

Effect of 1,2,3-Trichloropropane as Tri-Functional Monomer on Thermophysical Properties of Poly(ethylene tetrasulfide)

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ABSTRACT: *In this study, the effect of 1,2,3-trichloropropane (TCP) as trifunctional monomer on thermophysical properties of synthesized poly(ethylene tetrasulfide) (PETS) is investigated. To this end, different amounts of TCP (0-40 mol. % of halide-containing monomer) were incorporated into the structure of polysulfide polymer via interfacial condensation polymerization. Measurement of gel, fraction showed that by the introduction of only 10 mol. % of TCP, synthesized structure is almost crosslinked. The X-Ray Diffraction (XRD) results revealed that all samples are semi-crystalline whereas the crystallinity of samples strongly depends on the amount of TCP. All samples showed a glass transition temperature (T_g) less than 0 °C followed by melting temperature (T_m). Higher amount of crosslinking monomer resulted in higher T_g while T_m and heat of fusion (ΔH_m) were reduced. According to ThermoGravimetric Analysis (TGA) results, all samples exhibited a two-stage degradation process. Although, the introduction of 10 mol. % TCP into the structure of PETS resulted in lower thermal stability of obtained polymer, adding higher amounts of TCP led to the higher thermal stability of polymers.*

KEYWORDS: *Polysulfide; Poly(ethylene tetrasulfide); 1,2,3-trichloropropane; Crosslinking; Thermo-physical properties.*

INTRODUCTION

Among different elastomers, polysulfide polymers have high resistance to environmental degradation, fuels, solvents, and water [1-4]. They also have a variety of curing methods, good performance at low temperatures, and excellent cohesion to many surfaces [5-9]. These properties candidate polysulfide polymers for different applications such as adhesives [10], lithium batteries [11], nanocomposites [12], etc. Solid polysulfide polymers are high-molecular-weight rubbers [13] which are prepared

via polycondensation of organic polyhalids with mineral polysulfides in water medium [14]. In this field, different polysulfide polymers including poly(*p*-xylylene tetrasulfide) [15], poly(ethylene tetrasulfide) [16], etc. have been synthesized via interfacial polycondensation and their different properties have been investigated. Poly(ethylene tetrasulfide) is known as an elastomeric polymer with the ability of self-healing which can be used in different applications such as adhesives,

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preparation of nanocomposites, etc. However, it has been used almost in fabrication of nanocomposites via in situ polymerization process [12-13, 16-17].

In liquid polysulfide polymers, 1,2,3-trichloropropane (TCP) has been used to aim of branching and completing curing processes where its content is less than 5% [18]. Also, effect of multifunctional monomer on the properties of different polymers has been established completely [19-20]. Although some works have been studied particle formation in polymerization of TCP [21], there is no mentionable work in the case of solid polysulfide polymers related to effect of multifunctional monomer.

In current study, different amounts of TCP as trifunctional monomer are used to investigate the effect of multifunctional monomer on the properties of synthesized crosslinked structure. To this end, 0-40 mol. % of TCP is used in interfacial polymerization of 1,2-dichloroethane (DCE) with aqueous solution of disodium tetrasulfide (Na_2S_4). Gel fraction of each sample was determined via Soxhlet extraction using boiling dimethyl sulfoxide (DMSO). Crystalline structure of samples was analyzed by XRD method and thermal transitions were measured by Differential Scanning Calorimetry (DSC). Also, thermal stability of samples was studied using TGA.

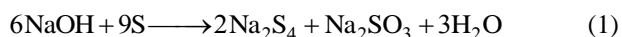
EXPERIMENTAL SECTION

Materials

1,2-dichloroethane (DCE, Sigma-Aldrich, 99.8%), 1,2,3-trichloropropane (TCP, Sigma-Aldrich, 99%), sodium hydroxide (NaOH, Mojallali, 97%), dimethyl sulfoxide (DMSO, Sigma-Aldrich, 99.9%), sulfur (S, Merck, 99%) and hydrochloric acid (HCl, Mojallali, aqueous solution, 37%) were used as received.

Synthesis of disodium tetrasulfide (Na_2S_4)

Sodium hydroxide (8 g, 0.20 mol) and deionized water (200 mL) were placed in a 250-mL flask and heated to boiling point. Then, sulfur (9.61 g, 0.3 mol) was added to the flask and reaction was performed for 3 h to obtain a monotone dark brick solution. After cooling, unreacted sulfur was filtered and aqueous Na_2S_4 was obtained *via* Equation (1):



Synthesis of polysulfide polymers

To prepare poly(ethylene tetrasulfide) (PETS, CPS00), a fresh solution of Na_2S_4 (12 mL) was poured into a four-necked round-bottom flask placed in oil bath at 70 °C. DCE (5.2 mL) was added dropwise and reaction was performed for 3 h. To prepare crosslinked polymers, same procedure was used where different amounts of TCP as crosslinking agent were utilized and added to reaction with DCE. To remove sodium chloride salt formed during the reaction, product was washed by distilled water and HCl (37%) several times. Finally, obtained polymer was vacuum-dried at 40 °C for 24 h. Samples were named as CPSYY where YY was the mol. % of TCP (00, 10, 20, 30, and 40).

