Macromolecules **2004,** *37,* 3287−3291

Highly Softened Polyurethane Elastomer Synthesized with Novel 1,2-Bis(isocyanate)ethoxyethane

Ken Kojio,[†] Tomoya Fukumaru,[‡] and Mutsuhisa Furukawa*[,‡]

Department of Materials Science and Engineering, Faculty of Engineering, and Department of Materials Science, Graduate School of Science and Technology, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-8521, Japan

Received December 26, 2003; Revised Manuscript Received February 6, 2004

ABSTRACT: A novel diisocyanate, 1,2-bis(isocyanate)ethoxyethane (TEGDI), whose backbone is ether bonds was used for the preparation of polyurethane elastomers (PUEs). 1,6-Hexamethylene diisocyanate (HDI) was also used as a control. The PUEs were prepared with either TEGDI or HDI, poly(oxytetramethylene) glycol (PTMG), and curing agent by a prepolymer method. Differential scanning calorimetry, infrared spectroscopy, and wide-angle X-ray diffraction revealed that the phase separation of the network TEGDI-based PUEs was much weaker compared with that of the HDI ones. Highly softened TEGDI-based PUEs were successfully prepared on account of flexibility of TEGDI itself and weaker phase separation.

Introduction

Polyurethane elastomers (PUEs) are widely used because they can show quite interesting properties with a changing chemical structure of starting materials, molecular weight of polymer glycol, preparation conditions, and so on.[1−8] The PUEs are usually prepared from polymer glycol, diisocyanate, and curing agent. Numerous starting materials have been used for the preparation of the PUEs to give them excellent properties. Hard segments possess a more different chemical nature than soft segments and separate into domains which act as physical cross-links. Hard domain morphology is well-known that it can be varied by changing starting materials, hard segment content, degree of cross-linking, thermal history, and so on.

The chemical structure of diisocyanate can be distinguished into two kinds. One is aromatic diisocyanate, and the other one is the aliphatic one. The PUEs prepared with aliphatic diisocyanate has the feature that the PUEs obtained do not show the change of color by UV light and heat aging.[9] However, these PUEs with aliphatic diisocyanate, such as 1,6-hexamethylene diisocyanate, usually give hard materials because of its high crystallizability. Thus, the development of the aliphatic diisocyanate-based PUEs does not satisfy the demands in our life. Recently, the 1,2-bis(isocyanate)ethoxyethane (TEGDI) was synthesized to attain novel properties of polyurethanes. This isocyanate has ether bonds in it. Ether groups have flexibility in comparison with the methylene chain. Thus, it is expected that the PUEs exhibit various properties that we do not know.

In this study, the effect of TEGDI on molecular aggregation state and mechanical properties of the PUEs was investigated using infrared spectroscopy, wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), dynamic viscoelastic measurement, and tensile test. We shall describe the intriguing properties of the obtained PUEs here.

