

PROPERTIES OF POLYURETHANE ELASTOMERS BASED ON POLY (OXYETHYLENE-*co*-OXYTETRAMETHYLENE) DIOL*

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Abstract Polyurethane elastomers derived from 4,4'-methylene bis(phenyl isocyanate), butylene glycol and the low oxyethylene moiety content copolyether of tetrahydrofuran and ethylene oxide, obtained by copolymerization using heteropolyacid-ethylene oxide initiator system, were prepared. The polyurethanes exhibited an increased water absorption and much better low temperature resilience, which remained high even at a temperature of -3°C , while that of polyurethane based upon poly(tetramethylene ether) glycol of the same molecular weight, i.e. being 2000, and molecular weight distribution, i.e. in the range of 1.4–1.5, starts to decrease dramatically at 5°C .

Keywords Polyurethane, Poly(oxyethylene-*co*-oxytetramethylene) diol, Low temperature resilience, Heteropolyacid-ethylene oxide initiator system

INTRODUCTION

Segmented polyurethane block copolymers are an important class of thermoplastic elastomers^[1]. They are composed of short alternating blocks of soft and hard segment units. The hard segment unit is normally an aromatic diisocyanate that has been chain-extended with a low molecular weight diol or diamine to form a urethane or urethane urea segment with a molecular weight ranging from 500 to 3000. The soft segment is typically a polyester or polyether diol with a molecular weight between 500 and 5000. The macroglycol and the chain extended diisocyanate then combine to form an $(AB)_n$ type block copolymer. A wide range of physical properties and morphologies for such kinds of block copolymers are obtainable by varying the composition and chemical structure of the hard and soft segments. The potential of tailoring their physical properties for a specific application has initiated the interest of investigation in this field.

Polyester diol or polyether diol has been widely used as the soft segment in polyurethane (PU). Poly(tetramethylene ether) glycol (PTMG) prepared by ring-opening polymerization of tetrahydrofuran (THF) is a representative example of useful polyether diol. Superacids (e.g. fluorosulfuric acid, perchloric acid-acetic anhydride, fuming sulfuric acid, etc.) were commonly used as the polymerization catalysts. Aside from the requirement for selecting acid-resistant construction materials, there are the problems of neutralizing the acids and the proper disposal of the salts (by-product). In the last decade, various research groups have found that heteropolyacids (HPAs), strong acids with complex polyanions, are the suitable initiators for cationic polymerization. These initiators are also of interest because they are readily available, nonvolatile, not particularly corrosive, stable in open air, and soluble in a number of organic solvents. Furthermore, they can be recovered and reused. However, their activity of initiation is low, and a large amount of HPA is required in order to get a suitable reaction rate. Even so, the polymerization conversion is lower than 30%^[2].

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In our previous paper^[3], we found that by using ethylene oxide (EO) as the promoter, the polymerization rate and conversion of THF were effectively increased while the amount of HPA used was only 1/5–1/20 of that used in the literature^[4]. The molecular weight of the product could be controlled within the range of 1000–3000 by varying the concentration of water, and its molecular weight distribution ($M_w/M_n \cong 1.4$) was relatively narrow. The melting point of the product was about 20°C lower than that of PTMG having the same molecular weight. However, there were about 16 mol% (11 wt%) oxyethylene moieties incorporated into the chains of product, which may influence the properties of polyurethane elastomer prepared thereby.

The copolyether containing up to 50 mol% (38 wt%) oxyethylene moieties is described in the patent literature as preferable for the soft segment of PU elastomers, such as Spandex^[4]. And the decreased melting point of the copolyether is beneficial for handling^[5]. Tonomura^[6] pointed out that the low temperature resilience of the PU elastomer was improved due to the relatively narrow molecular weight distribution of PTMG.

