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Thioether Functional Chain Extender for Thermoplastic Polyurethanes[*]

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Abstract In this study, a novel three functional chain extender (TATATRIOL) was synthesized from the reaction of 1,3,5-tri(prop-2-en-1-yl)-1,3,5-triazinane-2,4,6-trione (TATA) with 2-sulfanylethanol. Then new thermoplastic polyurethanes (TPUs) were synthesized by a one-step bulk polymerization from the reaction of 1,1'-methanediylbis(4-isocyanatocyclohexane) (H_{12}MDI), a poly(ethylene adipate) based polyester polyol and a chain extender. Butane-1,4-diol (BD) and the newly synthesized monomer, TATATRIOL, were used as chain extenders. The effects of TATATRIOL on the properties of the TPU were investigated and compared to those of the TPU prepared with BD. The TPUs which derived from the sulfur containing chain extender displayed lower modulus and high elongation at break values than the analogous TPUs derived from BD. Moreover sulfur containing TPUs exhibited higher thermal stability.

Keywords: Elastomers; Thermogravimetric analysis (TGA); Differential scanning calorimetry (DSC); Polyurethanes.

INTRODUCTION

Owing to the wide range of available polyols and isocyanates, today polyurethanes (PURs) rank among the most versatile and diversified polymers. Since their first discovery in 1937 by Prof. Dr. Otto Bayer, there has been a tremendous progress in polyurethane chemistry. Today PURs have a wide range of applications, from rigid foams for thermal insulation systems to flexible foams for furniture, from coatings to paints, from automotive industry to adhesives, from packaging to composites, *etc*[1–5].

Although polyurethanes are generally thermoset materials, the versatility in PUR chemistry allows researchers to prepare thermoplastic polyurethanes (TPUs). TPUs are linear segmented multi-block copolymers which consist of alternating hard and soft segments. Due to the immiscibility of these soft and hard domains, a so-called phase separation phenomenon takes place[6]. While the soft segments are responsible for the elasticity, crystalline hard segments disperse in the soft segments and form physical crosslinks. These crosslinks are thermo-reversible and they bring TPUs rubber-like properties. Therefore they can be processed *via* conventional techniques such as injection molding and extrusion, in contrast to rubbers[7–9]. TPUs are generally characterized by their good abrasion resistance, flexibility and good mechanical properties[10–12]. TPUs also tend to have high transparencies. In commercial TPUs, short diols like BD, and isocyanates like 1,1'-methanediylbis(4-isocyanatobenzene) (MDI) make up the hard segments while long and flexible polyether or polyester based diols are used as soft segments[13]. In literature several examples of polyether or polyester based diols which have different chemical structures and different chain lengths, along with the examples of vegetable based diols[14, 15] and polycarbonate based diols[16] can be found. Moreover several studies focus on the preparation TPUs with

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new unconventional chain extenders[1, 4, 6, 17].

Recently several sulfur containing TPUs have been prepared from either thioether linkages containing diols or dithiols as chain extenders[4–6, 13, 18, 19]. These relatively new polymers, especially the derivatives of dithiols, can be regarded as new classes of thermoplastic elastomers[13]. It is well known that sulfur containing polymers have interesting features like elastomeric properties, excellent optical clarity, good electrical and mechanical properties, improved adhesive properties and good biocompatibility[18].

In this study, a three functional chain extender (TATATRIOL) was synthesized from the reaction of 1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TATA) with 2-mercaptoethanol in the presence of methanol. BD or TATATRIOL were used as chain extenders in the preparation of TPUs. The effects of TATATRIOL on the properties of the TPUs were investigated and compared to those of the TPUs prepared with BD. The chemical composition of TATATRIOL was characterized by ATR-FTIR, ^{1}H-NMR and ^{13}C-NMR techniques. Thermo-oxidative stability and the glass transition/melting temperatures of TPUs were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements, respectively. Mechanical properties were characterized by tensile measurements.

