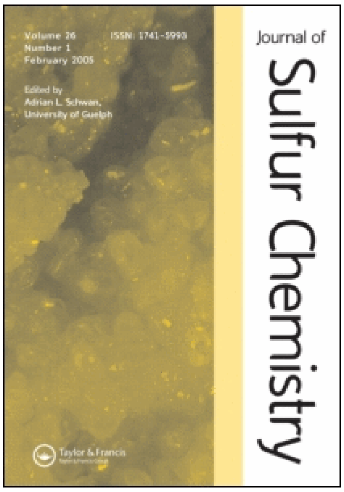

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Polymerization of ethylene dichloride and sodium tetrasulfide: synthesis and kinetic studies

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In this work, the kinetics of the condensation polymerization of ethylene dichloride and sodium tetrasulfide is studied. The resulting polymer is characterized by FT-IR, thermogravimetric analysis (TGA), differential thermal analysis (DTA), elemental analyses (CHN), and differential scanning calorimetry (DSC) analysis. The activation energy of the condensation polymerization obtained from an Arrhenius plot is 97.2 kJ mol^{-1}, and the pre-exponential frequency factor is $A = 24.2\ \mathrm{min}^{-1}$ at a temperature range of 50–70 °C.

Keywords: polysulfide polymer; condensation polymerization; kinetic; synthesis

1. Introduction

In 1840, Lowig discovered that an elastic material was produced when ethylene dichloride (EDC) was reacted with potassium polysulfide (*1*). Eighty-five years later, Patrick started investigating the rubbery elastic substances synthesized by 1,2-dichloroethane with sodium polysulfide in a caustic solution and established the backbone of the polysulfide polymer industry (*2–5*). This linear polysulfide rubber constitutes an important class of commercial polymers with wide industrial applications, particularly in coatings and sealants where excellent oil and solvent resistance are needed. Owing to their low cost of manufacturing and good physical and mechanical properties, they are also widely used in the rubber industry for manufacturing of various kinds of hoses and in aerospace industries for oil resistance linings, especially for fuel tanks (*6–10*).

Despite the long history of their production and commercial use, a detailed study of the kinetics of their polymerization has not been published in the open literature. This could be attributed to the insolubility of this polymer in common organic solvents, and hence, difficulties in their characterization by common accessible and required analytical techniques such as NMR and gel permeation chromatography (GPC) (*10–12*).

In this paper, the polymerization and kinetic study of EDC and sodium tetrasulfide is presented.

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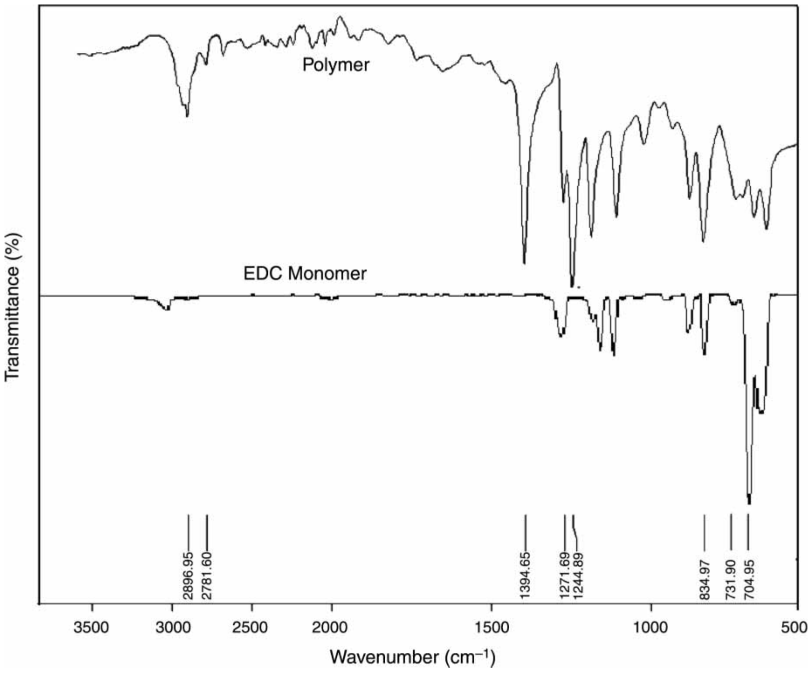


Figure 1. FT-IR spectra of EDC and polysulfide polymer.

2. Results and discussion

2.1. *FT-IR spectra of the polymer*

FT-IR spectra of the polysulfide polymer and EDC are shown in Figure 1. The formation of polymeric product was confirmed by the disappearance of the strong C–Cl stretching absorption at $705\,\text{cm}^{-1}$.

