

Synthesis and properties of thermotropic liquid crystalline polyurethane elastomers

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Abstract

High molecular weight thermoplastic polyurethane elastomers (TPEs), which consist of crystalline polycaprolactone soft segment and hexamethylene diisocyanate (HDI)/4,4'-dihydroxy biphenyl (DHBP) based mesogenic hard segment, were effectively synthesized by polyaddition reaction in dimethyl sulfoxide. These TPEs had an enantiotropic mesophase in the hard domain, when the content of hard segment was 40 wt.% or higher. Differential scanning calorimetry, polarizing microscopy, X-ray scattering analysis, dynamic mechanical test, tensile test were carried out to examine liquid crystalline, thermal, and mechanical properties and shape memory effect of these TPEs. The results were discussed and compared with those of previous articles, where low molecular weight HDI/DHBP based polyurethane or polycaprolactone diol/4,4'-diphenylmethane diisocyanate/1,4-butanediol based TPEs were examined. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Thermoplastic polyurethane elastomers (TPEs) are linear segmented copolymers whose chain is composed of a rubbery soft segment and a rigid, polar hard segment. A TPE has a characteristic microphase separated structure due to the incompatibility of the hard and soft segments, and the hard segment domains act as the tie points for the flexible soft segment. Extensive investigations have been devoted to the structure–property relationships of TPEs, because a wide range of monomeric materials are now commercially available and tailor-made properties can be obtained from well-designed combinations of monomeric materials [1,2].

It is well known that hard segment of TPE can form thermotropic liquid crystalline phase when properly selected diisocyanate and diol are used for polyaddition reaction, and that its liquid crystalline behavior is influenced by the content and the structure of soft segment. The hard segments prepared from 4,4'-dihydroxy biphenyl (DHBP)/hexamethylene diisocyanate (HDI) [3], 4,4'-bis-(6-hydroxyhexoxy)biphenyl (BHHBP)/4,4'-diphenylmethane diisocyanate (MDI) [4], 4,4'-bis-(2-hydroxyethoxy)biphenyl/toluene

diisocyanate (TDI) [5], BHHBP/TDI [6] pairs are examples of thermotropic liquid crystalline polyurethanes.

In this article, we synthesized TPEs, whose molecular weight is high enough to measure mechanical properties, and which are based on HDI, mesogenic DHBP as chain extender, and polycaprolactone (PCL) diol as crystalline soft segment. The differences in liquid crystalline properties due to high molecular weight were compared with those of previous articles about HDI/DHBP based polyurethanes [3,7,8] and the mechanical properties and shape memory effect were compared with those of our previous article about PCL/MDI/1,4-butanediol (BD) based TPEs [9], mainly at soft PCL segment-rich compositions where the hard segment can hardly form a mesophase.

2. Experimental

2.1. Materials

The PCL diol (from Daicel) with number average molecular weight of 4000 was dried under vacuum at 80°C for 12 h. Dimethyl sulfoxide (DMSO) was used after dehydration with 4 Å molecular sieve for 2 days. Hexamethylene diisocyanate (HDI), 4,4'-dihydroxy biphenyl (DHBP), and

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Table 1
Characteristics of TPEs prepared

Sample designation	Hard segment (HDI + DHBP) content (wt.%)		[η] (dl/g)
	In feed	In polymer ^a	
TPE-4	4	–	0.58
TPE-20	20	19.6	0.60
TPE-30	30	28.3	0.61
TPE-40	40	37.1	0.64
TPE-50	50	46.0	0.64
TPE-60	60	54.3	0.65
TPE-70	70	62.1	0.73
TPE-80	80	71.7	0.78
TPE-100	100	–	0.81

^a Determined by ¹H NMR analysis.

dibutyltin dilaurate (DBTDL) (all from Aldrich) were used as-received.