EXPERIMENTAL

Materials

1,3,5-Tri(prop-2-en-1-yl)-1,3,5-triazinane-2,4,6-trione, 2-sulfanylethanol, methanol and BD were purchased from Sigma Aldrich and used as received. 1,1'-Methanediylbis(4-isocyanatocyclohexane (H_{12}MDI, Vestanat H12MDI) and Oxyester T-568 which is a linear, 2,2-dimethylpropan-1,3-diol based saturated polyester polyol, were obtained from Evonik. It has an OH number of 56 mg KOH/g and an average molecular weight of 2000 g/mol.

Characterization Methods

FTIR spectrum was recorded on a Perkin Elmer Spectrum100 ATR-FTIR spectrophotometer. Each FTIR spectrum was collected with 4 scans with a resolution of 4 cm^{-1} in the range of 380–4000 cm^{-1}.

^{1}H-NMR and ^{13}C-NMR spectra of the newly synthesized monomer were recorded on a Varian T-60 NMR spectrometer. All samples were dissolved in $CDCl_3$ containing tetramethylsilane as internal standard.

TGA was performed using a Perkin-Elmer thermogravimetric analyzer Pyris 1 TGA model. Samples were run from 30 °C to 750 °C with heating rate of 20 K/min under air atmosphere.

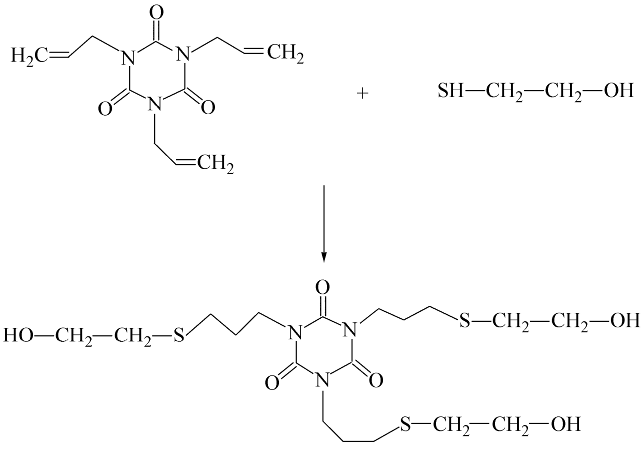
DSC was used to investigate the melting behavior, and establish the glass transition temperatures. DSC measurements were carried out with a Perkin Elmer Pyris Diamond. The samples were analyzed under a nitrogen atmosphere in the temperature range −50 °C to 200 °C at a heating rate of 10 K/min and cooling rate of 100 K/min. 8–10 mg of sample was placed in an aluminum pan. Glass transition temperature (T_g) was obtained from midpoint of the specific heat increment in the curve of the second heating run.

Mechanical properties of thermoplastic polyurethane elastomers were determined by standard tensile stress-strain tests to measure modules, ultimate tensile strength and elongation at break. Standard tensile stress-strain experiments were performed at room temperature on a Materials Testing Machine Z010/TN2S, using a crosshead speed of 2 mm/min. Stress-strain tests were carried out according to ASTM D638 and the results are given as an average of five different specimens' measurements.

Shore hardness of TPUs was measured with a HT-6510A model shore durometer at ambient conditions. An average of five measurements was reported.

Synthesis of the Sulfur Containing Chain Extender: TATATRIOL

For the synthesis of the sulfur containing chain extender; TATATRIOL, an ionic thiol-ene reaction was performed similar to a procedure adopted in a previous study[20]. Briefly, into a 250 mL, round-bottomed flask, 20.0 g (0.08 mol) of 1,3,5-triazine-2,4,6 (1H,3H,5H)-trione (TATA), 18.81 g (0.24 mol) of 2-mercaptoethanol, 120 mL of methanol and a stirring bar were placed. The mixture was stirred at room temperature for 30 min and then the solvent was removed under reduced pressure at 60 °C to give 38 g (98 %) of transparent product. The synthetic procedure is depicted in Scheme 1.