Also the absorption bands corresponding to C–S and S–CH_2 stretching appeared at around 730 and $1250\,\text{cm}^{-1}$, respectively. The olefin, C–H and CH_2 stretching was observed at around 2900 and $725\,\text{cm}^{-1}$, respectively.

2.2. *Elemental analyses (CHN)*

The stoichiometric calculation of elemental C and H in a $(C_2H_4S_4)_n$ polymer is C, H (15.4%, 2.5%). The experimental data shows C, H (14.8%, 2.2%).

2.3. *Polymerization kinetics*

Polysulfide polymer is produced by polymerization of sodium tetrasulfide and EDC as:

$$n\text{ClCH}_2\text{CH}_2\text{Cl} + n\text{Na}_2\text{S}_4 \xrightarrow{k} -[\text{CH}_2\text{CH}_2\text{S}_4] - \text{NaCl}$$

In the kinetic study of this polymerization, determination of conversion is of utmost importance. By assuming that this polymerization reaction could be reduced to the standard reaction of A–A and B–B, thus:

$$n\text{A} - \text{A} + n\text{B} - \text{B} \xrightarrow{k} \text{Polymer} + \text{Byproduct}$$

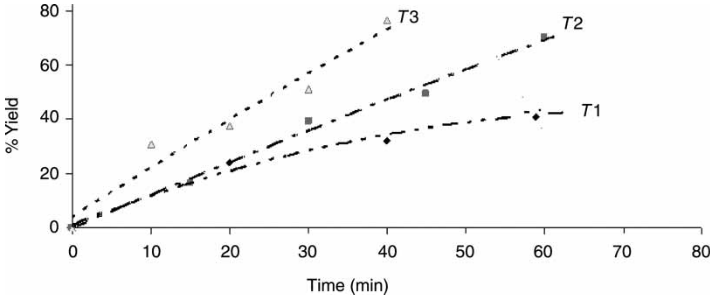


Figure 2. Influence of temperature and reaction time on conversion (♦ = 50°C, ■ = 60°C, ▲ = 70°C).

and, based on the stoichiometric ratio between A–A and B–B, conversion of polymer (x) can be calculated by employing ordinary weighting method, as follows (*13*, *14*):

$$x = \frac{\text{Weight of polymer}}{V_{\text{EDC}}}.$$

Thus, we were able to obtain the kinetic parameters at different temperatures. Figure 2 shows the conversion versus time of the reaction of EDC with sodium tetrasulfide at 50°C, 60°C and 70°C.

To determine the kinetic order of the polycondensation polymerization reaction, log C, $1/1 - P$ and $1/C2$ were plotted against time where log C, $1/1 - P$ and $1/C2$ represent first, second and third-order kinetics, respectively. The kinetic order was evaluated graphically by plotting the values of the kinetic equations vs. time. In the case of $1/1 - P$ and P, they are calculated 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_0 is the initial functional group of the polymer. The best-fitted line was sought for the experimentally obtained data when the quantity log C is used. The best-fitted curve suggests a first-order reaction with a slope equal to the rate constant k. The summary of resulting data is given in Table 1.

To study the effect of temperature on the rate of reactions, the Arrhenius equation was used:

$$\ln k = \ln A - \frac{E_a}{R}\frac{1}{T},$$

where k is the rate constant, A the pre-exponential frequency factor, E_a the activation energy, R the gas constant and T the temperature (in K). Thus, the activation energy E_a and the frequency factor A are obtained from the slope and the zero intercept of the straight line plot of ln K versus inverse of temperature. For the polysulfide polymer produced in this work, the obtained value of the activation energy is $E_a = 97.2$ kJ/mol and the frequency factor is $A = 24.2\,\text{min}^{-1}$.

Table 1. Summary of kinetic data.

T (°C)	k	$\log C = -\log C_0 + kt$	R^2
25[a]	–	–	–
50	0.0134	$y = 0.0134x + 0.28$	0.998
60	0.0078	$y = 0.0078x + 0.28$	0.986
70	0.0037	$y = 0.0037x + 0.28$	0.998
80[b]	–	–	–

Notes: [a] In this temperature, the rate of polymerization was extremely low. [b] Since this temperature is near to the boiling point of EDC, it was impossible to obtain reproducible data.

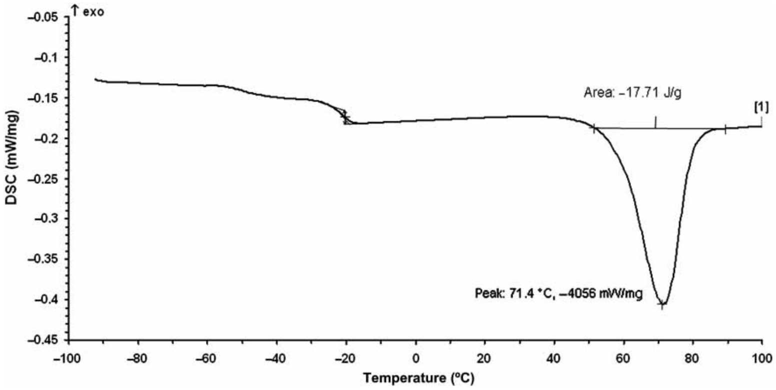


Figure 3. DSC plot for polysulfide polymer.