Experimental Section

The PUEs were prepared from poly(oxytetramethylene) glycol (PTMG: $M_n = 2000$, Nippon Polyurethane Industry Co., Ltd., Japan), TEGDI ($OCN-(CH_2CH_2O)_2CH_2CH_2-NCO$, Nippon Polyurethane Industry, Co., Ltd., Japan), and a mixture of 1,4-butanediol (BD, Wako Chemical Co., Ltd., Japan) and 1,1,1-trimethylolpropane (TMP, Wako Chemical Co., Ltd., Japan) by a prepolymer method. The purities of the TEGDI were greater than 99%. 1,6-Hexamethylene diisocyanate (HDI, $OCN-(CH_2)_6-NCO$, 99%, Nippon Polyurethane Industry Co., Ltd., Japan) was also used to prepare the PUE for the comparison with the TEGDI-based PUE. The ratio of curing agents (BD and TMP) was 75/25 (w/w). The PTMG was dried with bubbling dried nitrogen under a reduced pressure. Prepolymers were prepared from PTMG and TEGDI or HDI with the ratios of $K = [NCO]/[OH] = 3.0$ and 4.0 at 80 °C for 3 h under a nitrogen atmosphere. One drop of dibutyltin dilaurylate (DBTL, Wako Chemical Co., Ltd., Japan) was added as a catalyst. The reaction was pursued by an amine equivalent method. Also, the number-average molecular weight (M_n) of prepolymer estimated with an amine equivalent method was 2400 and 2350 for TEGDI and HDI, respectively. These magnitudes correspond well to the summation of one PTMG molecule and either two TEGDI or HDI ones. Thus, it is conceivable that prepolymers include lots of isocyanate-terminated trimers. After finishing the reaction, the prepolymer was placed in a vacuum to remove the air involved inside. The prepolymer and curing agent were mixed well with the ratio of $[NCO]_{pre}/[OH] = 1.05$ for 90 s, and the viscous product was poured into a mold constructed by a spacer of 2 mm thickness and two aluminum plates heated at 80 °C. The PUEs were demolded after 2 h curing, and then they were postcured at 60 °C for 24 h in air. For the preparation of the linear TEGDI-based PUEs, BD was only used as a curing agent.

To understand the crystalline structure of the hard segment chain, regular polyurethanes were synthesized as a hard segment model. Samples were prepared by mixing either TEGDI or HDI and BD with $K = 1$ at 70 °C. $-(\text{TE-BD})_n-$ and $-(\text{HD-BD})_n-$ denote the hard segment model sample of TEGDI and HDI.

The gel fraction of the PUEs was determined from the original weight and the weight of dried sample after swollen to equilibrium state with benzene and *N*,*N*-dimethylacetamide (DMA) at 60 °C. The degree of gel fraction, g, was defined as $g = W_b/W$, where W_b and W are the weight of which the swollen sample is dried and original weight, respectively. The degree of swelling of the PUEs was determined from weight before

---

[†] Department of Materials Science and Engineering, Faculty of Engineering.

[‡] Department of Materials Science, Graduate School of Science and Technology.

* To whom correspondence should be addressed. E-mail: furukawa@net.nagasaki-u.ac.jp.

10.1021/ma0359988 CCC: $27.50

Table 1. Magnitudes of Density, Gel Fraction, Degree of Swelling, T_g, and Mechanical Properties of the TEGDI- and HDI-Based PUEs with $K = 3$ and 4

	molar ratio	HSC/	gel fraction [%]		degree of swelling		density	T_g	hardness	Young's modulus	tensile strength	strain at
sample[a,b]	DI/PTMG/BD/TMP	SSC[c]	DMA	benzene	DMA	benzene	[g/cm^3]	[°C]	[JIS-A]	[MPa]	[MPa]	break
TE-BT-3	3.0/1.0/1.4/0.3	28/72	90	93	4.37	5.21	1.06	−73.2	55.8	2.0	10.2	6.1
TE-BT-4	4.0/1.0/2.2/0.5	34/66	97	98	2.65	1.56	1.06	−73.1	57.4	2.4	5.5	4.4
HD-BT-3	3.0/1.0/1.5/0.3	25/75	83	97	5.95	3.71	1.05	−69.0	85.4	7.4	14.1	3.3
HD-BT-4	4.0/1.0/2.2/0.5	32/68	98	100	3.10	2.31	1.08	−68.9	88.8	14.3	16.6	3.4
TE-B-3	3.0/1.0/1.8/0.0	28/72					1.04		49.8	2.5	2.5	11.1
TE-B-4	4.0/1.0/2.9/0.0	34/66					1.05		53.6	2.5	2.7	10.6

[a] Sample name denotes the type of diisocyanate, curing agent, and *K*. [b] TE = TEGDI, HD = HDI, BT = BD/TMP, and B = BD. [c] HSC = hard segment content; SSC = soft segment content.

and after equilibrium swelling with benzene and DMA. The degree of swelling, q, was defined as $q = 1 + \{(W_a - W_b)/d_s/(W_b/d_p)\}$. Here, W_a, d_s, and d_p are the weight of sample swollen to equilibrium state, the density of solvent, and density of the PUEs, respectively.

