

Polythiourethane Polymers Using Castor Oil Tristhioglycolate as Crosslinking Agent

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Synopsis

Polythiourethane polymers were synthesized from a few glycol polythioglycolates and TDI or MDI. Castor oil tristhioglycolate, a new trithiol, was tried as a crosslinking agent. Mechanical and solvent resistance properties of the cured products are reported.

INTRODUCTION

Polythiourethane polymers, unlike their polyurethane and polyurea counterparts, have not been well investigated, although thiol-isocyanate reactions have long been known. As a part of our studies on the synthesis and applications of thiols, we studied the synthesis and a few properties of the polythiourethane polymers from bisthioglycolate esters of some polyethylene glycols and TDI or MDI. These studies proved interesting because we used castor oil tristhioglycolate,¹ a new polythiol, as the crosslinking agent in the polymer synthesis. In this paper, we report the synthesis and some properties of new polythiourethane polymers.

EXPERIMENTAL

General remarks: Tensile strength and elongation tests on vulcanisates were performed on dumbbell specimens at room temperature using a Scott tensile testing machine. Hardness was determined at room temperature using a Shore-A Durometer.

Tensile strength of vulcanisates is expressed in megapascals (MPa), the recommended SI unit.² The conversion factor is 1000 psi = 6.9 MPa. Melting points are uncorrected.

Materials

Castor oil and polyethylene glycols-200, 400, and 600 were used as received. Toluene-2,4-diisocyanate (TDI) was used without further purification. 4,4'-Diphenylmethane diisocyanate (MDI) was distilled under vacuum prior to use (mp 37°C). All solvents employed in solvent resistant studies of vulcanisates were purified by standard methods.

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Methods

Synthesis of Polyethylene Glycol Bisthioglycolates

A toluene or xylene solution (150 mL) of the glycol (0.1 mol), thioglycolic acid (0.25 mol), and *p*-toluene sulfonic acid (1–1.5% w/w) was refluxed in a three-necked flask equipped with a mechanical stirrer, a thermowell, and a Dean-Stark apparatus for the azeotropic removal of water. After all the water had been removed, the contents were cooled, washed with hot water, dried over anhy-Na₂SO₄, and stripped of the solvent under reduced pressure. As it was not possible to purify these compounds by distillation, all the compounds were dried under vacuum for long periods and then used. The physical properties of all these compounds are presented in Table I. The IRA spectra are:

$$1730\text{--}1740\text{ cm}^{-1}(\text{---}\overset{\text{O}}{\parallel}{\text{C}}\text{---O---}), \text{ and } 2515\text{ cm}^{-1}(\text{---SH})$$

Synthesis of Castor Oil Tristhioglycolate [COTT]

A toluene or xylene solution (400 mL) of castor oil (93.2 g, 0.1 mol) was heated with stirring in a flask at 85–90°C, and thioglycolic acid was added followed by *p*-toluenesulfonic acid (1–1.5% w/w of castor oil). The contents of the flask were refluxed to remove water azeotropically. After the complete removal of water, the mixture was refluxed for an additional 19 h. The reaction mixture, after cooling, was washed many times with hot water, dried over anhy-Na₂SO₄, and stripped of the solvent *in vacuo*. The product, pale yellow to pale red in color, was dried under vacuum on a water bath. The completion of the reaction was confirmed by the complete disappearance of —OH absorption, and the appearance of the ester band (1730 cm⁻¹) in IR. Physical properties of COTT are recorded in Table I. The IR spectrum of COTT is shown in Figure 1 (see Discussion).

TABLE I
Characteristics of Thioglycolates

| No. | Compound | Yield (%) | <i>d</i> | <i>n</i> _D | % SH ^a calcd (found) | Analysis | |
|-----|---|-----------|----------|-----------------------|---------------------------------------|----------|-------|
| | | | | | | Calcd | Found |
| 1 | Ethylene glycol bisthioglycolate | 89 | 1.33 | 1.514 | 31.49 (31.61) | C, 34.28 | 34.81 |
| | | | | | | H, 4.76 | 5.14 |
| | | | | | | S, 30.40 | 29.90 |
| 2 | PEG ^b -200 bisthioglycolate | 85 | 1.26 | 1.494 | 19.00 (19.18) | C, 42.10 | 42.07 |
| | | | | | | H, 6.49 | 7.01 |
| | | | | | | S, 18.71 | 18.80 |
| 3 | PEG-400 bisthioglycolate | 81 | 1.23 | 1.492 | 11.77 (11.90) | C, 46.92 | 47.13 |
| | | | | | | H, 7.40 | 7.72 |
| | | | | | | S, 11.39 | 11.60 |
| 4 | PEG-600 bisthioglycolate | 65 | 1.23 | 1.489 | 8.85 (8.90) | C, 48.70 | 48.93 |
| | | | | | | H, 7.05 | 7.43 |
| | | | | | | S, 8.60 | 8.89 |
| 5 | Castor oil tristhioglycolate | 95 | — | 1.489 | 8.595 (8.475) | C, 65.51 | 66.63 |
| | | | | | | H, 9.53 | 9.79 |
| | | | | | | S, 8.33 | 9.62 |