2.4. *Thermal analysis*

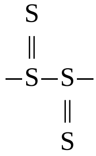
The thermal properties such as glass transition temperatures (T_g), crystalline melt temperatures (T_m) and the decomposition temperatures of the prepared polymers were obtained by TGA–DTA and DSC.

2.5. *Differential scanning calorimetry*

The DSC thermogram of the produced sample shows endothermic shift due to the glass transition with a T_g value of −18.5°C (Figure 3). This behavior has also been observed in other polymers with sulfur atoms along the aliphatic chain (*15*, *16*).

In order to have an idea for significance of this glass transition temperature, the T_g of this sample has been estimated by the approach of Van Krevelen (*17*), as follows:

$$T_{\underline{g}} = \frac{Y_g}{M} = \frac{\sum_i Y_{gi}}{M},$$

where M is the molar mass of the repeating unit (g/mol) and Y_g is the molar glass transition function. The expected T_g calculated by using the elemental data shown in Table 2 was −13.5°C. This small difference between experimental and theoretical T_g may be attributed to the lack of absolute molar mass data for  $-\overset{\overset{\displaystyle S}{\|}}{S}-\underset{\underset{\displaystyle S}{\|}}{S}-$ bonding structure group (*1–5*).

The polymer also shows a melting peak at around 71.4°C. For many unsymmetrical polymers, Beaman (*18*) have shown that the ratio of glass transition temperature to melting point (both

Table 2. Group contributions to Y_{gi} (*17*).

Group	Y_{gi}	M_i
$-CH_2-$	2.7	14.0
–S–	8	32.1
–SS–	16	64.2

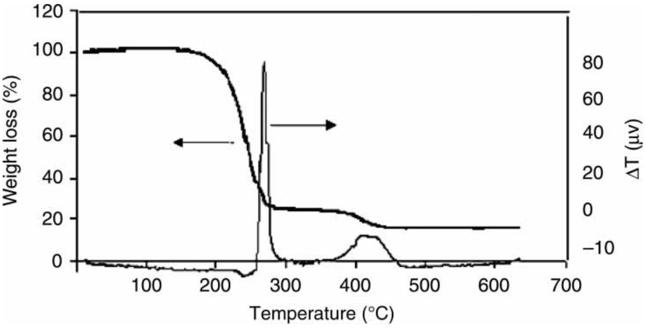


Figure 4. TGA–DTA thermograms of polysulfide polymer.

expressed in K) has a value of 0.75. Therefore, the melting point for our polymer should be 67°C, which is close to the observed value.

2.6. *Thermal degradation*

TGA–DTA has been used for the thermal degradation studies. TGA–DTA thermograms of the polysulfide sample are shown in Figure 4. Degradation temperature was observed near 274°C, and the DTA curve indicates an exothermic behavior.

Very few polymers, such as polyacrylonitrile, hydroxyl terminated polybutadiene and polysulfide polymers, are reported in the literature as undergoing exothermic degradation. The observed exothermic degradation behavior is caused by the thermal degradation products (*15*, *19*).

This feature of degradation in sulfur-containing polymers could be due to the difference in the degradation mechanisms and the product (*16*).

The apparent kinetic parameters of thermal decomposition of polysulfide rubber could be also determined using the DTG curve-fitting method (*20*). This method involves first measuring the weight loss behavior obtained using TGA, and then using the Arrhenius equation to fit the data obtained from the TGA measurement (Figure 4) as:

$$\left(\frac{\mathrm{d}W}{\mathrm{d}t}\right) = A\mathrm{e}^{-E/RT}(1 - W)^n,$$

Where, E, A and n are the apparent activation energy, the pre-exponential factor and the reaction order, respectively. Using DTG curve fitting, the apparent activation energy, E, of the produced polysulfide polymer was 263 kJ/mol.

3. Conclusion

The synthesis of a polysulfide polymer was studied at three different temperatures. All of the polycondensation polymerization reactions were carried out using EDC and sodium tetarasulfide as reacting monomers. Modeling the reaction shows a first-order rate with an activation energy of 97.2 kJ/mol. The structure of the synthesized polymer was confirmed through FT-IR and CHN techniques. Thermogravimetric results revealed that the synthesized polymer is stable up to 200°C. DSC thermogram of the polymer indicates that the polysulfide polymer has a melting temperature of 71.4°C and was degraded at 274°C.