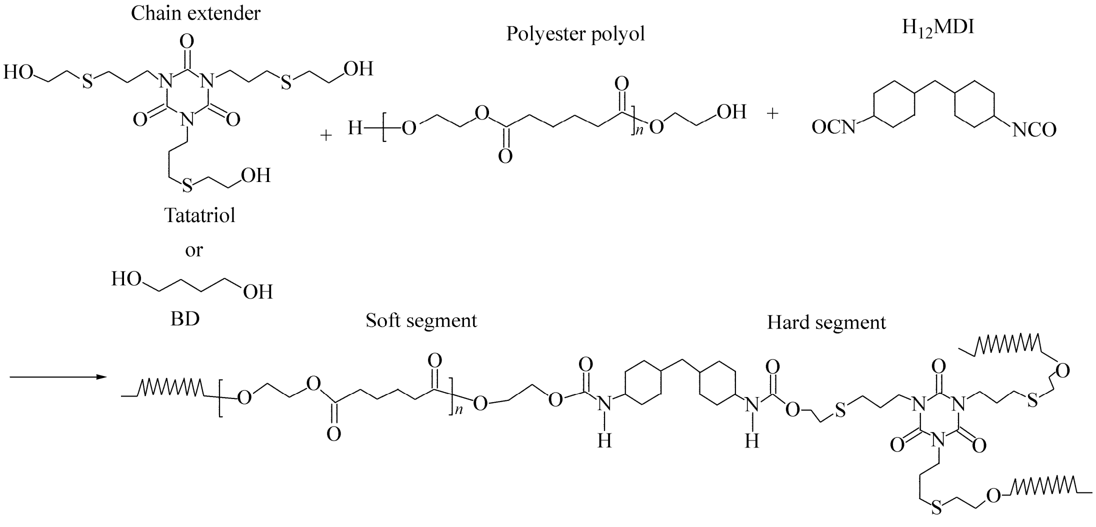
Scheme 1 Synthesis of TATATRIOL

Synthesis of Thermoplastic Polyurethane Elastomers

TPUs were synthesized by a one-step bulk polymerization. Calculated amounts of $H_{12}MDI$, Oxyester T-568 and the chain extender were added into a plastic container and mixed until homogenization. Then the mixtures were poured into Teflon® molds (5 cm × 1 cm ×1 mm). In order to remove air bubbles, molds were placed in a dessicator vacuum for 10 min. Finally samples were heated to 60 °C for 1 h in an oven. The composition of all formulations is given in Table 1. TATATRIOL containing TPUs were named as TPUTRIOL and BD based TPUs were abbreviated as TPUBD. The synthetic route to TPUs is shown in Scheme 2.

Table 1. Compositions of TPUBD and TPUTRIOL

Formulation		Oxyester T-568	1,4-Butanediol	TATATRIOL	$H_{12}MDI$
	Mol	0.0105	0.0219	–	0.0324
TPUBD	Equivalent	0.0211	0.0438	–	0.0649
	Weight (g)	20.00	1.47	–	8.94
	Mol	0.0105	–	0.0146	0.0324
TPUTRIOL	Equivalent	0.0211	–	0.0438	0.0649
	Weight (g)	20.00	–	7.0615	8.94



Scheme 2 General scheme of the TPU synthesis

RESULTS AND DISCUSSION

Previously Rogulska and her group synthesized several TPUs from aliphatic-aromatic chain extenders with sulfur atoms in their structure[4–6, 18]. These sulfur containing TPUs showed good resistance to organic solvents, low T_g values and good thermal stabilities. In this study we aimed to prepare sulfur containing crosslinked TPUs. By incorporating a three functional chain extender with thioeter linkages, we aimed to show that mechanical, thermal and optical properties of TPUs can be controlled.

In this study TPUs were prepared by a one-step bulk polymerization where BD or TATATRIOL were used as chain extenders and flexible, homogeneous and slightly yellowish elastomeric materials were obtained. TPUs prepared with TATATRIOL were transparent. On the other hand BD based TPUs were found to be translucent. This situation can be attributed to the sulfur linkages in the TATATRIOL containing TPUs and the reduced crystallinity.

Characterization of TATATRIOL

Thiol-ene reactions are useful tools for the modification and synthesis of new materials. Although the free radical pathway is much more studied, it was shown that the ionic thiol-ene reaction which can be viewed as a Michael-type addition reaction is a fast and an effective technique for the modification of electron-deficient species[20].