2.2. Synthesis of thermoplastic polyurethane elastomers

A 500 ml round-bottom, four-necked separable flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, and condenser with drying tube was used as a reactor. Segmented polyurethane elastomers were synthesized by solution polymerization in DMSO under dry N₂ by a prepolymer method. That is, PCL diol was reacted with HDI in the presence of DMSO and a catalytic amount of DBTDL for 9 h at 90°C, to prepare a prepolymer with terminal NCO group. The prepolymer was subsequently chain extended with DHBP for 20 h at 90°C. DMSO was added into the reactor occasionally when the viscosity of the reaction mixture was too high. The final polymer concentration

was about 25 wt.%. The mole ratio of HDI/(PCL + DHBP) was kept at 1.01/1.00 to yield a linear polymer. The residual isocyanate groups after polymerization were removed by the reaction with methanol (about 0.5 wt.% on solid base). Unsegmented hard segment type polyurethane was synthesized by the same method at the absence of PCL diol and the prepolymerization step.

Intrinsic viscosity [η] and hard segment contents of TPEs are shown in Table 1, where TPE-4 is a polymer obtained by the reaction of PCL diol only with HDI, and TPE-100 is unsegmented hard segment type polyurethane containing no PCL segment.

2.3. Characterization

The viscosity of TPE solution (0.2 g/dl) in DMSO was measured with a Ubbelohde viscometer at 60°C. Intrinsic viscosity was calculated by the equation of Solomon and Ciuta using the measured viscosity value [10].

¹H NMR spectra were obtained in DMSO-*d*₆ on a Varian Gemini-2000.

Differential scanning calorimetry (d.s.c) was carried out with a TA Instruments DSC-2100 at a heating or cooling rate of 10°C/min. All runs were carried out with a sample of ca. 5 mg.

The morphology of TPEs was observed with a Nikon Optiphot-I polarizing microscope fitted with a Linkham TMH 600 type heating stage at a heating or cooling rate of 10°C/min. Thin films of TPEs obtained by melting between slides were investigated.

X-ray scattering curves were obtained with a Rigaku Model D/Max-2400, using Ni-filtered CuK α radiation.

Films for the measurement of mechanical properties were prepared by the casting of TPE solution in DMSO on a glass plate. After the evaporation of DMSO at 120°C for 24 h, films were further dried at 80°C under 2–4 mmHg for the next 4 days.

Tensile tests were done using a tensile tester (Tinius Olsen Series 1000), attached with a constant temperature heating chamber. Microtensile specimen for test has the dimensions of 30 mm length, 5 mm width, and 0.5 mm thickness.

Dynamic mechanical properties were determined with a dynamic mechanical thermal analyzer (Rheometric Scientific DMTA MK-III), using a bending mode at a heating rate of 3°C/min and 11 Hz. The samples were compression molded at 120°C.

3. Results and discussion

3.1. Liquid crystalline and thermal properties of unsegmented polyurethane

The DSC thermograms of unsegmented hard segment type polyurethane, TPE-100, obtained on heating and subsequent cooling scans are shown in Fig. 1. The thermogram

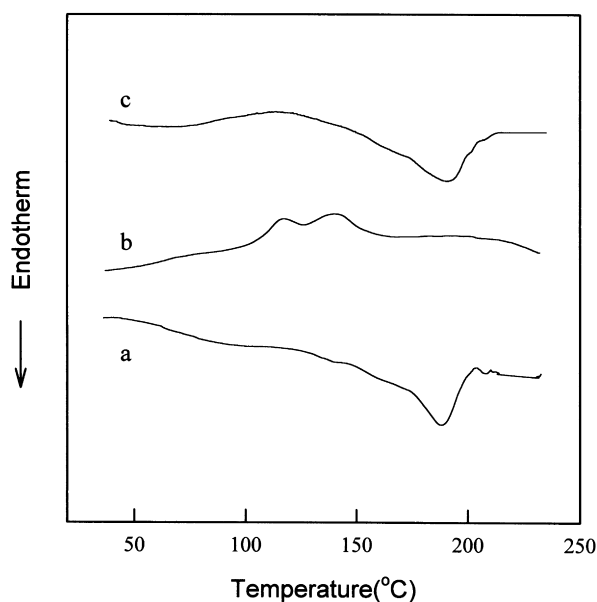


Fig. 1. DSC thermograms of TPE-100 obtained on: (a) first heating; (b) subsequent cooling; and (c) second heating scan.