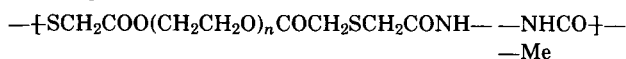
^a Ref. 14.

^b Poly(ethylene glycol).

TABLE II
 Characteristics of Thiourethanes from TDI and Glycol Bisthioglycolates^a

| Bisthioglycolate of | n | Physical state | Elemental analysis | | |
|------------------------|----|-------------------|--------------------|-------|------|
| | | | C (%) | H (%) | |
| Ethylene glycol | 1 | Solid (mp 174°C) | Calcd: | 46.87 | 4.16 |
| | | | Found: | 46.6 | 4.58 |
| PEG ^b -200 | 4 | Solid (mp 92°C) | Calcd: | 48.84 | 5.42 |
| | | | Found: | 49.96 | 6.47 |
| PEG-400 | 9 | Viscous liquid | Calcd: | 49.86 | 6.43 |
| | | | Found: | 50.02 | 7.2 |
| PEG-600 | 13 | Viscous liquid | Calcd: | 51.31 | 7.01 |
| | | | Found: | 51.53 | 7.65 |

^a General structure of products:



^b Poly(ethylene glycol).

Synthesis of Polythiourethane Polymers from Glycol Bisthioglycolates and TDI

The glycol bisthioglycolate (0.01 mol) and TDI (1.74 g, 0.01 mol) were heated under vacuum (1–0.5 torr) at 92–93°C for 6–7 h to obtain the polymer. The characteristics of all these polymers are recorded in Table II.

Synthesis of polythiourethane polymers employing COTT as the crosslinking agent is described below.

Synthesis of Polythiourethane Polymers from Glycol Bisthioglycolate, COTT, and TDI

The procedure, described here for the synthesis of polythiourethane polymer employing PEG-200 bisthioglycolate, COTT, was followed for other glycolates. PEG-200 bisthioglycolate (0.01 mol, 3.52 g) and COTT (0.01 mol, 11.54 g) were dried by heating under vacuum on a water bath for a long time. Further polymerization with the diisocyanate was performed in bulk. TDI (0.025 mol, 4.35 g) was added and the contents were heated under vacuum for a period of 7–8 h

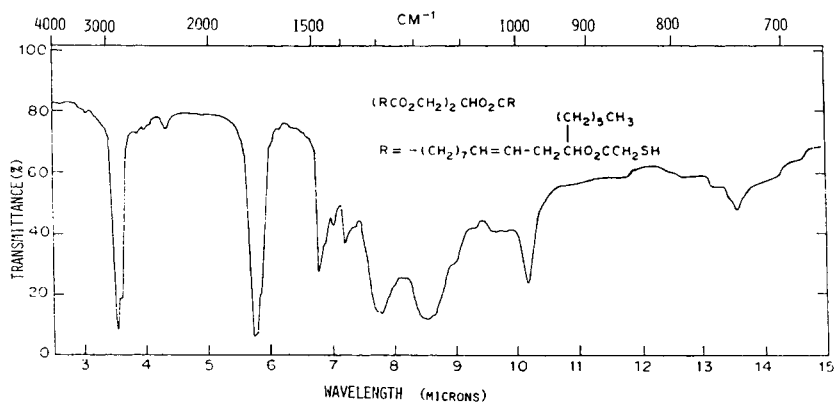


Fig. 1. IR spectrum of casto oil tristhioglycolate.