TATATRIOL was synthesized from the reaction of TATA with 2-mercaptoethanol. The structure of TATATRIOL was characterized by ATR-FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopies. The ATR-FTIR spectrum of TATATRIOL is given in Fig. 1, along with the spectra of the precursors; TATA and 2-mercaptoethanol. The absence of the absorption bands at 2555 cm^{-1} and 1640 cm^{-1} which correspond to thiol groups in mercaptoethanol and allyl double bonds in TATA, respectively, indicate that the reaction was performed successfully. Furthermore in the spectrum of TATATRIOL, the absorption bands at 3380 cm^{-1} is due to newly formed hydroxyl groups. In this spectrum the carbonyl stretching vibrations can also be seen at around 1690 cm^{-1}. In all spectra the peaks at around 2917 cm^{-1} and 2864 cm^{-1} were attributed to aliphatic (—CH—) asymmetric and symmetric stretching vibrations, respectively.

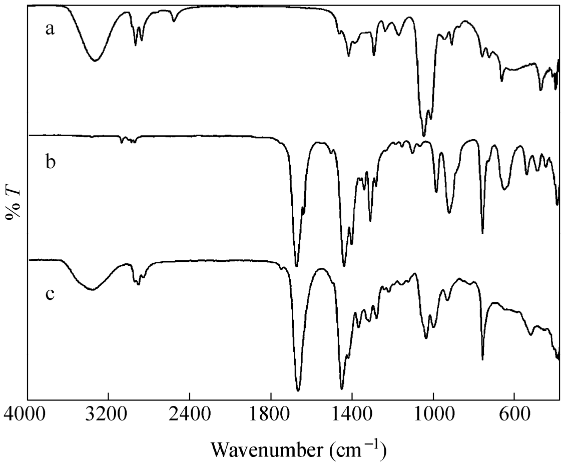


Fig. 1 FTIR spectra of (a) 2-sulfanylethanol, (b) TATA and (c) TATATRIOL

^{1}H-NMR and ^{13}C-NMR spectra of TATATRIOL are given in Fig. 2 and Fig. 3, respectively. It can be seen from the proton spectrum of TATATRIOL that the protons (Ha) on the carbon atom which is attached to the nitrogen atoms resonate at around δ = 3.90–4.0. While the β protons (Hb) with respect to nitrogen atoms resonate at δ = 1.87–1.94, the peaks at δ = 2.51–2.56 were assigned to the Hc protons. The protons (He) on the carbon atom that is attached to the hydroxyl group were found to resonate at δ = 3.64–3.67 in triplets. Finally the peaks at around δ = 2.64–2.67 were related to the β protons (Hd) with respect to hydroxyl functionality.