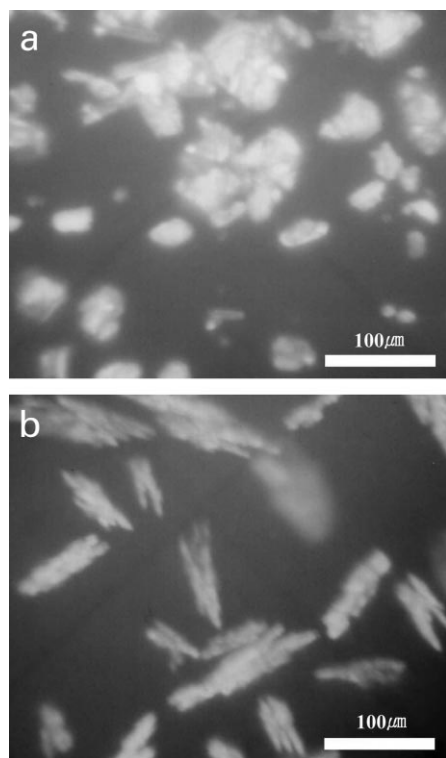


Fig. 2. Liquid crystalline morphologies of TPE-100 observed by polarizing microscope: (a) at 180°C on heating; and (b) at 132°C on cooling (bar represents 100 μm marker).

on heating scan shows a broad endotherm whose peak lies at 189°C. This result is somewhat different from those of previous articles on the same HDI-DHBP based liquid crystalline polyurethanes, where discrete double endothermic behavior were reported and the lower and higher temperature peaks were ascribed to crystal-smectic mesophase (T_m) and mesophase–isotropic transition (T_i), respectively. However, the morphology observed by polarizing microscope showed a texture due to birefringence (Fig. 2(a)) after crystal melting at 170°C and this texture disappeared on further heating above 192°C (Table 2). This result suggests that the broad endothermic peak of Fig. 1 includes

two closely located T_m and T_i . Because the polyurethanes with higher molecular weight exhibit a narrower temperature range of the mesophase [11], and the intrinsic viscosity of TPE-100, 0.81 dl/g (Table 1) suggests high molecular weight [12–14], this much narrowed mesophase temperature range compared with those of previous articles [7,8], where the molecular weight of synthesized liquid crystalline polymer were less than 10 000, seems to be due to higher molecular weight. The higher solubility of HDI-DHBP based liquid crystalline polyurethane in DMSO during polyaddition reaction compared with that in dimethylformamide [8] or in methyl ethyl ketone [7] might be a cause of higher molecular weight.

The DSC thermogram obtained on cooling of TPE-100 (Fig. 1(b)) has two exothermic peaks. The examination of morphology by a polarizing microscope revealed that the higher temperature peak is that of isotropic-mesophase transition (T_{ci}) and the lower temperature peak is that of mesophase-crystal transition (T_{cm}). The transition temperatures and the mesophase morphology of TPE-100 observed by the polarizing microscope on cooling are given in Table 2 and Fig. 2(b), respectively. The second heating scan (Fig. 1(c)) also showed a similar thermogram as in first heating scan. However Haridas et al. [8] reported somewhat different results on the same liquid crystalline polyurethane that only one crystallization peak was observed between T_m and T_i on cooling, and no T_m was observed on the second heating. These differences seems to be caused by the thermosetting reaction due to the thermal instability of low molecular weight liquid crystalline polyurethane synthesized by Haridas et al.

Fig. 3 represents the wide-angle X-ray scattering patterns of TPE-100. The film slowly cooled from the isotropic state exhibits sharp peaks at $2\theta = 12$ – 13 and 20 – 25° ranges (Fig. 3(a)) [3]. However, when the film was quenched from the mesophase (Fig. 3(b)), these peaks were broadened and weakened, and a sharp and small peak at 3° was clearly observed. These results suggest that the former peaks are those of the crystalline phase. The peak at 3° suggests the possibility that the mesophase has a smectic texture [8,15].

