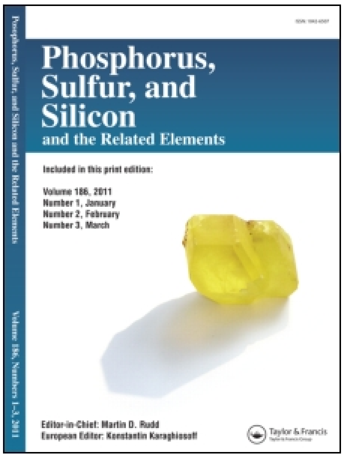

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POLYMERIZATION OF METHYLENE DICHLORIDE AND SODIUM TETRASULFIDE: SYNTHESIS AND KINETIC STUDIES

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The kinetics of the condensation polymerization of a novel polysulfide polymer based on methylene dichloride and sodium tetrasulfide is studied. The results of the experiments indicated that the reaction order is two. The activation energy obtained from the Arrhenius plot is 1.879 kcal mol^{-1}, and the pre-exponential frequency factor is A = 27.11 min^{-1} at temperature range of 40∼60°C. The polymer is characterized by using Fourier transform-infrared and CHN analysis. Thermal properties were evaluated by differential scanning calorimetry. The TGA-DTA was used to find out the thermal stability of polymer. The solvent resistance of the polymer was investigated by the swelling method.

Supplemental materials are available for this article. Go to the publisher's online edition of **Phosphorus, Sulfur, and Silicon and the Related Elements** ***to view the free supplemental file.***

Keywords Characterization; polysulfide polymer; synthesis

INTRODUCTION

Sulfur-containing polymers are increasingly important because their interesting properties make them useful in a wide range of application.[1,2] Aliphatic polysulfide polymers constitute an important class of commercial polymers with wide industrial applications, particularly in sealants, which have excellent resistance to solvents such as ketones, alcohols, acids, hydrocarbon solvents, water, etc. They also have low permeability to gases, and show superior resistance to the effects of sunlight, ozone, aging, and weathering.[1–3] Hence, they are heavily used in coatings, adhesives, sealants, insulators, and other applications. Their wide applications are in hose industries to manufacture spray paint hoses, gasoline

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hoses, and hose nozzles. They are also used as sealants to fuel tanks and de-icers on wings of airplanes.[4–7]

Polymers containing sulfur can be prepared by different methods such as ring-opening polymerization or polycondensation reactions. The polysulfide polymers are aromatic and aliphatic polymers. The aliphatic polysulfide polymers are high molecular weight solid elastomers. Among the various methods of preparation, synthetic methods such as reaction of dihalides with dihalides, polymerization of episulfides, and reaction of dihalides with inorganic polysulfides have been applied routinely.[8–17] The following article describes the kinetic study and characterization of the linear poly(methylenetetrasulfide).

RESULTS AND DISCUSSION

In this study, the synthesis and kinetic properties of polysulfide polymer from methylene dichloride were investigated (Scheme 1). Elemental analysis data of the polymer are shown in Scheme 1.

$$\mathrm{Cl\text{-}CH_2\text{-}Cl} + \mathrm{Na_2S_4} \xrightarrow{k} \left(\mathrm{CH_2S_4}\right) + \mathrm{NaCl}$$

Scheme 1 Synthesis of poly(methylenetetrasulfide).

The percentages of carbon and hydrogen of the polymer observed [C, H (7.98%, 1.26%)] are in accordance with the calculated values [C, H (8.45, 1.41)].

The influence of the temperature also was examined. In the kinetic study of polymerization, the determination of conversion is very important; the conversion of polymer can be calculated by the weighting method. For this, the kinetic parameters were obtained at different temperatures. Figure 1 shows the conversion versus time of the reaction of methylene dichloride with sodium tetrasulfide at 40, 50, and 55°C.