TABLE III
 Mechanical Properties of Polythiourethane Polymers

| Polymer no. | From COTT ^a and bithioglycolate of | | Shore A hardness | Relative extension (%) | Tensile strength (MPa) |
|-------------|---|--------------|------------------|------------------------|------------------------|
| | | Diisocyanate | | | |
| I | PEG-200 | TDI | 80 | 50 | 10.39 |
| II | PEG-200 | MDI | 85 | 55-60 | 10.93 |
| III | PEG-400 | TDI | 78 | 55 | 9.7 |
| IV | PEG-400 | MDI | 80 | 70 | 9.98 |
| V | PEG-600 | TDI | 70 | 60 | 8.07 |
| VI | PEG-600 | MDI | 75 | 75 | 8.57 |

^a Castor oil tris(thioglycolate).

until a solid, rubbery product resulted. The product, which was pale yellow in color, was removed from the flask and kept overnight before testing for its physical properties.

Polymers from the mixtures of COTT (0.01 mol) with PEG-400 bithioglycolate, or PEG-600 bithioglycolate (0.01 mol) with TDI were prepared similarly.

Polymers from the mixture of a glycol bithioglycolate and COTT with MDI were also prepared employing the above procedure.

Testing

The rubbery products were passed through a two-roll laboratory mill to get a sheet. Then each sheet was mixed with MDI (crosslinking agent, 10 parts to rubber by wt) and again given several passes to get a sheet. The sheet was then pressed out in a metal mold in a hydraulic press at 145°C for 30 min. Dumbbell specimens were cut out from the vulcanizates using a standard dumbbell punch of width 0.125 in. Tensile strength and elongation were determined at room temperature according to ASTM designation D 412-68. Shore-A hardness was determined according to the ASTM designation D 2240-68. These results are presented in Table III.

Solvent resistance of the vulcanizates was determined in the solvents, Table IV, as percent weight increase after 15 days of immersion according to the ASTM designation D 471-64.

 TABLE IV
 Solvent Resistance of Polythiourethane Polymers (wt % Increase)

| Solvent | Polymer ^a | | | | | |
|---------------------------------------|----------------------|------|-------|------|------|------|
| | I | II | III | IV | V | VI |
| Acetone | 22.0 | 42.9 | 25.8 | 51.0 | 30.2 | 59.5 |
| CCl ₄ | 78.3 | 55.0 | 64.37 | 40.5 | 43.2 | 27.4 |
| Ethyl acetate | 35.8 | 25.6 | 36.1 | 26.2 | 36.7 | 28.2 |
| Toluene | 48.2 | 37.0 | 44.4 | 32.1 | 37.4 | 25.0 |
| 20% aq H ₂ SO ₄ | 5.2 | 10.3 | 3.81 | 8.5 | 2.2 | 6.4 |
| 10% aq NaOH | D ^b | D | D | D | D | D |
| Water | 6.3 | 3.8 | 6.8 | 4.1 | 7.0 | 4.5 |

^a See Table III.

^b D = complete degradation.

DISCUSSION

Polyurethane polymers have been the focus of universal attraction bedecked with a host of properties that can be engineered to a variety of diversified applications. The important properties of this type of polymers based on the reaction of isocyanates with active hydrogen compounds, viz., $-\text{OH}$, $-\text{NH}_2$, or $-\text{SH}$, have been attributed to the presence of $-\text{NHCOX}-$ linkage, where X = O, NH, or S.

Apart from polyurethanes (X = oxygen) and polyureas (X = NH), the study of polythiourethane polymers has not been looked into extensively. The studies by Mitchell,³ Bertozzi,⁴ and others⁵ were aimed at the synthesis and study of some polythiourethane polymers and also their applications. In 1975, Zochniak et al.⁵ reported their studies on two polyglycol thioglycolate-based polythiourethane polymers. These polymers were high melting solids exhibiting good water and thermal resistance, and dielectric properties. The present study was undertaken to gain further knowledge regarding the synthesis and a few properties of polythiourethane polymers using readily available materials. The salient feature of these studies was our attempts to use a new polythiol, COTT, as the cross-linking agent.

A few words on the characteristics of COTT seem appropriate. In castor oil, the double bonds are *cis*. The IR spectrum of pure castor oil has a broad band at 740 cm^{-1} ($13.6\ \mu$) characteristic of *cis*-double bonds. On esterification, however, the 740 cm^{-1} band decreases in intensity, and a sharp band of medium intensity appears at 980 cm^{-1} ($10.2\ \mu$). This band is characteristic of the double bond with *trans* configuration. Thus we could conclude that the esterification of castor oil with thioglycolic acid is accompanied by *cis-trans* isomerization. However, we could not determine the relative amounts of *cis* and *trans* isomers. Although we were more interested in the immediate applications of COTT for our experiments, we think that a study of the effect of such isomerization on the further properties of the COTT-based products might prove interesting.