Table 2
Thermal properties of TPEs

Sample	T_{ms}^a (°C)	ΔH_{ms}^a (J/g-soft segment)	T_m^b (°C)	T_i^b (°C)	ΔH_h^a (J/g-hard segment)	T_{cm}^b (°C)	T_{ci}^b (°C)	ΔH_c^a (J/g-hard segment)
TPE-4	59	78	–	–	–	–	–	–
TPE-20	57	71	–	–	24	–	–	–
TPE-30	50	69	–	–	32	–	–	20
TPE-40	47	67	163	178	45	110	125	29
TPE-50	45	45	160	180	47	113	127	33
TPE-60	42	36	163	185	70	112	131	42
TPE-70	41	22	167	188	76	113	135	55
TPE-80	38	11	168	187	77	120	140	53
TPE-100	–	–	170	192	71	126	143	58

^a Measured by DSC

^b Observed by polarizing microscope.

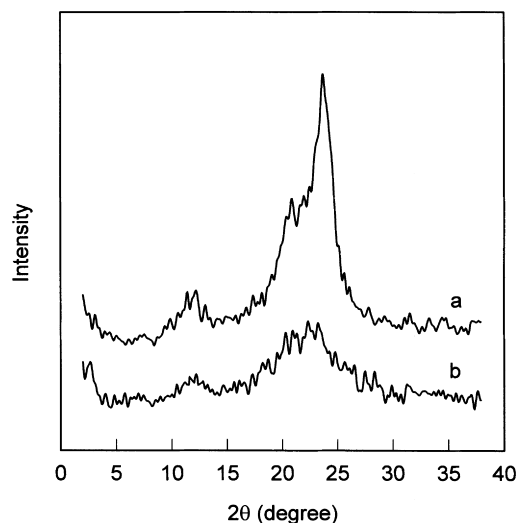


Fig. 3. Wide-angle X-ray diffraction patterns of TPE-100 film: (a) cooled slowly from isotropic state; and (b) quenched from mesophase.

3.2. Liquid crystalline and thermal properties of segmented polyurethanes

In Fig. 4, the DSC thermograms of TPEs containing crystalline PCL soft segment are shown. The thermograms from heating scan show the melting endothermic peak of PCL soft segment (T_{ms}) at the temperature from -30 to 60°C . As can be seen in Fig. 4, the T_m/T_i and T_{cm}/T_{ci} behaviors of

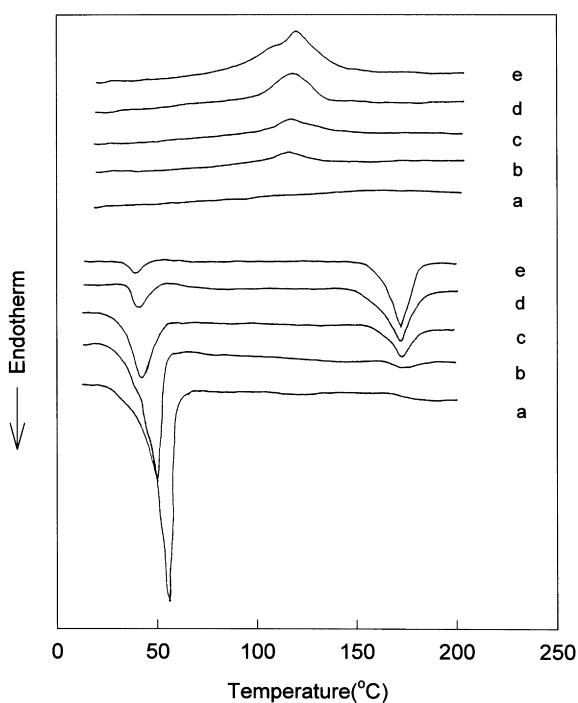


Fig. 4. DSC thermograms of TPEs obtained on heating (lower thermograms with endothermic peaks) and subsequent cooling (upper thermograms with exothermic peaks) scan: (a) TPE-4; (b) TPE-30; (c) TPE-50; (d) TPE-70, and (e) TPE-80