The state of hydrogen bond of the hard segment in the PUEs was investigated by attenuated total reflection Fourier transform infrared spectroscopy (ATR-FT-IR). ATR-FT-IR spectra were obtained with an FTS-3000 EXCALIBUR (Digilab Japan Co., Ltd., Japan) equipped with a TGS detector using an ATR cell (MIRacle, PIKE Technologies, Inc.). All spectra were collected with 32 scans and at a resolution of 4 cm^{-1}.

Molecular arrangement of the PUEs was evaluated using wide-angle X-ray diffraction (WAXD). RINT2200 (Rigaku Co., Ltd., Japan) was employed. WAXD profiles were obtained with a 2θ scan mode. Voltage and current of an X-ray source were set to be 40 kV and 40 mA, respectively.

Differential scanning calorimetric (DSC) measurement was performed to understand the thermal behavior of the PUEs. DSC thermograms were obtained with a DSC (Rigaku DSC 8230, Rigaku Denki Co. Ltd., Japan) in the temperature range from −130 to 250 °C with a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. As-prepared samples were simply cooled around −140 °C, and then measurements were started.

Temperature dependence of dynamic mechanical properties was measured with DMS 6100 (Seiko Instruments, Co., Ltd., Japan). The size of samples used is 20 mm × 5 mm × 2 mm. Measurements were performed in the temperature range from −150 to 250 °C with a heating rate of 2 °C min^{-1} in nitrogen. Imposed strain and frequency were set to be 0.2% and 10 Hz, respectively.

Tensile test was performed with an Instron type tensile tester (Shimadzu, Autograph; AGS −100A, Japan) at 20 °C. The size of samples used is 60 mm × 5 mm × 2 mm. An initial length and elongation rate were set to be 15 mm and 5 mm min^{-1}, respectively.

Results and Discussion

Appearances of the TEGDI- and HDI-based PUEs were transparent and milky opaque, respectively. Table 1 shows density, gel fraction, and degree of swelling, T_g, and mechanical properties of the TEGDI- and HDI-based PUEs with formulation ratios of $K = 3$ and 4. The abbreviation of the PUEs denotes the kind of isocyanate and *K*. TE, HD, BT, and B denote TEGDI, HDI, BD/TMP, and BD, respectively. An obvious difference was not observed for the density of both PUEs. Gel fraction and degree of swelling of both PUEs increased and decreased with an increasing *K*, respectively. This can be attributed to the increasing in hard segment content with stronger cohesion force. Hardness of the HDI-based PUE increased with an increasing *K*, but that of the TEGDI-based PUE did not show any obvious trends.

