Synthesis and Characterization of Polysulfide Rubber Using Phase Transfer Catalyst

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Summary: Poly(alkyltetrasulfide) is prepared via reaction of ethylene dichloride with sodium tetrasulfide (Na_2S_4) in the presence of methyl tributyl ammonium chloride as phase transfer catalyst (PTC). The polysulfide polymer is characterized by CHN analysis, FT-IR, TGA, DTA and DSC techniques.

Keywords: Phase Transfer Catalyst; Poly (alkyltetrasulfide); Polysulfide rubber; synthesis

Introduction

Polysulfide polymers are one of the important classes of polymers with excellent thermal stability, weather-ability, solvent and oil resistance.[1–3] Due to these characteristic properties, they are used in coatings, adhesives, sealants, insulators, and other applications.[4–7]

Phase transfer catalysis is a very interesting approach in organic and polymer synthesis.[8–12] The feature of this technique is to allow the reagents present in different phases to react with the aid of a catalyst, which transfers anions, from the aqueous phase into the organic phase, and the reaction with water-insoluble hydrophobic species takes place in organic phase. Quaternary ammonium and phosphonium salts, crown ethers, poly (ethyleneglycol)s, and cryptates have been used as phase transfer catalysts. Phase transfer catalysis is also used successfully in the synthesis of several kinds of polymers. This technique offers important advantages with respect to other polymerization methods, because mild conditions are usually required.

Herein, we report a new method for synthesis of poly (alkyl tetrasulfide) using methytributyl ammonium chloride as phase transfer catalyst.

Experimental Part

Materials

Sodium hydroxide, sulfur, ethylene dichloride (EDC) and methyl tributyl ammonium chloride were purchased from Merck and used as received.

Synthesis of Polymers

A fresh solution of sodium tetrasulfide (250 ml) was added in a 500-ml, four-necked round bottom flask equipped with a stirrer, a dropping funnel, a condenser, and a thermometer. Agitation was provided by a double-impeller shaft. The flask was heated to 70 °C with constant stirring at 300 rpm, and of methyl tributylammonium chloride (2.25 ml) was added. During this time the temperature of solution was increased to 80 °C for 15 minutes, and then ethylene dichloride (80 ml) was added dropwise through the dropping funnel during one hour, after which the reaction system was stirring for another one hour. The obtained polymer dispersion was washed by hot water followed by decantation. This procedure was repeated twice to remove inorganic salts. The synthesized polymers are of yellow

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color, with the low odor which is characteristic of polysulfide polymers.

Measurements

FT-IR spectra of the polymer were recorded on a Bruker, Equinox 55 spectrometer. Elemental analyze (C and H) was performed on PerkinElmer 2400 Series II CHNS/O Elemental Analyzer. Thermogravimetric analysis (TGA) was performed using a PL-STA-1500 thermal analysis unit attached with differential thermal analysis. The experiments were carried out in a nitrogen atmosphere at a heating rate of 10 °C/min. The glass transition temperature and melting point of the polymer was performed using the NETZSCH DSC 200 F3 instrument. The experiments were carried out in N_2 atmosphere (flow of 50 ml/min) at a heating rate of 5 °C/min.

Elemental Analyses (CHN)

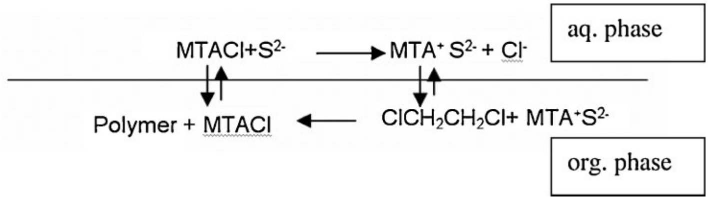
The result of elemental analyses of the polysulfide rubber is given below.

$(C_2H_4S_4)_n$ $(156)_n$: calculated. C, H (15.41%, 2.52%); found C, H (15.82%, 2.82%).

The Effect of PTC on the Kinetic of Polymerization

To study of effect of phase transfer catalyst on the rate of polytmerization reaction, two set of reaction were performed in the presence and absence of methyl tributyl ammonium chlorideunder same reaction conditions.