The copolyether of tetrahydrofuran with high content of oxyethylene moieties around 50 mol% (38 wt%) was used for the preparation of PU^[7, 8] and the elastomer thus obtained offered an improved resistance against organic solvent. Although the copolyether still shows no industrial importance for the property loss of elastomer product thereof^[9]. No studies on PU thermoplastic elastomer based on copolyether of low oxyethylene moiety content (< 20 wt%) could be found in the literature.

In the present article we prepared PU elastomers based upon the low oxyethylene content copolyether which was obtained by polymerization of THF using heteropolyacid-ethylene oxide as initiator system^[3]. The copolyether contains more than 80% of the total end groups, these being the oxyethylene hydroxyls. The properties of elastomers were characterized and compared with those of PU based upon PTMG available from Du Pont Co. under the trade name "Teracol".

EXPERIMENTAL

Materials

Copolyether diol prepared in our laboratory by the procedure described in the literature^[3] and PTMG (Teracol 1000 and Teracol 2000) were dried in vacuum at 100°C for 6 h. DMF was refluxed with CaH_2 for 2 h and distilled under vacuum. 4,4'-Methylene bis(phenyl isocyanate) (MDI) and butylene glycol (BG) were distilled under reduced pressure.

Polymerization

0.1 mol MDI was added to a 100 mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet tube and a distilling condenser. The flask was heated to 60–70°C to melt MDI under nitrogen atmosphere. Then the copolyether or PTMG was introduced dropwise into the flask. After 15 min, BG was added very slowly and stirred till the viscosity of the system remained unchanged. 20 mL DMF was added to dissolve the polymer and the resulting solution was poured into water. The spongiiform product was immersed in water for 24 h and then dried in vacuum at 50°C for 4 h.

The ingredients of PUs are shown in Table 1.

Table 1. Ingredients for PU preparation and $[\eta]$ of the product

Sample	Polyether		P(T):MDI:BG (molar ratio)	$[\eta]$ (dL/g)
	Kind ^a	<i>M</i>		
PU-1	T	1000	1:2:1	0.79
PU-2	P	1000	1:2:1	0.76
PU-3	T	2000	1:2:1	0.82
PU-4	P	2000	1:2:1	0.79
PU-5	P	1700	1:2:1	0.70
PU-6	P	2000	0.8:2:1.2	0.67
PU-7	P	2000	0.7:2:1.3	0.68

^a T = PTMG (TeracolTM), P = Poly(THF-co-EO) diol^[3]

Film Preparation

PU was dissolved in THF to form 10 wt% solution and poured into a polytetrafluoroethylene mould. After 24 h a film was formed, which was subsequently dried in vacuum at 50°C for 4 h to remove the solvent. The film thickness was about 0.1–0.15 mm.

Characterization

Differential scanning calorimetry (DSC) was conducted at −100°C to 100°C using a TA DSC2010 instrument with a heating rate of 10 K/min. The intrinsic viscosity was measured with an Ubbelohde viscometer using DMF as the solvent at 25°C.

The resilience of PU was determined as follows: A 50 × 1 × 0.1–0.15 mm sample of PU with a gripper distance of 1.5 cm was stretched to a length of 4.5 cm and held for 10 min. Then it was released and left for 10 min at various temperatures. The length (l) of the released sample was then measured. The resilience was calculated according to Eq. (1)

$$\text{Recovery} = \frac{4.5 - (l - 1.5)}{4.5} \times 100\% \quad (1)$$

The mechanical properties of PUs were measured using an Instron 5500 at 16°C. The moving speed of the crosshead was 200 mm/min. The sample size was 40 × 4 mm and the gripper distance was 15 mm.

Water absorption of the sample was calculated from its weights before and after immersion in water at 25°C for 24 h or 1 week^[10].

RESULTS AND DISCUSSION

Copolyether

The copolyether diols prepared by polymerization of THF with heteropolyacid-ethylene oxide as the initiator system^[3] were characterized and their results are shown in Table 2.

