about 250°C with $T_{d,max}$ of 296°C and degradation continues until 313°C . Low thermal stability of synthesized polymer can be related to its oxygen-containing groups, weak C-S bonds, aliphatic carbon structure and also its low molecular weight as obtained via ^1H NMR results.

4 Conclusion

In this work, sunflower oil was halogenated via benzoyl peroxide-catalyzed reaction with hydrochloric acid to obtain halogenated oil. FT-IR and ^1H NMR results were used to approve the halogenation step. Also, EDX results were further confirmed the halogenation process. Then, halogenated oil was used as precursor and reacted with Na_2S_3 polysulfide to produce sunflower oil-based polysulfide polymer. ^1H NMR analysis showed that the molecular weight of polysulfide polymer is about 8800 g/mol and EDX analysis revealed that around 21 wt.% of S exist in polymer structure. Also, DSC analysis showed that the T_g of synthesized polymer is about 5.2°C . According

to TGA result, two stages of degradation are observed. The first stage of degradation was related to the decomposition of oxygen-containing moieties of oil structure and the main stage of degradation is ascribed to random chain scission.

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