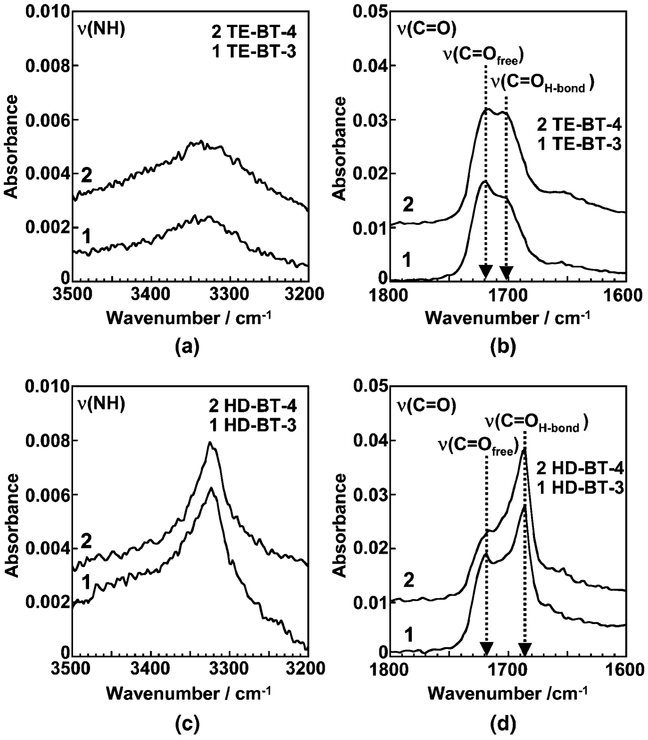

Figure 1. ATR-FT-IR spectra of the network TEGDI- and HDI-based PUEs with $K = 3$ and 4. The mixture of 1,4-butanediol (BD) and 1,1,1-trimethylolpropane (TMP) was used as a curing agent. (a, c) NH stretching band region. (b, d) Carbonyl stretching band region.

Figure 1 shows the ATR-FT-IR spectra of the NH stretching band region for the network (a) TEGDI- and (c) HDI-based PUEs with $K = 3$ and 4. Peaks of the NH stretching band (ν(NH)) of the network TEGDI- and HDI-based PUEs were observed at 3330 and 3325 cm^{-1}, respectively. In this region, hydrogen-bonded NH groups with ether oxygen ($\nu(\mathrm{NH}_{\mathrm{ether}})$) and urethane carbonyl groups ($\nu(\mathrm{NH}_{\mathrm{carbonyl}})$) and free one ($\nu(\mathrm{NH}_{\mathrm{free}})$) are generally observed at around 3290−3310, 3300−3350, and 3450 cm^{-1}, respectively.[10,11] Thus, most of NH groups in the network TEGDI- and HDI-based PUEs form a hydrogen bond with either ether oxygen or urethane carbonyl oxygen. The peak width of the network TEGDI-based PUE was much broader than for the HDI one. Hence, it is likely to consider that NH groups in the network TEGDI-based PUE form many kinds of hydrogen bonds with ether and carbonyl groups, but most of those in the network HDI one form a hydrogen bond with carbonyl groups. Figure 1 also shows the ATR-FT-IR spectra of the carbonyl stretching band region for the network (b) TEGDI- and (d) HDI-based PUEs with $K = 3$ and 4. One can see three peaks at 1687, 1704, and 1719 cm^{-1}, which can be assigned to the hydrogen-bonded carbonyl stretching band ($\nu(\mathrm{C{=}O}_{\mathrm{H-bond}})$) and free one ($\nu(\mathrm{C{=}O}_{\mathrm{free}})$).[10,11] For the both network PUEs, the ratio of peak intensities ($\nu(\mathrm{C{=}O}_{\mathrm{H-bond}})/\nu(\mathrm{C{=}O}_{\mathrm{free}})$) in-

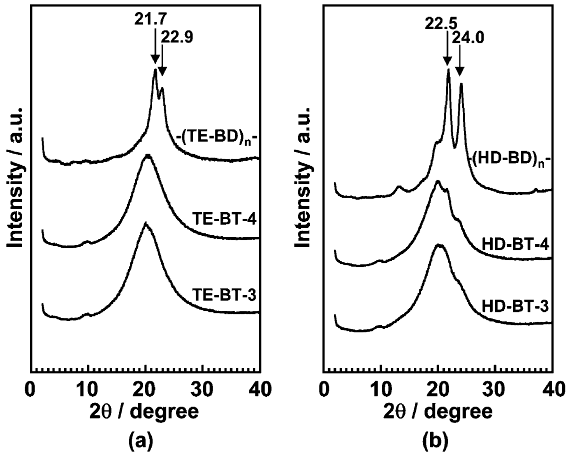

Figure 2. WAXD profiles for the network (a) TEGDI- and (b) HDI-based PUEs with $K = 3$ and 4 as well as hard segment model polyurethanes ($-(\text{TE-BD})_n-$ and $-(\text{HD-BD})_n-$).

creased with an increasing K. This trend indicates that the hard segment chains aggregate more with an increasing K. The wavenumber of $\nu(\text{C=O}_{\text{H-bond}})$ in the network HDI-based PUEs is lower than for the network TEGDI-based ones. The peak intensity of $\nu(\text{C=O}_{\text{H-bond}})$ was much higher than that of $\nu(\text{C=O}_{\text{free}})$ for the network HDI-based PUEs; on the contrary, these intensities were comparable for the network TEGDI-based PUEs even at $K = 4$. From these results, ATR-FT-IR measurement revealed that the hydrogen-bonded hard segment domains were formed well in the network HDI-based PUEs, but those were not done in the network TEGDI-based ones.