It can be assumed that in the presence of methyl tributyl ammonium chloride (MTACl) as PTC, poly(alkyltetrasulfide) is produced by polycondensation of sodium tetrasulfide and ethylene dichloride according to the following scheme:



Results and Discussion

Poly(alkyltetrasulfide) was prepared by the reaction of ethylene dichloride and sodium tetrasulfide using methytributyl ammonium chloride as phase transfer catalyst.

FT-IR Spectra of the Polymer

FT-IR of polysulfide are shown in Figure 1. The formation of polymeric product was confirmed by the disappearance of strong $C-Cl$ stretching absorption at 623 cm^{-1}.

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

The yields of polymer were determined using gravimetric method. The results summarized in the Table 1. These results showed that, the addition of PTC reduces the reaction time and increase the yield Xp_i of polymer.

Also the effect of concentration of the PTC on the yield was studied, and the results are showed in Figure 2. According to these data, the yield of the reaction is increased upon increasing of the concentration of PTC.

Thermal Analysis

The thermal properties such as decomposition temperature, glass transition temperature (T_g) and crystalline melting temperature (T_m) of the prepared polymers were

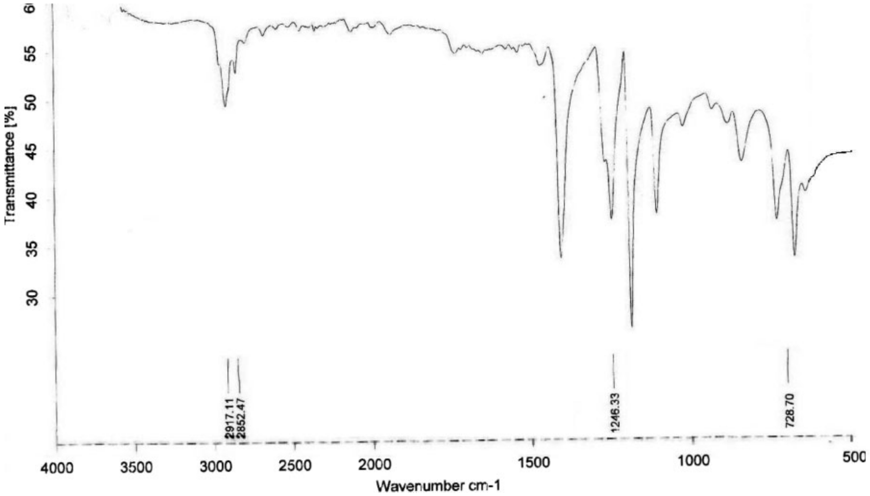


Figure 1.
FT-IR spectra of the polysulfide.

Table 1.
The effect of PTC on conversion.

Time(min)	Xp_1 [%] (No PTC)	Xp_2 [%] (PTC)
0	0	0
10	30	31
20	49	54
30	57	72
40	73	90

studied by thermogravimetric analysis and differential scanning calorimetric.

Thermal Degradation

Thermogravimetric analysis (TGA-DTA) has been extensively used for thermal degradation studies of polymers. TGA-DTA thermograms of the poly(alkyltetrasulfide) sample was shown in Figure 3. In the present study, the synthesized polymer

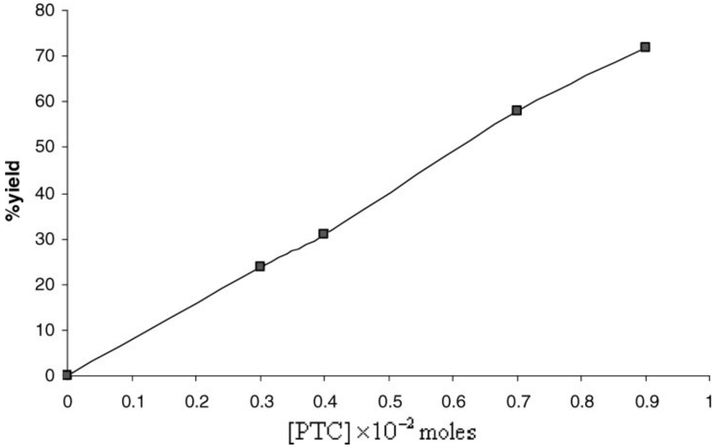


Figure 2.
Effect of the variation of the PTC concentration on Conversion.