Gel content

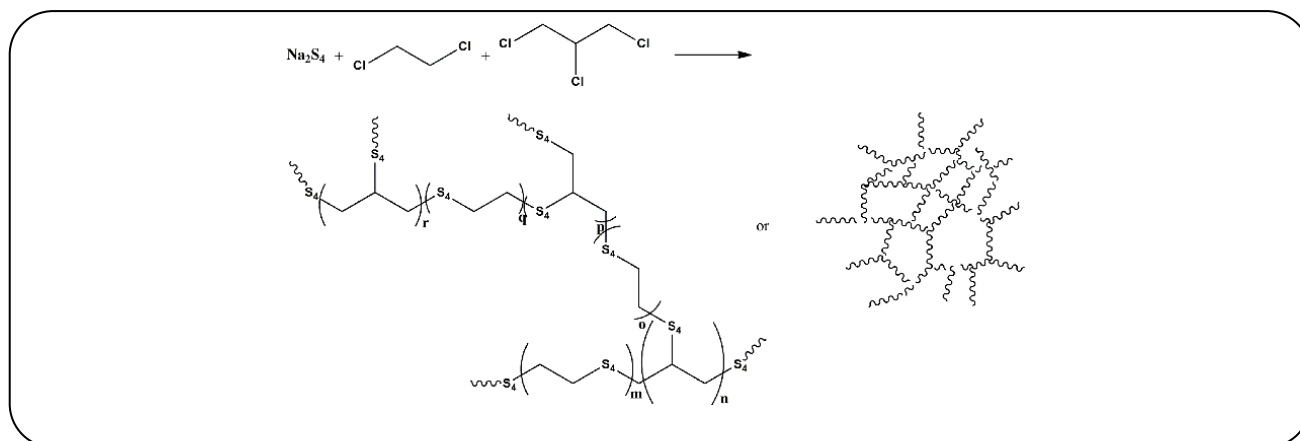
To determine gel content of each sample, 1.0 g of dried sample were placed in a 0.2- μm Regenerated Cellulose (RC) bag (pre-weighted) and non-crosslinked chains were extracted via Soxhlet extraction using boiling DMSO. After extraction, sample-containing cellulose bag was vacuum-dried at 70 °C for 48 h. The gel fraction was calculated via Equation (2):

$$\text{Gel fraction (\%)} = \frac{\text{weight of the dried sample after extraction}}{\text{weight of the dried sample before extraction}} \times 100 \quad (2)$$

To determine gel fractions, three measurements were performed for each sample.

Characterization methods

X-ray diffraction (XRD) spectra were collected on an X-ray diffraction instrument (Siemens D5000) with a Cu target ($\lambda = 0.1540$ nm) at room temperature. The system consists of a rotating anode generator which operated at 35 kV and 20 mA. The samples were scanned from $2\theta = 10^\circ$ to 40° at the step scan mode. The diffraction pattern was collected using a scintillation counter detector. Differential scanning calorimetry (DSC, NETZSCH DSC 200 F3, Netzsch Co, Selb/Bavaria, Germany) was carried out using nitrogen purging at a rate of 50 mL/min. Aluminum pans containing 2-3 mg of the samples were sealed using the DSC sample press. The samples were heated from ambient temperature to 180 °C at a heating rate of 10 °C/min and then were cooled at the same rate down to -50 °C with subsequent heating to 180 °C.



Scheme 1: Schematic of reaction to prepare crosslinked polysulfide polymer.

T_g was obtained as the inflection point of the heat capacity change in second stage of heating. Thermal gravimetric analyses were carried out by means of a PL thermo-gravimetric analyzer (Polymer Laboratories, TGA 1000, UK). All samples (about 10 mg) were heated from ambient temperature to 600 °C at a heating rate of 10 °C/min and nitrogen as the purging gas was used at a flow rate of 50 mL/min.