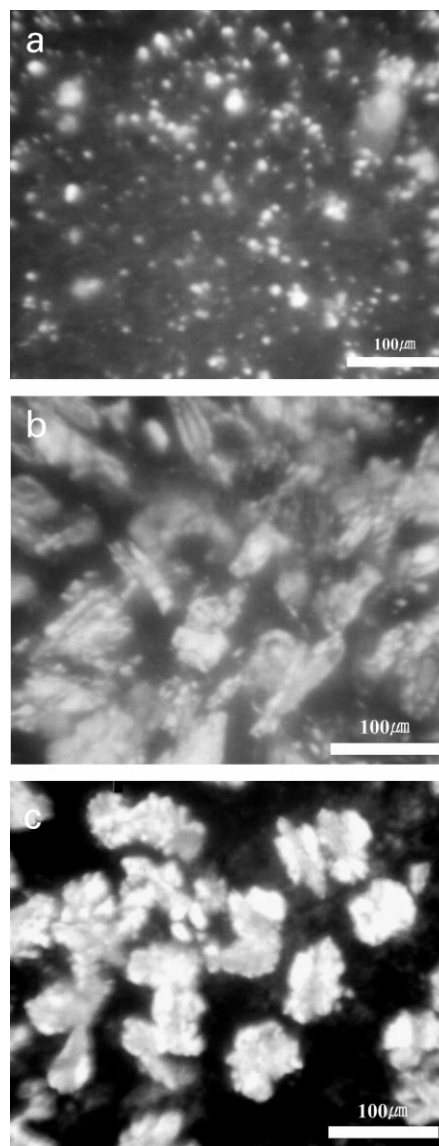


Fig. 5. Liquid crystalline morphologies of: (a) TPE-40 (172°C); (b) TPE-60 (175°C); and (c) TPE-80 (175°C) observed by polarizing microscope on heating (bar represents $100\ \mu\text{m}$ marker).

the TPEs are more obscure than Fig. 1 of unsegmented polyurethane.

We could observe the texture due to birefringence after crystal melting by the polarizing microscope when the liquid crystalline hard segment content was 40 wt.% or higher. The texture observed on heating and transition temperatures observed by the polarizing microscope are given in Fig. 5 and Table 2, respectively.

The T_{ms} and the heat of fusion at T_{ms} (ΔH_{ms}) shown in Table 2 generally decrease as the content of liquid crystalline hard segment is increased. This might be due to the hindered crystallization and reduced crystal perfectness and reduced crystal size of PCL segment by the restricted chain mobility in the presence of rigid hard segment.

In Table 2, T_m , T_i , T_{cm} , T_{ci} , the total endothermic heat of

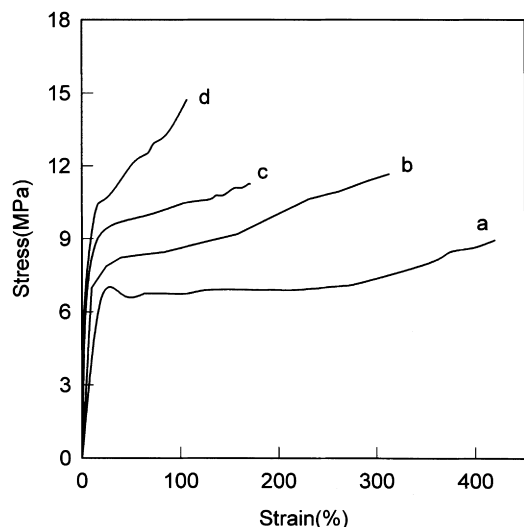


Fig. 6. Stress–strain curves of: (a) TPE-20; (b) TPE-30; (c) TPE-40; and (d) TPE-50 obtained at room temperature.

transitions at T_m and T_i (ΔH_h), and the total exothermic heat of transitions at T_{cm} and T_{ci} (ΔH_c) generally decrease as the content of PCL soft segment is increased. As the content of soft segment is increased, the average length of hard segment is decreased [16], and this seems to cause the decrease in transition temperatures [4,6,17]. However, the changes in mesophase temperature ranges, T_i-T_m or $T_{ci}-T_{cm}$, were not so evident. Reduced ΔH_h and ΔH_c support the diminishing of liquid crystallinity and crystallinity of hard segment as the content of PCL soft segment is increased.

