Polyurethane Urea Elastomer Having Monodisperse Poly(oxytetramethylene) as a Soft Segment with a Uniform Hard Segment

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Introduction

Poly(oxytetramethylene) glycol (PTMG) in the molecular-weight range from 500 to 4000 is often used as the soft segment of high-performance multiblock-type elastomers such as polyurethanes, polyether−esters, and polyether−amides because of its low glass transition point (T_g), good rubbery elasticity, and high strength. The crystallinity of PTMG provides the high strength of the PTMG elastomers. However, studies on the isothermal crystallization of PTMG network polymers[1] show that a cold crystallization phenomenon (cold hardening) is sometimes observed, which restricts their applications.

In the case of multiblock-type elastomers, segment distribution and composition ratios of monomers are important parameters for control of physical properties. Effects of the chain length and distribution of hard segments on the physical properties of elastomers have been examined by using well-characterized hard segments.[2−5] There have been reports[6] on the effect of unreacted tolylene diisocyanate (TDI) on the domain structure of a polyurethane urea elastomer consisting of PTMG, TDI, and aromatic diamines. On the other hand, there have been few reports[7] on physical properties of elastomers having a monodisperse soft segment (M_w/M_n < 1.1). In using polydisperse PTMG, with its index from 1.5 to 3.8, the effect of the molecular weight distribution of the soft segment on the polyurethane properties has been examined.[8]

In the present paper, synthesis and properties of an elastomer having monodisperse PTMG unit with uniform hard segment are described. The resulting data clearly showed that the elastomer properties could be controlled by changing the molecular weight distribution of the soft segment and the hard segment distribution.

Experimental Section

Materials. Monodisperse PTMG was prepared by fractionation of commercial PTMG (PTG 1000SN, Hodogaya Chemical Co. Ltd.) according to the literature.[9] Polydisperse PTMG (Terathane 2000) was obtained from DuPont Chemical Co. Other reagents are commercially available and used as received.

Synthesis of Polyurethane Urea with Unimodal Hard Segment Distribution. PTMG was reacted with an excess of 2,4-TDI (6-fold for PTMG) at 60 °C under argon. After 3 h, unreacted TDI was removed under reduced pressure (0.1 mmHg) at 150 °C. The adduct was kept at 80 °C and added to 4,4′-methylenebis(2-chloroaniline) (MOCA) at 120 °C (isocyanate/amine = 1.05). The mixture was injected to the mold held at 120 °C for 30 min, followed by heating at 100 °C for 24 h. The sample was stood at room temperature for 7 days for measurement of properties.

Measurements. Size exclusion chromatographic (SEC) analysis was carried out using a Tosoh SC8010 apparatus with a refractive index detector using the following conditions: TSKgel G5000HXL and GMHXL (×2) columns and tetrahydrofuran eluent at a flow rate of 1.0 mL/min. The calibration curves for SEC analysis were obtained using polystyrene standards. As to the 1:2 adduct of PTMG and TDI, the capping with methanol was performed before the measurement. Hardness was measured using a Kobunshi keiki microdurometer with model MD-1. Tensile tests were carried out using a Orientec RTC-1225A with model U-4310 at 23 °C in tension speed of 100 mm/min. Wide-angle X-ray diffraction (WAXD) profiles were recorded at room temperature on a Rigaku RAD-B diffractometer. A sealed X-ray tube generator with a Cu target operated at 40 kV and 100 mA provided the source of X-rays. Intensities were counted in the Bragg angle (2θ) from 10 to 30° at scan rate of 4°/min. Dynamic viscoelasticity was measured using a thermal mechanical analysis system of Seiko EXSTRA 6000/DMS 6300 in a range from −100 to +220 °C at 3 °C/min heating rate. DSC analysis was preformed under nitrogen using a Seiko EXSTRA 6000/DSC 6200 apparatus calibrated with an indium reference standard. The measurement was made at a heating rate of 10 °C/min from −100 to 230 °C using 10 mg of the sample.

Results and Discussion

PTMG is synthesized by cationic ring-opening polymerization of tetrahydrofuran. Under appropriate reaction conditions, the polymerization proceeds in a living fashion to give monodisperse polymers. However for synthesizing oligomers with degree of polymerization from 10 to 40, strict control of molecular weight distribution is difficult; several patents show that the lowest value of M_w/M_n with oligomers was about 1.3.[10,11] The quantitative introduction of a hydroxyl group at both polymer ends is also required for use as soft segments. In this study, therefore, monodisperse PTMG was prepared by fractionation of commercially available PTMG with M_n and M_w/M_n of 1000 and 1.5, respectively, using methanol solutions containing different concentration of urea.[8] M_n and M_w/M_n of the fractionated PTMG sample, determined by hydroxyl value and SEC, were 2000 and 1.1, respectively.