To determine the kinetic order of the reaction for the polycondensation process, logC, $1/1-P$, and $1/C^2$ versus time was plotted, where log C, $1/1-P$, and $1/C^2$ represent first, second, and third-order kinetics, respectively. The kinetic order was evaluated graphically by plotting the values of the kinetic equations versus time. In the $1/1-P$, P is calculated

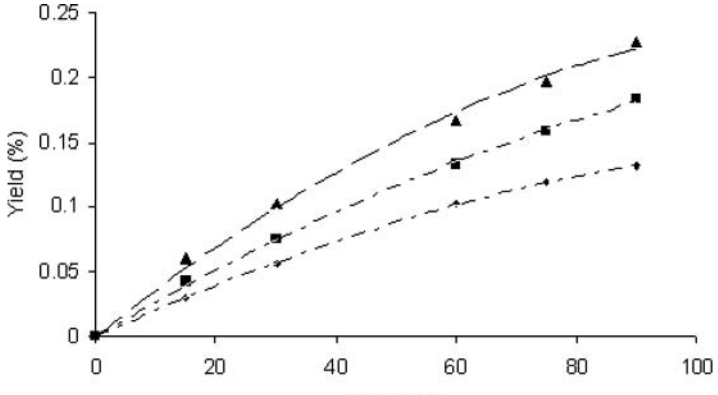


Figure 1 Influence of temperature and reaction time on conversion (◆ = 40°C, ■ = 50°C, ▲ = 550°C).

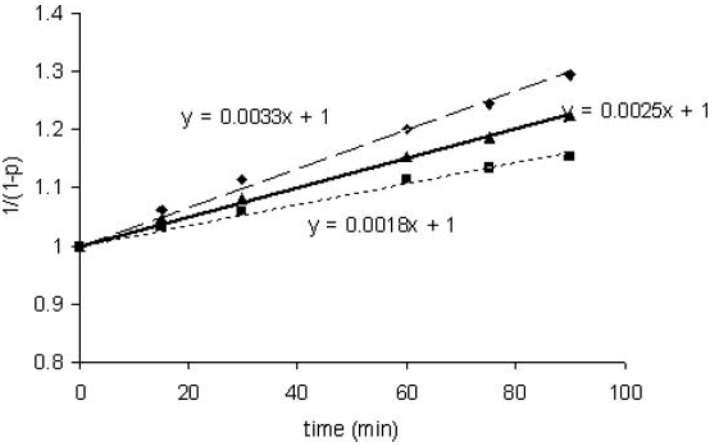


Figure 2 Order of the reaction for the polymerization of polysulfide rubber (♦ = 40°C, ■ = 50°C, ▲ = 55°C).

from the formula $\rho = 1-C/C_0$, where C is the concentration of functional group of the polymer at a given reaction time, and C_o is the initial functional group of the polymer. Plots of the polycondensation of methylene dichloride with sodium tetrasulfide at 40, 50, and 55°C are shown in Figure 2.

A straight line is obtained for the experimentally obtained data when the quantity $1/(1-P)$ is used. This indicates a second-order reaction with slope equal to the rate constant k. The Arrhenius plot of log k versus the reciprocal thermodynamic temperature gave the value of the initiation energy $E = 1.879$ kcal mol^{-1}, and the frequency factor is $A = 27.11$ min^{-1}, as shown in Figure S1 (available online in the Supplemental Materials).

The IR spectrum of the polymer is shown in Figure 3. The IR spectrum of the polymer is in good agreement with the assigned structure. The alkyl halide absorptions are absent,

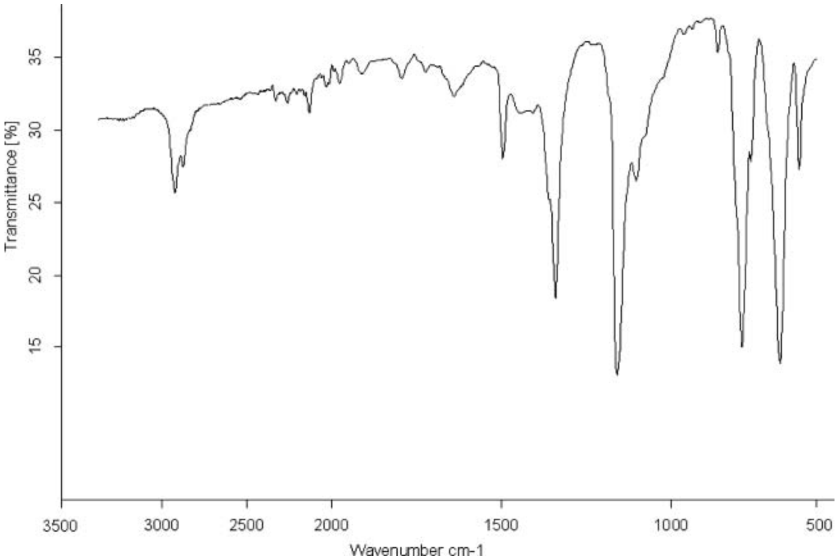


Figure 3 Infrared spectra of the polysulfide.

and no hydroxyl absorptions are observed. These spectra when compared to similar linear polysulfides show the typical characteristic absorptions.