WAXD measurements were carried out to evaluate the crystalline state of the PUEs. Figure 2 shows WAXD profiles for the network TEGDI- and HDI-based PUEs with $K = 3$ and 4. WAXD profiles of the TE-BT-3 and TE-BT-4 exhibited only amorphous halo at around $2\theta = 20°$. On the other hand, two small peaks as well as an amorphous halo were observed at $2\theta = 22.5°$ and 24.0° for the HD-BT-3 and HD-BT-4. The intensity of these two peaks apparently increased with an increasing K. To investigate the molecular aggregation state of the hard segment part, the hard segment model ($-(\text{TE-BD})_n-$ and $-(\text{HD-BD})_n-$) was synthesized with diisocyanate and BD. WAXD profiles for these two hard segment models were also shown in Figure 2. WAXD profiles for both model samples showed two crystalline peaks. Peaks positions in these profiles were $2\theta = 21.7°$ and 22.9° for the $-(\text{TE-BD})_n-$ and 22.5° and 24.0° for the $-(\text{HD-BD})_n-$. Since these peak positions of the $-(\text{HD-BD})_n-$ corresponded well to those obtained from the network HD-BT-3 and HD-BT-4, it is likely to consider that two peaks are from the crystallized hard segment domain. These results clearly suggest that the network HDI-based PUEs have crystalline hard segment domains in them. In contrast, even if the $-(\text{TE-BD})_n-$ is in a crystalline state at room temperature, they cannot form the crystal structure in the network TEGDI-based PUEs.

Thermal properties of the PUEs were investigated using DSC. Figure 3 shows the DSC thermograms for the network TEGDI- and HDI-based PUEs with $K = 3$ and 4. T_gs of the soft segment chain were observed at around −70 °C. Here, T_g of the original PTMG used in this study was −85 °C. T_gs of the soft segment in network TEGDI-based PUEs were lower than those of the network HDI-based ones. This is because the TEGDI has a much higher affinity with PTMG on account of ether bonds and has flexibility. For the network TEGDI-based PUEs, unusual behaviors were observed. With an increasing temperature, strong exothermic and endothermic peaks because of crystallization due to rearrangement and melting of crystal of soft segments were observed at around −30 and 18 °C, respectively. In contrast, the network HDI-based PUE did show only broad endothermic peak due to melting of the soft segment. Also, the endothermic peaks due to the melting of hard segment domains were observed at around 130 °C only for the HD-BT-3 and HD-BT-4. The reason that the TE-BT-3 and TE-BT-4 showed crystallization due to reorganization during the heating process can be explained as follows. In the case of the general crystallizable PUEs like HD-BT-3 and HD-BT-4, the soft segment can be crystallized with cooling before DSC measurement because they have a phase-separated structure; that is, each phase is composed of a rich phase. However, the soft segment in the TE-BT-3 and TE-BT-4 cannot be crystallized during the cooling process due to the presence of a large amount of hard segment component in the soft phase. Therefore, it seems reasonable to conclude from IR, WAXD, and DSC that the network HDI-based PUEs have a strong microphase separation, but the network TEGDI-based ones do not, that is, have a phase mixing trend.