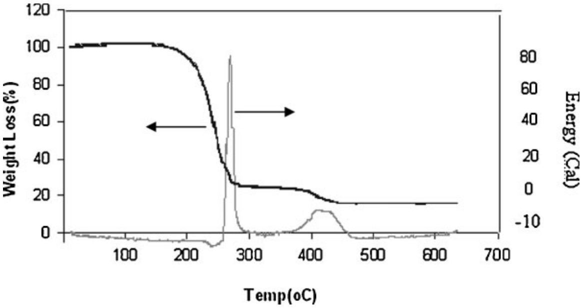


Figure 3.
TGA-DTA Thermograms of Polysulfide Rubber.

was showed exothermic degradation in two steps in 262 °C and 423 °C.

The observed exothermic degradation behavior is caused by the thermal degradation products.[4] Only a few polymers, such as polyacrylonitrile (PAN), hydroxyl terminated polybutadiene (HTPB), and polysulfide polymers, are reported in the literature as undergoing exothermic degradation.[14–16]

The apparent kinetic parameters of thermal decomposition of poly (alkyltetrasulfide) could be also determined using the DTG curve fitting method.[17] This method involves first measuring the weight loss behaviour obtained by using thermogravimetry (TGA), and then using the Arrhenius equation to fit the data obtained from the TGA measurement as following:

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

Where E, A and n are the apparent activation energy, the pre-exponential factor and the reaction order, respectively.

Using DTG curve fitting, the apparent activation energy, **E**, was obtained as follow:

At 0–350 °C: $E_1 = 263$ kJ/mol, A1 = 2.8×10^{15} and the order of reaction equal to 0.9
At 350–600 °C: $E_2 = 64$ kJ/mol, A1 = 1.2×10^{13} and the order of reaction equal to 0.46 related to first and second step of exothermic degradation of polymer respectively.

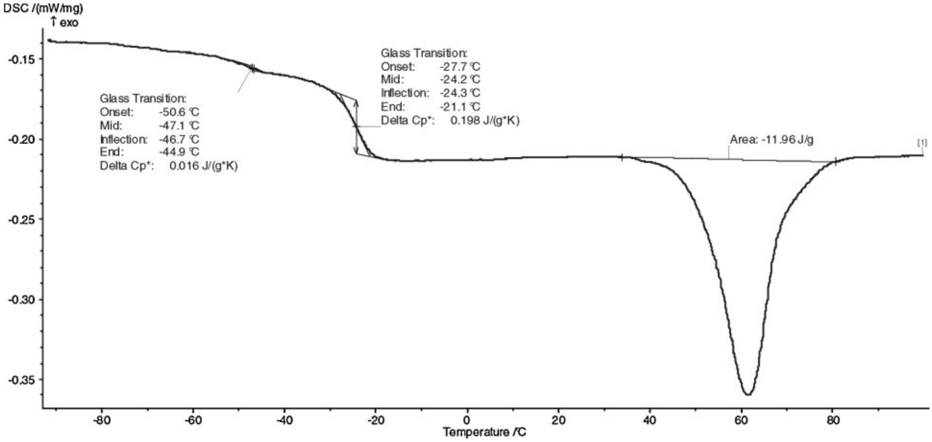


Figure 4.
DSC plot for a Polysulfide-type Rubber.

Table 2.
Group Contributions to Y_{gi}.

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

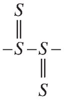
Differential Scanning Chalorimetry

The glass- transition temperature of this polymer is below room temperature and the value for poly (alkyltetrasulfide) is shown in −21 °C. Also it's melting point is 61.2 °C. Figure 4, shows DSC plot for the polymer.

In the thermograms obtained by DSC, poly (alkyltetrasulfide) showed the endothermic step due to the glass transition. This behavior is observed also in polymer with sulfur atoms along the aliphatic chain.[14,16]

In order to have an idea for significant range of glass transition temperature, the T_g of this sample has been estimated by the approach of Van Krevelen and Hoftyzer,[17,19] as follow:

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

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 was calculated approximately by using the Table 2, $T_g = -13.5\,°C$. 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, $\Delta H = -11.96\,\mathrm{kJ/g}$. 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 play an important role in 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[19] for unsymmetrical polymers is $T_g/T_m = 0.75$, therefore for our polymer should have a melting point around 62.3 °C, close to the experimentally determined value.