RESULTS AND DISCUSSION

To synthesize crosslinked polysulfide polymers, different amounts of TCP were added to the polymerization medium of DCE and Na_2S_4 as depicted in Scheme 1. Total molar number of functional groups were kept constant whereas amount of TCP was varied between 0 and 40 mol. %. The gel fraction values of samples are summarized in Table 1. Results show that higher amount of TCP as crosslinker leads to higher gel fraction of synthesized polymer where by using 10 mol. % of TCP (or higher) in halide-containing monomer, a crosslinked polymer is synthesized. It is noteworthy that CPS00 also shows a gel fraction of 6.3 wt. % which may be attributed to solubility problem of polysulfide polymers in different solvents [22].

Crystalline structure of the polymers was investigated by X-ray diffraction (XRD) as results are shown in Fig. 1. The XRD pattern of all samples show a sharp peak at 20.7° related to crystalline structure of polymers due to existence of tetrasulfide units in the structure polymers [23]. However, by introduction of more crosslinking monomer into structure of sample, intensity of the peak decreases. To clarify the reason of such a phenomenon,

size of crystals was calculated by the Scherrer equation (Equation 3) as follow [24]:

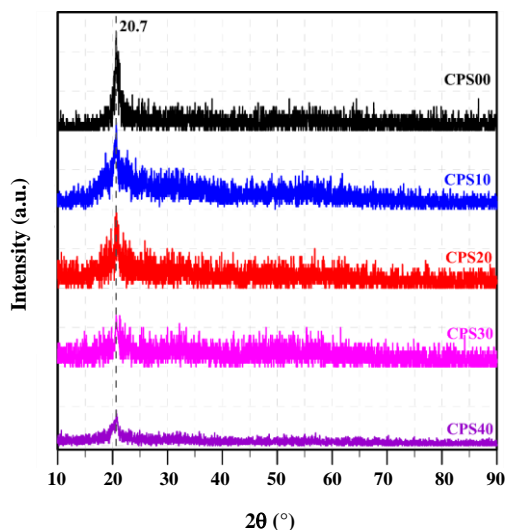
$$\tau = \frac{K\lambda}{\beta \cos \theta} \quad (3)$$

Where, τ is the mean size of crystalline domains, K is a dimensionless shape factor which is taken equal to unit, β is the line broadening at half the maximum intensity, and θ is the Bragg angle (in degrees). The size of crystals in synthesized polymers is presented in Table 1. As it can be seen from the results, size of crystals decreases by increasing the amount of TCP. This is attributed to the confinement effect of crosslinking process which prevents the formation of crystals originated from chain folding [25]. Additionally, the XRD peak becomes broader at higher amounts of crosslinker. This is attributed to the reduction of size of crystalline domains and presence of defects in structure of crystalline domains that results in deficiency of complete crystallization [26].

To further investigate the crystalline structure of samples, all samples were examined by means of DSC analysis and results are depicted in Fig. 2. All samples showed a glass transition temperature (T_g) less than 0 °C followed by a melting temperature (T_m). T_g is obtained -24.5, -20.0, -18.4, -15.6 and -14.5 °C for CPS00, CPS10, CPS20, CPS30, and CPS40 respectively, i.e. by incorporation of more crosslinking monomer into polymer structure, higher T_g was obtained. In fact, the crosslinker reduces mobility of amorphous segments that results in increase of T_g [27-28]. Also, by increasing amount of crosslinker, T_m and heat of fusion (ΔH_m) are reduced. CPS00 showed

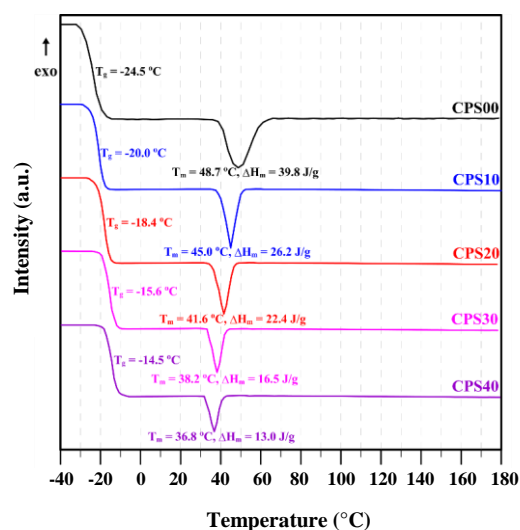
Table 1: Gel fraction values and crystal size of different samples prepared via polymerization of DCE/TCP and N_2S_4 .