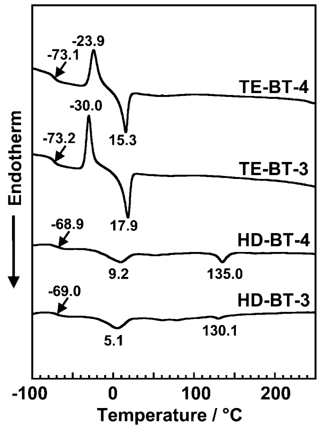

Figure 3. DSC thermograms for the network TEGDI- and HDI-based PUEs with $K = 3$ and 4.

Figure 4 shows the temperature dependence of storage modulus (E') and loss tangent ($\tan \delta$) for the network TEGDI- and HDI-based PUEs with $K = 3$ and 4. During the heating process, E' of the TE-BT-3 and TE-BT-4 once increased at around room temperature due to recrystallization of the soft segment. Both network PUEs exhibited a rubbery plateau region above room temperature. The magnitude of E' around the rubbery plateau region for the network HDI-based PUEs increased with an increasing K; on the other hand, that for the network TEGDI one showed a similar value. Also, the magnitude of E' for the network TEGDI-based PUEs was more than 1 decade smaller than for the network HDI-based PUEs. In the $\tan \delta$ curve, three peaks were clearly observed for the TE-BT-3. They might be assigned to a glass transition, crystallization due to reorientation and melting of soft segment chain from lower temperature side.

Mechanical properties of the network PUEs were investigated using the tensile test. Figure 5 shows the stress−strain curves for the TEGDI- and HDI-based

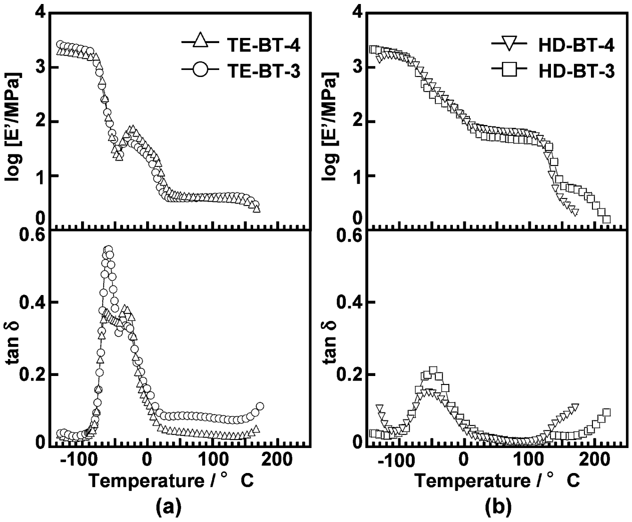

Figure 4. Temperature dependence of storage modulus (E') and loss tangent (tan δ) for the network (a) TEGDI- and (b) HDI-based PUEs with $K = 3$ and 4.

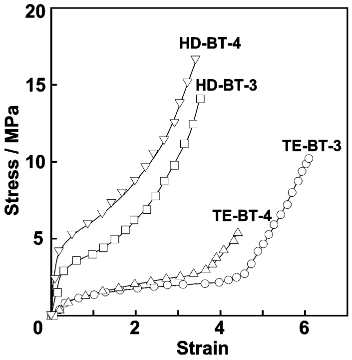

Figure 5. Stress−strain curves for the network TEGDI- and HDI-based PUEs with $K = 3$ and 4.

PUEs with $K = 3$ and 4. The initial slopes of the HD-BT-3 and HD-BT-4 exhibited a high magnitude and then the increasing slope because of elongation-induced crystallization was subsequently observed, as usually observed for general elastomers. In contrast, the initial slopes of the TE-BT-3 and TE-BT-4 were quite small and stress kept low magnitude by strain, $\epsilon = 4$. Subsequently, increasing slope was observed at higher elongation region ($\epsilon > 4$). As shown in Table 1, Young's modulus, tensile strength, and strain at break of the TE-BT-3 were 2.0 MPa, 10.2 MPa, and 6.1, respectively. Those magnitudes of the HD-BT-3 were 7.4 MPa, 14.1 MPa, and 3.3, respectively. That is, the network TEGDI-based PUEs showed quite low Young's modulus and large elongation, indicating the network TEGDI-based PUEs are highly softened ones. As far as we know, this PUE can be classified as one of the most softened PUEs.