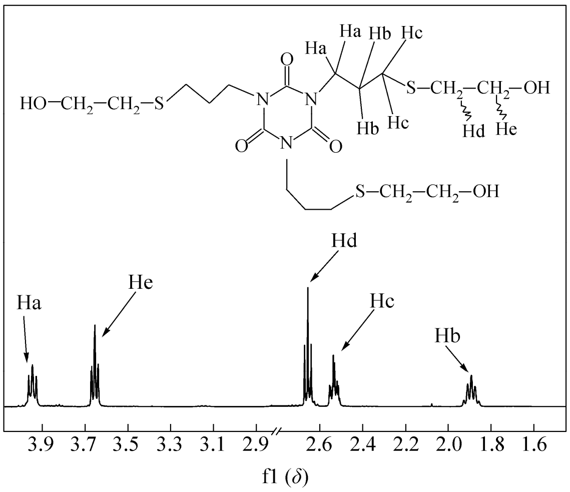


Fig. 2 ^{1}H-NMR spectrum of TATATRIOL

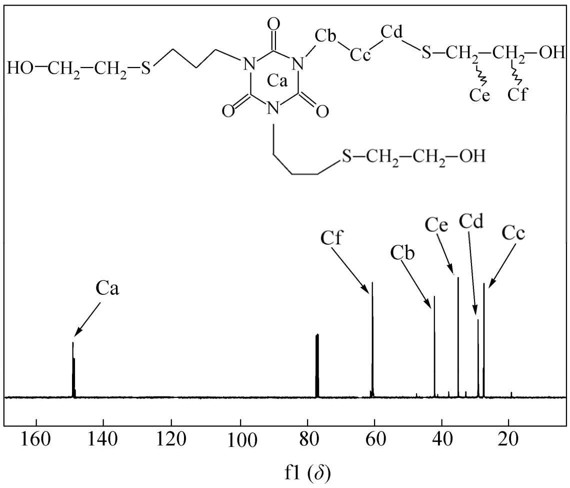


Fig. 3 ^{13}C-NMR spectrum of TATATRIOL

It can be seen from the ^{13}C-NMR spectrum that the peaks of the carbonyl groups resonate at δ = 148.7–149.8. The peaks at δ = 61.5–61.8 correspond to the carbon atom (Cf) which is attached to oxygen. The peaks at δ = 33.8 are due to β carbon atoms (Ce) with respect to the hydroxyl group. The chemical shifts at 28.3 and 26.4 were attributed to the Cd and Cc carbon atoms, respectively. The carbon atoms adjacent to nitrogens resonate at δ = 40.8.

All spectroscopic analysis results are in good accordance with literature results[20]. In conclusion it can be said that according to the spectroscopic analysis, TATATRIOL was synthesized successfully.

Thermal Properties

Thermal properties of TATATRIOL or BD containing polyester polyol based TPUs are given in Table 2. Figure 4 shows the thermal degradation behavior of TPUTRIOL and TPUBD under air atmosphere, respectively. Both TPUs displayed similar thermograms. As it can be seen from the results that the incorporation of the three functional, sulfur containing chain extender resulted in an improvement in the thermal properties when compared to the BD based TPUs. It can be seen that the maximum weight loss temperature was shifted from 361 °C to 381 °C. Although all TPUs resulted in negligible char yields, it is also clear from the results that the char yield of TPUTRIOL is two times the char yield of TPUBD. Due to the presence of thioether bonds in the polymer matrix and also due to the crosslinked structure of the TATATRIOL containing thermoplastic polyurethanes, an enhancement in the thermal properties was achieved. To sum up, it can be said that TATATRIOL increased the thermo-oxidative stability of the system by increasing the activation energy that is required for the thermal degradation of the polymer chains.

Table 2. Thermal properties of TPUTRIOL and TPUBD

Samples	10% weight loss temperature (°C)	Max. weight loss temperature (°C)	Char yield (%)	T_g^1 (°C)	T_g^2 (°C)	T_m (°C)
TPUBD	323	361	0.15	−8.5	65	167
TPUTRIOL	330	381	0.3	−16	64	155

Melting and glass transition temperatures of TPUTRIOL and TPUBD were determined by DSC. T_g and T_m of TPUs are given in Table 2. In the DSC thermogram of TPUBD three main thermal transitions were observed at −8.5 °C, 65 °C and 167 °C which correspond to the glass transition temperature of the soft segments (T_g^1), the glass transition temperature of the hard segments (T_g^2) and the melting temperature of the hard segments of TPUBD, respectively. As can be seen from Table 2, the T_g^1 of TPUTRIOL was found to be lower than that of

TPUBD and found as −16 °C. It can also be seen from the results that the T_g^2 and the melting temperatures were shifted to lower temperatures when TATATRIOL was used as chain extender. These decreases in the thermal transitions of TPUTRIOL can be attributed to the presence of flexible thioether bonds. As it is known from literature; thioether bonds are characterized by their flexibility[21]. Furthermore the decrease in the melting point of TPUTRIOL indicates that the crystallinity was also reduced. This reduced crystallinity can be related with the increased transparency of the TPUTRIOL, as noted earlier.