Resistance to Solvent

The polysulfide polymers exhibit superior solvent resistance compared to other synthetic rubbers. This is due to a backbone structure. According to swelling method the organic polysulfide polymer tested in ethyl alcohol, acetic acid, acetone and water. For this purpose specimen in the form of 2-mm-thick circular discs of 40 mm in diameter were immersed in solvent, and

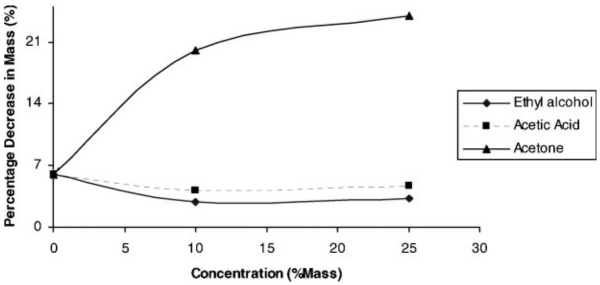


Figure 5.
% swelling of polymer in solvents, at 25 °C after 1 month.

the diameters of the swollen samples were measured. For the determining of solvent resistance properties of the specimens, each solvent tested at three different concentrations at 25 °C, Figure 5.

Conclusion

Polysulfide rubber was synthesized from ethylene dichloride and sodium tetarasulfide by polycondensation technique using methyltributyl ammonium chloride as phase transfer catalyst, (PTC). Using of PTC employed to increase the rate of conversion of the synthesis of polysulfide polymer and improving the physical properties of the product. The structures of synthesized polymers were confirmed through, FTIR and CHN, techniques. Thermogravimetric results indicate that the synthesized polymers are stable up to 200 °C. DSC analysis of the polymer reveals that the polysulfide polymer meltable in the range from 40–80 °C, with the onset of thermal degradation at about 150 °C.

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[1] S. Ellerstein, in: "*Handbook of Polymer*", 3rd ed., J. Wiley & Sons, New York **1985**, *13*, pp. 187–196.
[2] T. C. P. Lee, Properties and Applications of Elastomeric Polysulfides, Rapra, **1992**, ISBN: 1-85957-158.
[3] A. Mahon, J. Terence, J. Robert, *Polymer Degradation and Stability* **1998**, *62*, 15–24.
[4] C. Lee, Process for Manufacturing a Polysulfide Polymer, United States Patent 5432257, (**1995**).
[5] A. V. Tobolsky, "*The Chemistry of Sulfides*", Wiley-Interscience, New York **1968**.
[6] C. A. Bahh, *Material and Design* **2000**, *21*, 211–215.
[7] H. Lucke, "*Aliphatic Polysulfides*", Huthing & Wepf, **1994**.
[8] J. M. J. Frechet, M. D. Smet, M. J. Farrall, *J.Org .Chem* **1979**, *44*, 1774.
[9] M. Makosza, *Pure Appl. Chem.* **2000**, *72*(7), 1399–1403.
[10] L. H. Tagle, F. R. Diaz, J. C. Vega, P. Valenzuela, *European Polymer Journal* **2003**, *39*, 407–410.
[11] B. Mancai Xua, *Reactive & Functional Polymers* **2001**, *48*, 85–95.
[12] C. Berti, A. Celli, E. Marianucci, *European Polymer Journal* **2002**, *38*, 1281–1288.
[13] S. Sundarrajan, K. Ganesh, K. S. V. Srinivasan, *Polymer* **2003**, *44*, 61–71.
[14] S. Sundarrajan, K. S. V. Srinivasan, *Macromolecular Rapid Communi.* **2004**, *25*, 1406–1409.
[15] S. Sundarrajan, M. Surianarayanan, K. S. V. Srinivasan, *Journal of Polymer Science* **2005**, *43*, 638–649.
[16] C. Berti, A. Celli, E. Marianucci, *European Polymer Journal* **2002**, *38*, 1281–1288.
[17] J. Yang, R. Miranda, C. Roy, *Polymer Degradation and Stability* **2001**, *73*, 455–461.
[18] D. W. Krevelen, "*Properties of polymers*", 3rd ed., Amsterdam, Elsevier **1990**.
[19] R. G. Beaman, *J. Polymer Sci.* **1953**, *9*, 472.