Why do the network TEGDI-based PUEs show such interesting properties? To understand the reason, we investigated the properties of hard segment model polyurethane and the "linear" TEGDI-based PUEs (B series) because these samples seem to have more simplified structure. For the synthesis of the linear TEGDI-based PUEs, BD was only used as a curing agent in the synthetic procedure. As already shown in Figure 2, the hard segment model polyurethane of TEGDI (−(TE-BD)$_n$−) is in a crystalline state at room temperature. Also, DSC measurement revealed that the melting point of the −(TE-BD)$_n$− was around 80 °C (not shown). This melting point is quite lower than 180 °C for the −(HD-BD)$_n$−.

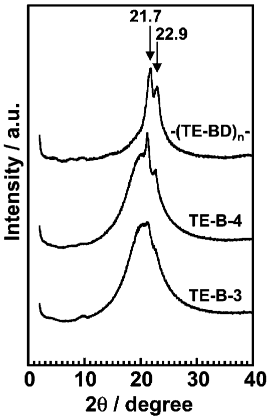

Figure 6. WAXD profiles for the linear TEGDI-based PUEs with $K = 3$ and 4 as well as the TEGDI hard segment model urethane (−(TE-BD)$_n$−). 1,4-Butanediol (BD) was used as a curing agent for the preparation of linear TEGDI-based PUEs.

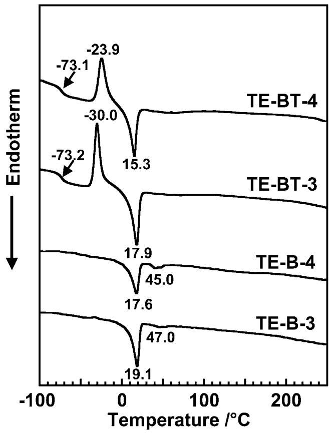

Figure 7. DSC thermograms for the linear and network TEGDI-based PUEs with $K = 3$ and 4.

Figure 6 shows WAXD profiles for the linear TEGDI-based PUEs with $K = 3$ and 4. In these cases, two crystalline peaks were observed at $2\theta = 21.7°$ and 22.9°, being different from the network TEGDI-based PUEs (Figure 2). Since these peak positions correspond well to those for the −(TE-BD)$_n$−, it is likely to consider that these two peaks are from crystallized hard segment domains in the linear TEGDI-based PUEs. The intensities of crystalline peaks for the TE-B-4 is much larger that for the TE-B-3. In the ATR−FT-IR spectra (not shown), the ratio of carbonyl peak intensities ($\nu(\mathrm{C{=}O_{H-bond}})/\nu(\mathrm{C{=}O_{free}})$) for the linear TEGDI-based PUEs were slightly larger than for the network ones. Figure 7 shows DSC curves for the linear TEGDI-based PUEs with $K = 3$ and 4. DSC curves for the network TEGDI-based PUEs were also shown for the comparison. Two endothermic peaks were only observed around 18 and 45 °C. The lower peak can be assigned to the melting of the soft segment, as observed for the network TEGDI-based PUEs. On the contrary, since the melting point of the −(TE-BD)$_n$− is 80 °C, it seems that the higher endothermic peak observed at 45 °C for the TE-B-4 and TE-B-3 is from melting of the hard segment domain. This melting of the hard segment was observed for the linear TEGDI-based PUEs, but not for the network ones. For the linear TEGDI-based PUEs, the exothermic peak, which is observed for the network TEGDI-based PUEs, was not observed. As the linear

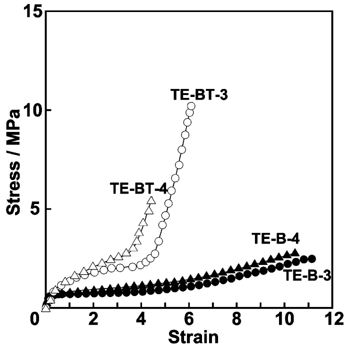

Figure 8. Stress−strain curves for the linear and network TEGDI-based PUEs with $K = 3$ and 4.