In the synthesis of polyurethane urea by the conventional method, the addition reaction of free diisocyanate and the chain extender resulted in the formation of the polydisperse hard segment. In this study, the polyurethane urea with uniform hard segment was synthesized according to Scheme 1. The obtained sample (**1**) had monodisperse soft segment with unimodal hard segmental distribution. For comparison, two samples were synthesized: one (**2**) having polydisperse PTMG unit (M_n = 2000, M_w/M_n = 2.0) with unimodal hard segmental distribution and the other (**3**) having the polydisperse PTMG unit with polydisperse distribution of the hard segment. The latter was obtained by the conventional method (reaction of PTMG and TDI (1:2 feed molar ratio) and subsequent polymerization of the resulting prepolymer with MOCA. Composition (content of soft and hard segments) of **1** was almost the same as that of **2** or **3**. The analytical value and physical properties of **1**−**3** are summarized in Table 1.

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Scheme 1

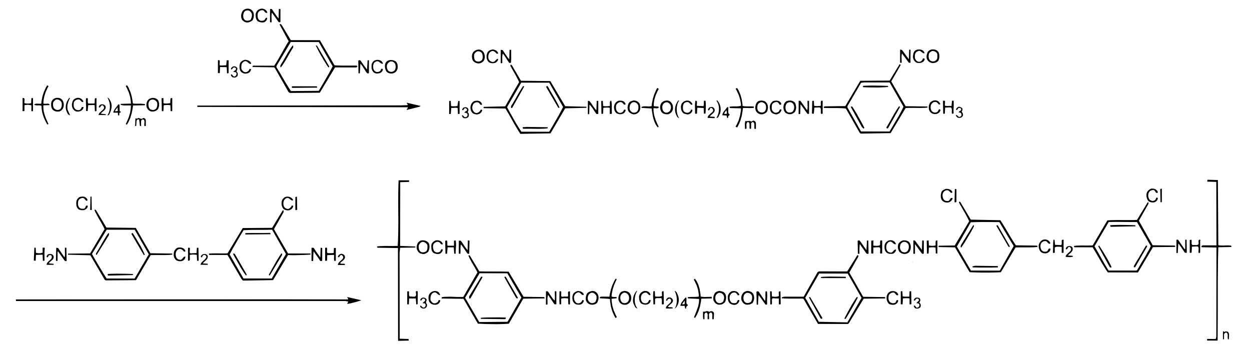

Table 1. Properties of PTMGs, Prepolymers and Elastomers

	PTMG		prepolymer			elastomer					
sample	$M_n{}^a$	$M_w/M_n{}^b$	NCO (%)	free TDI (%)	$M_w/M_n{}^b$	$H_s{}^c$ (A)	$T_b{}^d$ (MPa)	$E_b{}^e$ (%)	$T_g{}^f$ (°C)	$T_m{}^g$ (°C)	$T_s{}^h$ (°C)
1	1989	1.08	3.63	0.07	1.13	68	32.2	460	−60.9		161
2	2036	2.03	3.58	0.08	1.90	72	37.8	490	−67.0	5.3	179
3	2036	2.03	3.58	1.11	1.91	81	44.7	510	−71.5	5.8	190

[a] Calculated from the hydroxyl value by titration. [b] Determined by SEC on the basis of calibration with standard polystyrene. [c] Hardness, measured by a microdurometer. [d] Tensile strength at break. [e] Elongation at break. [f] Glass transition temperature, determined by DSC. [g] Melting point of soft segment, determined by DSC. [h] Softening temperature, determined by DMS (as half of the E′ value at 20 °C).

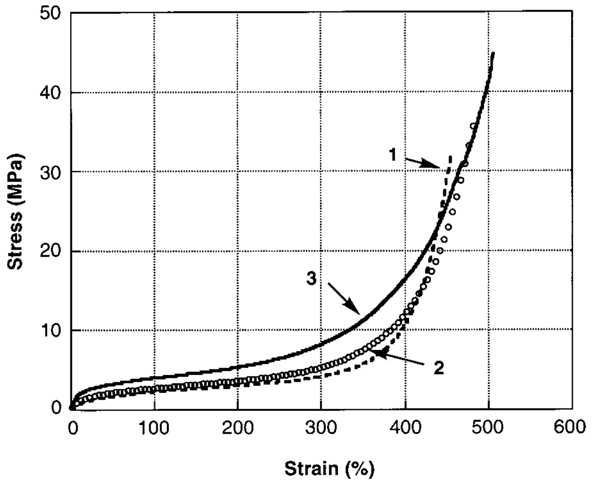

Figure 1. Stress–strain curves of elastomers **1**–**3**.

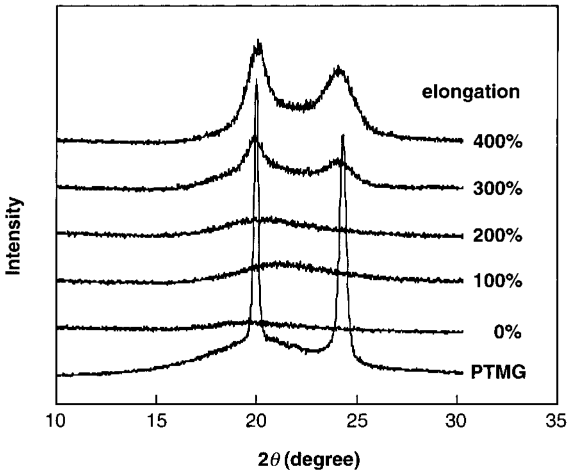

Figure 2. WAXD profiles of **1** at different elongation rate.