3.3. Mechanical properties

The stress–strain properties of TPEs at PCL segment-rich compositions where the hard segment can hardly form a mesophase are shown in Fig. 6 and Table 3. As the content of rigid hard segment is increased, we can observe that the modulus and yield strength generally increase and the elongation at break decrease. Compared with PCL/MDI/BD based TPE in our previous article (Run No. 4-50) [9], whose content and molecular weight of PCL segment is same with TPE-50 and its tensile modulus and elongation at break were 52 MPa and 610%, TPE-50 has about 5-fold value of tensile modulus and much reduced value of elongation at break. Much enhanced rigidity of hard segment seems to be the cause of these differences [12,18] In our

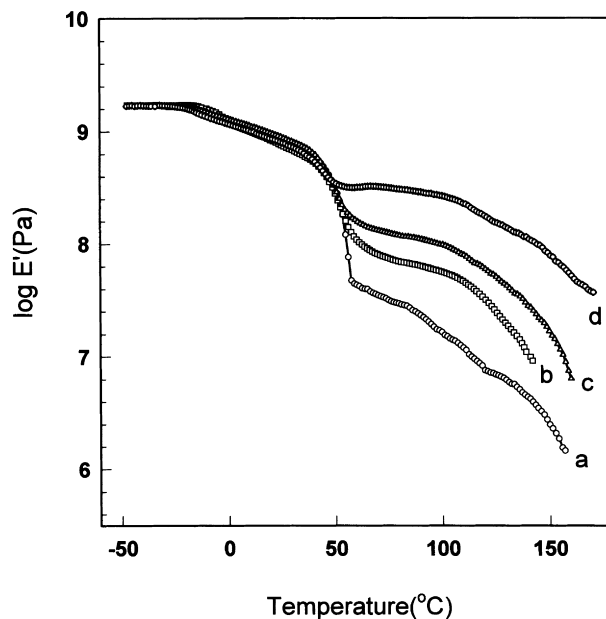


Fig. 7. Tensile storage modulus of: (a) TPE-20; (b) TPE-30; (c) TPE-40; and (d) TPE-50.

previous article [9], the tensile modulus of PCL/MDI/BD based TPE was increased as the content of PCL soft segment was increased due to the predominant contribution of PCL crystallinity on the tensile modulus. However, in this PCL/HDI/DHBP based TPEs, the tensile modulus increased as the content of hard segment is increased. This shows that the contribution of hard segment on tensile modulus is much more dominant than that of PCL crystallinity.

The changes of tensile storage modulus, E' in TPEs on heating are shown in Fig. 7. Gradual decrease of E' at the temperature range between glass transition temperature (T_{gs}) of PCL segment (-21 – -10°C) and T_{ms} , and a sudden drop at T_{ms} can be observed. The T_{gs} s of this PCL/HDI/DHBP based TPEs are higher than those of PCL/MDI/BD based TPEs whose T_{gs} s are near -50°C [9]. This shows the enhanced dissolution of the mesogenic hard segment into the soft segment domain [19]. Compared with PCL/MDI/BD based TPE in our previous article (Run No. 4-70) [9], whose content and molecular weight of PCL segment is same with TPE-30, the modulus below T_{ms} and rubbery plateau modulus of TPE-30 is about three and six times higher. This shows that HDI-DHBP based hard segment does its role as a physical crosslinking site or reinforcing filler more effectively.