4. Experimental

4.1. *Materials*

Sodium hydroxide, sulfur and EDC were purchased from Merck and used as received.

4.2. *Monomer synthesis*

Two grams of sodium hydroxide was dissolved in 50 ml of distilled water and was heated to the boiling point. Four grams of sulfur was added to the solution and was stirred till the sulfur was dissolved completely. As the sulfur content of the sodium polysulfide increases the liquid turns from light yellow to dark brown. After 5 min, the solution was cooled and the un-dissolved sulfur from the dark brown liquid was filtered by filter paper.

4.3. *Polymer synthesis*

A fresh solution of sodium tetrasulfide (250 ml) was added in a 500 ml, four-necked round-bottom flask equipped with a double-impeller stirrer, a dropping funnel, a condenser and a thermometer. The flask was heated to 70°C with constant stirring at 300 rpm. EDC (80 ml) was added dropwise, after which the reaction mixture was stirred for another hour. During this time, the condensation of the EDC and sodium tetrasulfide was completed and a tetrasulfide polymer was produced. The dispersed polymer was filtered out of the solution and was washed by hot water followed by decantation. This procedure was repeated twice to remove the inorganic salts. The synthesized polymer was yellow in color, with a characteristic odor of polysulfide polymers.

4.4. *Measurements*

The FT-IR spectrum of the polymer was obtained from a Bruker, Equinox 55 spectrometer. Elemental analysis (C and H) was performed using a Perkin-Elmer 2400 Series II CHNS/O Elemental Analyzer. The glass transition temperature and the melting point of the polymer were obtained using a NETZSCH 200 F3 differential scanning calorimeter in a nitrogen environment (flow of 50 ml/min) and a heating rate of 5°C/min. The TGA spectrums were obtained using a PL-STA-1500 thermal analysis unit attached to a differential thermal analyzer, in a nitrogen environment and a heating rate of 10°C/min.

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References

(1) Lucke, H. *Aliphatic Polysulfides;* Huthing & Wepf: New York, 1994.
(2) Patrick, J.C.; Morrisvil, Pa. United States Patent 2278128, 1940.
(3) Patrik, J.C.; Morrisvil, Pa.; Harry, R.; Ferguson, T.; Tremton, N.J. United States Patent 2466963, 1945.
(4) Fettes, E.M.; Jorczak, J.S. *Ind. Eng. Chem*. **1950,** *42* (11), 2217–2222.
(5) Maner, S.; Martin, J.R.; Patrick, J.C. *Ind. Eng. Chem*. **1936,** *28* (10), 1144–1176.
(6) Ellerstein, S. *Handbook of Polymer;* Wiley: New York, 1985; Vol. 13, pp 187–196.
(7) Lee, T.C.P. *Properties and Applications of Elastomeric Polysulfides*; Rapra Review Reports; Pergamon: New York, 1999.
(8) Mahon, A.; Kemp, T.J.; Coates, R. *J. Polym. Degrad. Stab*. **1998,** *62,* 15–24.
(9) Vietti, D.E. *Comprehensive Polymer Science;* Pergamon: New York, 1988; Vol. 3, p 31.

(10) Lee, C.; Chang, T.C.; Hui Huang, Y. United States Patent 5432257, 1995.
(11) Baah, C.A.; Baah, J.I.; Gianadda, P.; Fisher, C. *J. Mater. Design* **2000,** *21,* 211–215.
(12) Sundarrajan, S.; Ganesh, K.; Srinivasan, K.S.V. *Polymer*. **2003,** *44,* 61–71.
(13) Odian, G. *Principles of Polymerization;* John Wiley & Sons Inc: New York, 2004.
(14) Kumar, A.; Gupta, R.K. *Fundamentals of Polymer Engineering;* Marcel Dekker: New York, 2003.
(15) Sundarrajan, S.; Srinivasan, K.S.V. *Macromol. Rap. Commun*. **2004,** *25,* 1406–1409.
(16) Berti, C.; Celli, A.; Marianucci, E.; *Eur. Polym. J*. **2002,** *38,* 1281–1288.
(17) Van Krevelen, D.W. *Properties of Polymers*; Elsevier: Amsterdam, 1990.
(18) Beaman, R.G. *J. Polym. Sci*. **1952,** *9,* 470–472.
(19) Sundarrajan, S.; Surianarayanan, M.; Srinivasan, K.S.V. *J. Polym. Sci*. **2005,** *43,* 638–649.
(20) Yang, J.; Miranda, R.; Roy, C. *Polym. Degrad. Stab*. **2001,** *73,* 455–461.