TEGDI-based PUEs have a stronger phase separation, the soft segment can be crystallized during the cooling process of DSC measurement, resulting in not showing the exothermic peak due to the rearrangement of the soft segment through DSC measurement. From WAXD, ATR-FT-IR, and DSC results, it seems reasonable to conclude that the phase separation of the linear TEGDI-based PUEs series (B series) is much stronger than for the network series (BT series). Figure 8 shows stress−strain curves for the linear and network TEGDI-based PUEs with $K = 3$ and 4. Young's modulus of the linear TEGDI-based PUEs showed similar magnitude in comparison with the network ones. Surprisingly, the linear TEGDI-based PUEs were broken without showing elongation-induced crystallization at larger strain, although the linear PUEs have a strong phase separation. As stated above, the melting temperature of the $-(\text{TE-BD})_n-$ is quite low compared with general hard segment. Thus, it is conceivable that the molecular motion of the hard segment domains in the TEGDI-based PUEs might be activated even at room temperature. Therefore, it seems reasonable to consider that weaker cohesive force originate the plastic deformation for the linear TEGDI-based PUEs.

For the network TEGDI-based PUEs, the phase separation and the cohesive force in the hard segment domains are fairly weak. It seems that these TEGDI's intriguing property originates an interesting property of the network TEGDI-based PUEs.

Conclusions

A novel diisocyanate with ether group, TEGDI, was used for the preparation of the PUEs. The network TEGDI-based PUEs showed a weaker phase separation in comparison with the network HDI ones. Also, the network TEGDI-based PUEs have a quite larger strain at break and lower Young's modulus than the network HDI-based ones. The highly softened PUEs were successfully obtained by the introduction of the TEGDI as a diisocyanate. This is attributed to the unique properties of the hard segment. Since TEGDI has quite intriguing properties, this diisocyanate is expected to other applications such as functional paints, foams, and adhesive as well as elastomers.

References and Notes

(1) Petrovic, Z. S.; Ferguson, J. *J. Prog. Polym. Sci.* **1991**, *16*, 695.

(2) Ng, H. N.; Allegrezza, A. E.; Seymour, R. W.; Cooper, S. L. *Polymer* **1972**, *14*, 255.

(3) Koberstein, J. T.; Russell, T. P. *Macromolecules* **1986**, *19*, 714.

(4) Leung, L. M.; Koberstein, J. T. *J. Polym. Sci., Polym. Phys.* **1985**, *23*, 1883.

(5) Furukawa, M.; Komiya, M.; Yokoyama, T. *Angew. Makromol. Chem.* **1996**, *240*, 205.

(6) Furukawa, M.; Shiiba, T.; Murata, S. *Polymer* **1999**, *40*, 1791.

(7) Martin, D. J.; Meijs, G. F.; Renwick, G. M.; Gunatillake, P. A.; McCarthy, S. J. *J. Appl. Polym. Sci.* **1996**, *60*, 557.

(8) Furukawa, M.; Hamada, Y.; Kojio, K. *J. Polym. Sci., Polym. Phys. Ed.* **2003**, *41*, 2355.

(9) Schellenberger, C. S.; Stewart, F. D. *Adv. Urethane Sci. Technol.* **1975**, *4*, 68. (b) Gardette, J. L.; Lemaire, J. *Polym. Degrad. Stab.* **1984**, *6*, 135. (c) Gerlock, J. L.; Mielewski, D. F. *Polym. Degrad. Stab.* **1989**, *23*, 41.

(10) Lee, H. S.; Wang, Y. K.; Hsu, S. L. *Macromolecules* **1987**, *20*, 2089.

(11) Brunette, C. M.; Hsu, S. L.; MacKnight, W. J. *Macromolecules* **1982**, *15*, 71.

MA0359988