Table 3
Mechanical properties of TPEs

Sample	Tensile modulus (MPa)	Yield strength (MPa)	Tensile strength (MPa)	Elongation at break (%)
TPE-20	34	7.1	9.0	420
TPE-30	71	8.2	11.7	310
TPE-40	184	9.1	11.3	170
TPE-50	283	10.5	14.6	110

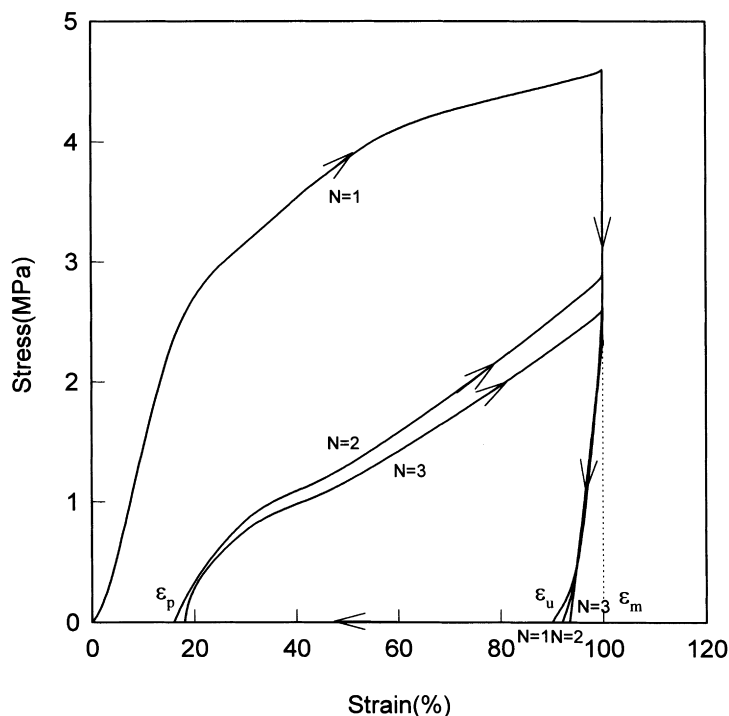


Fig. 8. Cyclic tensile behavior of TPE-20.

Shape memory polymers consist of two phases, frozen phase or fixed points and reversible phase [20]. In crystalline PCL soft segment based TPEs, the crystalline soft segment form a reversible phase, with T_{ms} being the shape recovery temperature, and hard domains become frozen phase or fixed point [9]. That is, when a cast or molded specimen is heated above T_{ms} but below the melting temperature of hard segment, it changes from a rigid crystalline state to a rubbery state at which it is highly flexible, allowing it to be deformed to a new shape that can be frozen in by cooling below T_{ms} . If the deformed part is subsequently heated above the T_{ms} , the specimen will remember its original shape and spontaneously return to that shape.

The result of cyclic tensile test to examine the shape memory effect of TPE-20 is shown in Fig. 8 [9]. Sample was elongated at 65°C to 100% strain (ϵ_m) at a constant elongation rate of 10 mm/min. While maintaining the strain at ϵ_m , sample was cooled to 25°C and unloaded. Upon removing the constraint at 25°C small recovery of strain to ϵ_u occurs. The sample was subsequently heated to 65°C in 5 min, and stayed at that temperature for the next 10 min, allowing recovery of strain. This completes one thermomechanical cycle ($N = 1$) leaving a residual strain, ϵ_p , where the next cycle ($N = 2$) starts. Compared with PCL/MDI/BD based TPE, the stress for elongation at 65°C is much higher, as anticipated from the result of E' (Fig. 7). However, ϵ_u or ϵ_p values were not so much different from those of PCL/MDI/BD based TPE [9].

4. Conclusions

1. High molecular weight TPEs based on PCL diol whose molecular weight is 4000, HDI, and DHPB had an enantiotropic mesophase in the hard domain, when the content of hard segment was 40 wt.% or higher
2. The tensile storage moduli of these TPEs, both at the crystalline state below the melting temperature of PCL segment and at the rubbery state above the melting temperature of PCL segment, were much higher than those of PCL/MDI/BD based TPEs
3. Shape memory effect of this TPE, using crystalline PCL domain as reversible phase and hard segment as frozen phase, was similar to that of PCL/MDI/BD based TPE.

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