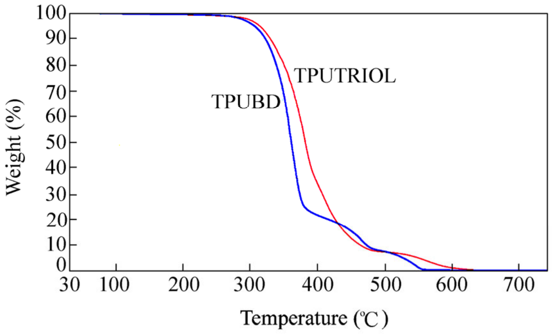


Fig. 4 TGA curves of (a) TPUTRIOL and (b) TPUBD

Mechanical Properties

E-modulus, tensile strength and the elongation at break values of TPUTRIOL and TPUBD are given in Table 3. Also the comparison of the mechanical properties of the two TPUs prepared in this study is plotted in Fig. 5. Generally thermoplastic polyurethanes are elastomeric materials which are characterized by moderate modulus and high elongation at break values. As can be seen from the results, TPUTRIOL has a lower modulus and higher elongation at break values than TPUBD. Although TATATRIOL containing thermoplastic polyurethanes are crosslinked, due to the presence of flexible thioether bonds, TPUTRIOL became much more elastic. On the other hand, the tensile strength of TPUTRIOL was more than 2.5 times of that of TPUBD. This increased tensile strength can be attributed to the crosslinked structure of the system.

Table 3. Mechanical properties of TPUTRIOL and TPUBD

Samples	E-module (MPa)	Tensile strength (MPa)	Elongation at break (%)	Tear strength (kN/m)	Shore A hardness
TPUBD	14.9 ± 1.1	2.6 ± 0.4	175.6 ± 20	20.8	70
TPUTRIOL	3.6 ± 0.3	7.0 ± 0.7	438.7 ± 35	7.1	45

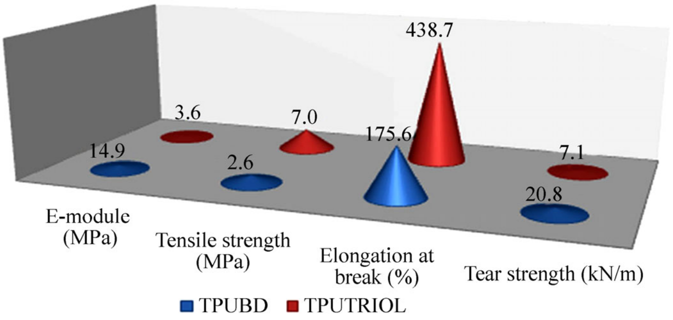


Fig. 5 Comparison of the mechanical properties of TPUTRIOL and TPUBD

Tear strength is the resistance of a material to tear propagation and indicates a TPU's ability to counter break and distortion[22]. Tear strengths of the TPUTRIOL and TPUBD were found as 7.1 and 20.8 kN/m, respectively. Thus it can be said that due to the rigid structure of the BD, TPUBDs are much more resistant to tear propagation.

Moreover the shore hardness values (Table 3) were measured to investigate the effect of the chain extender type on the surface hardness of the TPUs. As can be seen from Table 3 BD containing TPUs have higher shore hardness values than TPUTRIOL which is related to the relatively rigid, more crystalline structure of TPUBD and the rather flexible structure of TPUTRIOL. Thus it can be interpreted that the presence of BD decreases the segmental mobility of the polymer chains.

CONCLUSIONS

In this study, a three functional chain extender (TATATRIOL) was synthesized by using an ionic thiol-ene addition reaction. TATATRIOL was obtained from the reaction of 1,3,5-triazine-2,4,6 (1H,3H,5H)-trione (TATA) with 2-mercaptoethanol. Two different TPUs were prepared by using either BD or TATATRIOL as chain extenders. The effects of TATATRIOL on the properties of the TPUs were investigated and compared to those of the TPUs prepared with BD. The chemical structure of TATATRIOL was confirmed by ATR-FTIR, ^{1}H-NMR and ^{13}C-NMR techniques and the reaction was proven to be successful. Although a three functional chain extender was used and the resulting TPUs are thus crosslinked, due to the presence of flexible thioether linkages, the TPUs derived from the sulfur containing chain extender displayed lower modulus and high elongation at break values than the analogous TPUs derived from BD. Also TATATRIOL containing TPUs showed lower shore hardness and tear strength values, but better transparency than TPUBD. Due to the flexible and viscoelastic thioeter bonds in the structure of TPUTRIOL, these TPUs were found to have lower thermal transition temperatures.

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