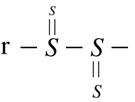
The absorption bands corresponding to C-S and S-CH_2 stretching appeared at around 830 cm^{-1} and 1250 cm^{-1}, respectively. Also, the methyl deformational at around 1380 cm^{-1}, 1270 cm^{-1}, 1250 cm^{-1} and olefin stretching (CH) 2900 cm^{-1} and (CH_2) 730 cm^{-1} were observed.

The thermal properties of the polymer were studied by thermogravimetry and DSC.

Figure S2 (Supplemental Materials) shows the DSC trace of poly(methylenetetrasulfide). The T_g and T_m values are –19.8°C and 77.3°C, respectively.

This behavior is observed also in polymer with sulfur atoms along the aliphatic chain.[18–20] In order to have an idea of the significant range of glass transition temperature, the T_g of this sample has been estimated by the approach of Van Krevelen and Hoftyzer,[21] as follows:

$$T_g = \frac{Y_g}{M} = \frac{\sum_i^{Y_{gi}}}{M}$$

where M is the molar mass of the repeating unit (g/mol) and Y_g is called the molar glass transition function. The expected glass transition temperatures were calculated approximately by using the Table I, $T_g = -17.5$°C. This small difference between experimental and theoretical T_g, may be attributed to the absence of absolute molar mass data for  $-\overset{\overset{S}{\|}}{S}-\underset{\underset{S}{\|}}{S}-$ bonding structure group.

The polymer also shows a melting peak at around 61.2°C, $\Delta H = -65.91$ kJ/g. This may be attributed to the incorporation of sulfur linkages in the backbone of polysulfide polymer, which facilitate crystallization. These results indicate that the type of polysulfide plays an important role in the thermal stability of the prepared polymers.

Also in order to have an idea of a significant range of melting temperatures, it has been observed that the ratio of glass transition temperature to melting point (both expressed in K) has about the same value for many polymers by the approach of modification of Boyer and Beaman[22]; for unsymmetrical polymers the value is $T_g/T_m = 0.75$, therefore our polymer should have a melting point around 65.3°C, close to the experimentally determined value.

Figure S3 (Supplemental Materials) shows the thermograms of the polymer. The temperatures corresponding to 10% and 50% weight loss and char residue remaining at 800°C are 190.18, 252.76, and 4.86, respectively.

The synthesized polymer showed exothermic degradation in two steps at 262°C and 423°C. Only a few polymers, such as polyacrylonitrile (PAN), hydroxyl terminated polybutadiene (HTPB), and polysulfide polymers, are reported in the literature as undergoing exothermic degradation; it is possible to assume that the thermal decomposition of

Table I Group contributions to Y_{gi}

Group	Y_{gi}	M_i
$-CH_2$-	4.3	14.0
$-S-$	8	32.1
$-SS-$	16	64.2

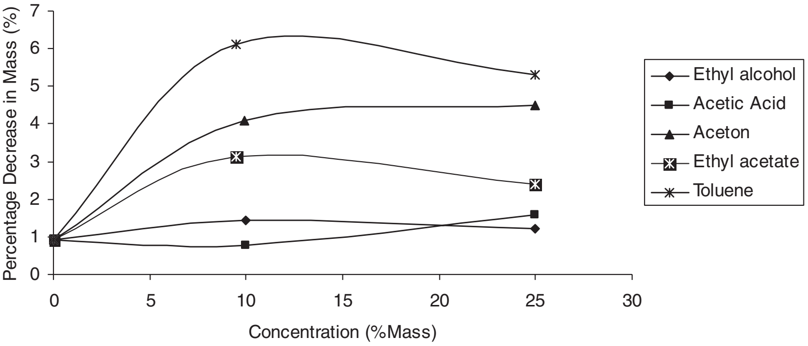


Figure 4 Percent swelling of polymer in solvents, at 25°C after 1 month.