Table 2. Characterization of copolyether glycol

Sample	M_n	Content of EO moieties in chains		-EOH ^a - E -	[-EOH] ^b [-TOH]	T_m (°C)	M_w/M_n
		(mol%)	(wt%)				
1	1017	26.9	18.4	41.4	4.0	7.8	1.36
2	1943	22.7	15.2	25.3	4.6	11.9	1.37

^a Molar ratio of EO moieties attached to hydroxyl groups at chain ends and the total EO moieties in chain.

^b Molar ratio of the hydroxyl end-groups attached to EO moieties and THF moieties.

Copolyether glycols having M_n in the range of 1000 ± 50 or 2000 ± 100, as required commercially^[9], were prepared. The melting temperatures of copolyethers were determined by DSC to be about 20°C lower than those of PTMG having the same M_n ^[9]. The molecular weight distribution indices (M_w/M_n) of both samples verified by GPC^[3] to be around 1.4 were relatively narrow.

According to ¹H-NMR spectroscopic measurement^[11], the contents of EO moieties in the copolymers were 26.9% and 22.7%, respectively. Considering that 41.4% and 25.3% of the total EO moieties attached to the hydroxyl groups (−CH₂CH₂OH) at the ends of copolyether diols, respectively, the exact content of EO moieties distributed inside the chains was only about 16 mol% (11 wt%). About 80% of the hydroxyl end groups formed were the oxyethylene hydroxyl ones.

PU Preparation and the Thermal Transition of Products

A series of PUs were prepared based on MDI, BG and polyether of THF or its copolyether with EO in different amounts or by using the copolyether of different molecular weights (Table 1), and several DSC thermograms are shown in Fig. 1(a) (PU-1 and PU-2) and Fig. 1b (PU-3 and PU-4). The transition temperatures of the samples are summarized in Table 3. With the incorporation of EO moieties into the soft segments, the T_g of PUs was raised, which is in agreement with the results reported by Robinson^[7], who pointed out that the T_g of PU based on

copolyether containing EO moieties is higher than that based on PTMG.

Sample PU-3 exhibits a crystallization temperature at -20.5°C and a melting temperature at 8.5°C , which could be attributed to the ease of crystallization of the sufficiently long poly(tetramethyleneoxy) soft segments.

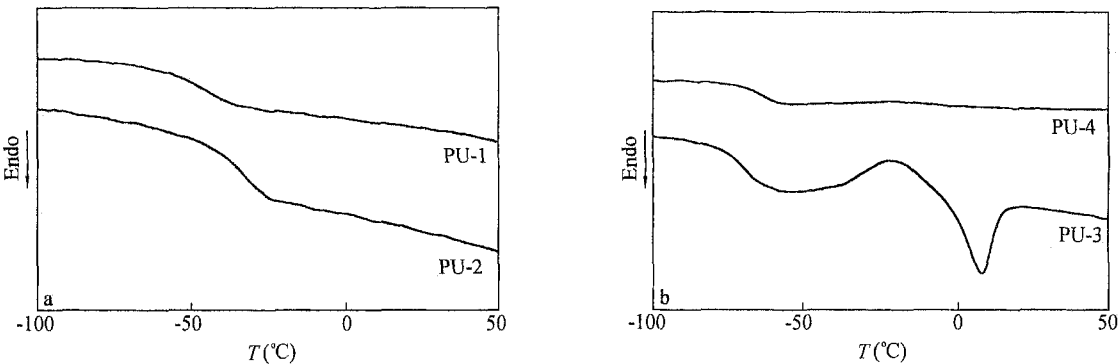


Fig. 1 DSC curves of PUs

Table 3. Thermal transition of PUs

Sample*	T_g ($^{\circ}\text{C}$)	Transition temperature of soft segment ($^{\circ}\text{C}$)	
		T_c	T_m
PU-1	-56.6	—	—
PU-2	-40.3	—	—
PU-3	-75.4	-20.5	8.5
PU-4	-69.5	—	—

* See Table 1

Mechanical Properties of PU

With the incorporation of EO moieties into the soft segments of the PU, the modulus and the tensile strength decrease and the elongation increases. However, on varying the formulation of the feed materials or by using the copolyether of lower molecular weight to increase the fraction of the hard segment composition, the mechanical properties increase.