Furthermore, COTT exhibits a strong propensity to form solid, insoluble, and transparent films on storage. Although oxidants may catalyze this reaction,¹ we thought of exploiting this inherent tendency of COTT for some useful purposes.¹ Some of the results have been already reported elsewhere.¹

The present work was undertaken to synthesize and study the tensile properties of a few new polythiourethane polymers employing COTT as one of the components. The synthesis was accomplished without the use of any solvent. Some of the conclusions that are immediately evident may be summarized as follows:

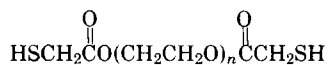
(i) Because of the equimolar quantities of the glycol bithioglycolate, COTT, and the diisocyanate, the number of thiourethane linkages, N_t , can be assumed to be constant for each elastomer. However, the concentration of thiourethane linkages, W_t , will vary for each elastomer.

(ii) Similarly the number of crosslinks imparted by COTT may be assumed to be constant for each elastomer, while the crosslink density, obviously, will be different.

(iii) Urethane groups contribute polarity, hydrogen bonding, rigidity, etc., into a polyurethane polymer.⁶ Since oxygen and sulfur occur in the same group in the periodic table (Group VI), a similar effect of the thiourethane linkage, $-\text{NHCOS}-$ on the properties of the polythiourethane polymer may be expected.

However, the effects of —NHCOO— and —NHCOS— would not be identical due to the inherent differences in the properties of O and S and, consequently, C—O and C—S bonds. These factors may affect the ultimate tensile properties and other related phenomena.

(iv) It is known that for a given series of polyurethane polymers from a diisocyanate and a series of aliphatic difunctional active hydrogen compounds in fixed molar quantities, ultimate properties, like T_g and tensile characteristics, are guided primarily by the structure of the aliphatic components.^{7,8} The above properties, viz., T_g and tensile strength, decrease with increasing chain length of the aliphatic component while the elongation at break increases. In the present case, the only variable factor in the synthesis of the title polymers is the structure of the glycol bistihioglycolate, the general structure of which may be represented as



where $n = 4$ for PEG-200, $n = 9$ for PEG-400, and $n = 13$ for PEG-600. Thus it may be considered that ultimate properties will be guided primarily by the numerical value of n .

From the above arguments, it is clear that although N_t is same for all the polythiourethane polymers based on the various glycol bistihioglycolates, W_t decreases in the order PEG-200 bistihioglycolate > PEG-400 bistihioglycolate > PEG-600 bistihioglycolate.

Edgar⁹ and Chichagova et al.¹⁰ consider that the ultimate properties of a polyurethane polymer are linearly dependent on the concentration of urethane linkages. Smith and Magnusson,⁷ while studying the properties of polyurethanes based on a particular series of polyalkylene glycols, found a linear dependence of T_g , and thus the tensile strength, on the concentration of urethane linkages. The results of Chen et al.⁸ further indicated, for a series of poly(ether glycol)-based polyurethanes, a reciprocal relationship of tensile strength with the length of polyether chain. The elongation, however, showed a linear relationship with the length of the polyether chain. Thus all these results suggest high tensile strength, hardness (a measure of degree of crosslinking) for the polythiourethane polymer from PEG-200 bistihioglycolate—COTT, which shall decrease with an increase in the mol wt of the glycol, whereas the elongation at break should show an opposite trend. The results in Table III amply support these expectations.

The effect of the aromatic unit and its length in imparting stiffness and raising the T_g of polymers is well known.¹¹⁻¹³ If more aromatic rings are present in the chain, these effects would be more pronounced. Thus, we can predict better strength and hardness for the polythiourethane polymers based on MDI compared to the TDI-based ones. These are also fully borne out by the results in Table III.

The complete degradation of the vulcanizates in 10% aqueous NaOH (2.5 N) solution might be due to the total hydrolysis of the ester linkages present in the elastomer. It was also found that all the virgin glycol bistihioglycolates show a high degree of susceptibility for hydrolysis even under mildly basic environment. This was one of the reasons that prompted us to resort to hot water washing of the reaction mixtures during the synthesis of glycol bistihioglycolates.

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