the polysulfide gives rise to the formation of compounds that interfere with the oxidation products.[16,17] The apparent kinetic parameters of thermal decomposition of polysulfide rubber could also be determined using the DTG curve fitting method.[21] This method involves measuring the weight loss behavior obtained by using thermogravimetry (TGA), and then using the Arrhenius equation to fit the data obtained from the TGA measurement (Figure S3, Supplemental Materials) as follows:

$$\left(\frac{dW}{dt}\right) = Ae^{-E}/RT_{(1-W)^n}$$

where E, A, and n are the apparent activation energy, the pre-exponential factor, and the reaction order, respectively. Using DTG, the E, A, and n are obtained from the curve fitting process. Results show that the kinetic parameters of the first peak were determined by fitting the left half of the peak (180–260°C), which gave 234 kJ/mol and 0.73 for E and n, respectively. The kinetic parameters for the second peak were determined to be 196 kJ/mol and 1.2 for E and n, respectively, through fitting the right half of the peak (260–330°C).

The solubility of the polymer was tested with various solvents. According to the swelling method, the organic polysulfide polymer was tested in ethyl alcohol, acetic acid, acetone, and water. For this purpose, specimens in the form of 2-mm-thick circular discs of 40 mm in diameter were immersed in the solvents, and the diameters of the swollen samples were measured. For the determination of solvent resistance properties of the specimens, each solvent was tested at three different concentrations at 25°C (Figure 4).

The presence of sulfur in the backbone enhances the solubility parameters (δ) of the poly(methylenetetrasulfide) ($\delta = 7.06$, calculated by the Hoftyzer and Krevelen method). The polymer is insoluble in ethyl acetate, toluene, ethylene dichloride, ethyl alcohol, acetic acid, acetone, and water.

CONCLUSION

The synthesis of poly(methylenetetrasulfide)was studied at three different temperatures. All these reactions were carried out from methylene dichloride and sodium tetarasulfide by the polycondensation technique. The features of this study are as follows: (1) A simple second-order rate law is capable of analyzing the reaction, the activation energy of the polycondensation was obtained from Arrhenius plot is 1.879 kcal mol^{-1}, and the pre-exponential frequency factor is A = 27.11 min^{-1}. (2) The structure of the polymer was confirmed by FT-IR spectroscopy and elemental analysis. (3) DSC analysis of the polymer reveals that the T_g value of this polymer is –19.8°C, and the polymer is capable of melting in the range of 77–160°C. (4) Thermal studies of the poly(methylenetetrasulfide) revealed that this polymer is stable up to 160°C, and 10% weight loss takes place after 185°C. (5) The unique thermal behavior of these materials, in that two thermal endotherms were observed, will require further investigation. (6) The polymer is insoluble in many solvents.

EXPERIMENTAL

Reagents

Methylene dichloride, sodium hydroxide, and sulfur were used as received from Merck.

Characterization Methods

FT-IR. Infrared spectra were taken on a Bruker, Equinox 55 spectrometer.

Elemental Analyses (CHN). Elemental analysis (C and H) was performed on PerkinElmer 2400 Series II CHNS/O Elemental Analyzer.

Differential Scanning Calorimetry (DSC). DSC measurement was performed on a Netzsch DSC 200 F3 instrument. The temperature was ramped at 5°C/min from –100°C to 100°C with a nitrogen atmosphere. The sample weight was approximately 5 mg. The glass transition temperature was determined by the intersection method, and the melting point was taken as the maximum in the endothermic peak. The peak area was measured as the enthalpy of the polymer.

TGA-DTA. Thermogravimetric analysis (TGA) spectrum was obtained using a PL-STA-1500 thermal analysis unit attached with differential thermal analysis. The experiment was carried out in a nitrogen atmosphere at a heating rate of 10°C/min.

Procedure of Synthesis of Polysulfide Polymer

To a 500 mL four-necked round bottom flask equipped with a stirrer, a dropping funnel, a condenser, and a thermometer, a fresh solution of sodium tetrasulfide (250 mL) was added. Agitation was provided by a double-impeller shaft. The flask was heated to 50°C with constant stirring at 600 rpm, and then methylene dichloride (80 mL) was added dropwise through the dropping funnel, after which the reaction mixture was stirred for 1 h. During this time, the condensation of methylene dichloride and sodium tetrasulfide was complete and a tetrasulfide polymer was formed. The obtained polymer dispersion was washed with hot water (150 mL) followed by decantation. This procedure was repeated twice to remove inorganic salts.

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