Hardness strongly depended on the microstructure; the hardness of **1**, where the hard segment was separated by the soft segment, was the smallest. Figure 1 shows stress–strain curves of elastomers **1**–**3**. For **3**, the initial stress rose sharply, whereas for **1** the initial stress increased the most slowly. In all the samples, a great increase of the stress is observed above 300%, indicating a rubberlike elasticity due to strain-induced crystallization of the soft segment. The order of the ultimate elongation was on the order of **1** < **2** < **3**. These data imply that the microstructure of the polyurethane urea affected the static mechanical properties.

Figure 2 shows WAXD spectra of **1** with different elongation rates. There were no peaks at less than 200% of the elongation rate, and two peaks were clearly observed at more than 300%, which agrees with those of PTMG. These data indicate that the crystallite formed by elongation was that of PTMG segment.

Storage modulus E′ and dissipation factor tan δ, as a function of temperature, are shown in Figure 3. As to the storage modulus, **1** had no shoulder around 0 °C, whereas there was a shoulder in **2** and **3**. In the DSC charts of the present elastomers (Figure 4), an endothermic peak was observed at ca. 5 °C in **2** and **3**. These data indicate that PTMG of **2** and **3** became crystallized at the low temperature (cold hardening), and hence, **2** and **3** cannot act as elastomers below the melting point. On the other hand **1** had no melting point at such a

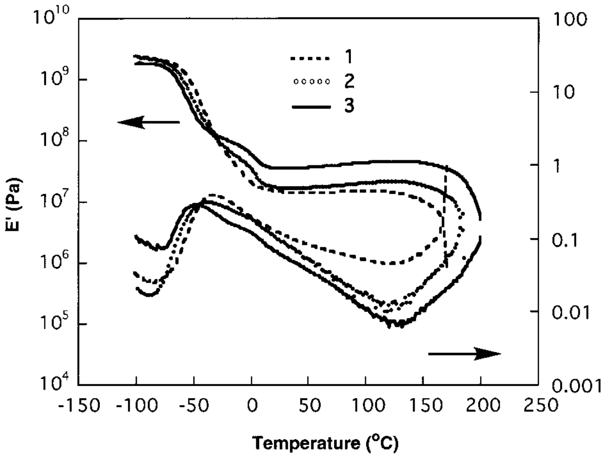

Figure 3. Temperature vs storage modulus (E′) and tan δ for elastomers **1**–**3**.

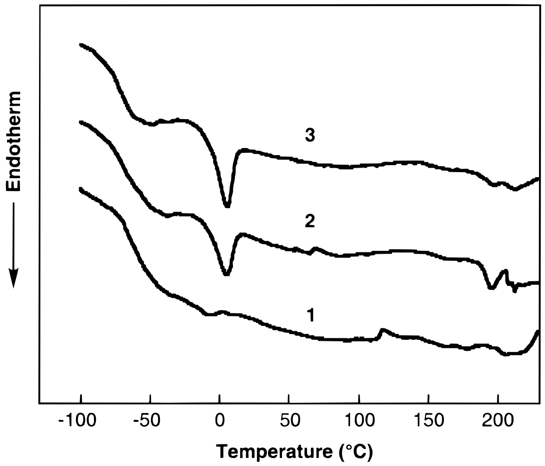

Figure 4. DSC curves of elastomers **1**−**3**.

temperature, maintaining good elasticity at a wide range of temperatures. From these data, it was found that elastic properties at low temperature were improved by introduction of the monodisperse soft segment.

The storage modulus of **1** at room temperature was the lowest, the tendency of which agrees with that of the hardness and initial stress of S−S measurement. The apparent softening temperature at the high-temperature region was on the order of **1** < **2** < **3**. This is probably due to the strong aggregation of the polydisperse hard segment in **3**.

In the case of polyurethanes and polyurethane ureas having crystalline soft segments, their crystallinity is reduced by extending the chain length of the hard segments. This means that a large amount of the hard segments is required, resulting in the increase of hardness and modulus. Natural rubbers show excellent properties such as high extensibility and mechanical strength, despite the elastomer having low hardness. In the polyurethane derivatives, especially with low hardness, it is often difficult to provide both properties with elasticity at low temperature and good mechanical strength. On the other hand, the present polyurethane urea (**1**) having a monodisperse PTMG unit with a uniform hard segment has both functions, suggesting that the control of soft and hard segmental dispersity is very important for physical and mechanical properties.

In conclusion, polyurethane urea having the monodisperse soft segment with a uniform hard segment was synthesized and characterized. Elastic properties, especially at low temperature, can be controlled by changing the dispersity of soft and hard segments. The present data are expected to provide a new concept for synthetic design of high-performance elastomers.

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