Table 4. Mechanical properties of PUs

Samples*	$[\eta]$ (dL/g)	Maximum strain (%)	Modulus (MPa) ^a	Modulus (MPa) ^b	Modulus (MPa) ^c	Stress at max. load (MPa)
PU-1	0.79	1060	2.252	1.825	2.454	60.44
PU-2	0.76	1087	1.401	1.444	1.846	46.42
PU-3	0.82	1316	1.001	0.879	1.183	48.15
PU-4	0.79	1792	0.530	0.377	0.339	27.70
PU-5	0.70	1831	0.662	0.589	0.648	24.58
PU-6	0.67	1644	0.818	0.820	0.855	32.79
PU-7	0.68	1547	1.012	1.128	1.029	29.50

* See Table 1

^a The modulus calculated at 100% elongation

^b The modulus calculated at 200% elongation

^c The modulus calculated at 300% elongation

Low Temperature Resilience of PU

Tomomura^[6] has pointed out that the molecular weight distribution of PU may influence its low temperature resilience. The resilience of PU elastomer derived from PTMG of molecular weight 2000 with $M_w/M_n = 2.1$ was significantly decreased at the temperature below 15°C , while that for PTMG of the same molecular weight with $M_w/M_n = 1.4$ started to decrease at 5°C . However, the resilience of PU derived from the copolyether with a small

amount of EO moieties having a molecular weight of 2000 and $M_w/M_n = 1.4$ still remained high even at a temperature of -3°C , as shown in Fig. 2. The deterioration of the low temperature resilience of PU-3 prepared by using PTMG ($M_w = 2000$) must be related to its crystallization at a temperature below 8°C , as shown in Table 3.

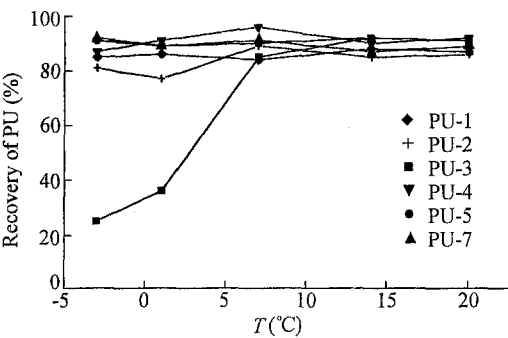


Fig. 2 The resilience of PUs

Water Absorption of PU

Due to the introduction of EO moieties into the soft segments of PU, the polarity of the soft segments increases, resulting in an increase of water absorption of PU, which might be preferable for use in Spandex fabrics with modified sweat absorption (Table 5). The absorption of water for PU based on copolyether was almost twice that for PU based on PTMG.

Table 5. Water absorption of PUs		
Samples *	Water absorption (24 h) (%)	Water absorption (1 week) (%)
PU-1	2.5	2.6
PU-2	4.5	4.6
PU-3	2.9	2.9
PU-4	4.3	4.5
PU-5	4.4	4.5
PU-6	3.8	3.9
PU-7	3.0	3.0

* See Table 1

CONCLUSIONS

PU elastomers derived from MDI, BG and low oxyethylene content copolyether of THF and EO obtained by copolymerization using a heteropolyacid-EO initiating system were prepared. The PUs derived from copolyether exhibit much better resilience at a temperature below 5°C than that derived from PTMG having the same molecular weight ($M_n = 2000$) and relatively narrow molecular weight distribution ($M_n = 1.4-1.5$). The PUs derived from copolyether exhibit a water absorption value twice that based upon PTMG. With the incorporation of oxyethylene moieties into the soft segments of PU the mechanical strength and modulus decreased. However, these could be enhanced by varying the prescription of feed materials or by using copolyether of decreased molecular weight.

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