Sample	CPS00	CPS10	CPS20	CPS30	CPS40
Gel fraction (%)	6.3 ± 0.2	83.5 ± 0.6	98.4 ± 0.7	100 ± 0.0	100 ± 0.0
Crystal size (nm)	12.8	10.7	8.4	7.0	6.8

**Fig. 1: XRD patterns of different samples prepared via polymerization of DCE/TCP and N_2S_4 .**

a T_m of 48.7°C whereas T_m of CPS40 was obtained 36.8°C . Formation of crosslinked junctions in amorphous phase disturbs reorganization and chain folding during crystallization process. This results in formation of imperfect crystallites with smaller size and less in content [25]. Conclusively, melting resistance of crystals decreases and T_m switches to lower temperatures. Also, low thermal energy is needed to melt crystalline structure that leads to decreasing ΔH_m . These results are also confirmed by XRD which shows lower size of crystals by increasing amount of crosslinker.

ThermoGravimetric Analysis (TGA) was used to study thermal stability of synthesized samples. Also, some of their thermal properties are summarized in Table 2. All samples exhibited a two-stage degradation process where the first step is ascribed to random chain scission [29-30] and the second degradation takes place due to pyrolysis process. Introduction of 10 mol. % TCP into structure of PETS results in lower thermal stability. This is attributed to increment of C-S bonds which are more thermal-labile than C-C bonds [31]. Also, crosslinking introduces tertiary carbons into polymer structure [32] which are prone to thermal degradation. However, by adding higher amounts of TCP, degradation temperature

**Fig. 2: DSC thermograms for different samples prepared via polymerization of DCE/TCP and N_2S_4 .**

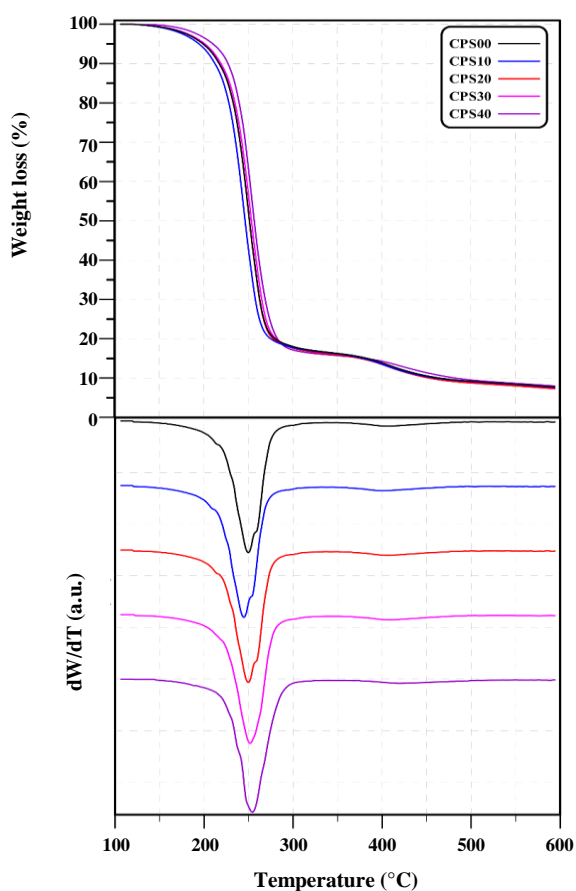
increases because of increasing of crosslinking density that causes higher resistance of structure to degradation at higher temperatures [33].

CONCLUSIONS

Different amounts of TCP as trifunctional monomer were introduced into structure of PETS to affect its thermophysical properties. Measurement of gel fractions revealed that adding 10 mol. % and higher amounts of TCP in halide-containing monomer results in crosslinked structure as expected. By introduction of more crosslinking monomer into structure, intensity of XRD peak decreased due to formation of smaller crystals originated from confinement effect of crosslinking process. All samples showed a T_g less than 0°C followed by a T_m where higher T_g was observed by incorporation of more crosslinking monomer into polymer structure related to reduced mobility of amorphous segments. Also, increasing amount of crosslinker led to lower T_m and ΔH_m values. This was ascribed to disturbing chain folding during crystallization process by crosslinked junctions and subsequently, formation of imperfect crystallites with smaller size and less in content.

Table 2: Summarized TGA results for different samples prepared via polymerization of DCE/TCP and N_2S_4 .

Sample	TGA			DTG	
	$T_{0.1}$ (°C)	$T_{0.5}$ (°C)	Char at 600 °C (wt. %)	$T_{d,max1}$ (°C)	$T_{d,max2}$ (°C)
CPS00	216.7	251.2	7.64	250.0	405.0
CPS10	212.5	246.2	7.57	245.0	400.0
CPS20	216.7	251.9	7.19	250.0	405.0
CPS30	219.2	253.3	7.40	251.7	410.0
CPS40	226.7	256.7	7.89	254.2	420.0

Fig. 3: TGA thermograms for different samples prepared via polymerization of DCE/TCP and N_2S_4 .

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