Shape memory polyurethane containing mesogenic moiety

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The mechanical and thermal properties, in particular the shape memory effect, of TPUs synthesized from diol-terminated poly(caprolactone) (PCL diol), 4,4′-diphenylmethane diisocyanate (MDI), and mesogenic chain extenders, 4,4′-bis-(2-hydroxyethoxy)biphenyl (BEBP) or 4,4′-bis-(6-hydroxyhexoxy)biphenyl (BHBP) were examined and compared with results for PCL diol/MDI/1,4-butanediol (BD) based TPUs in a previous study. Some results related to the rigid structure of BEBP or BHBP were observed in the thermomechanical properties. Shape fixity was related to the crystallization of the PCL phase. © *2000 Kluwer Academic Publishers*

1. Introduction

Shape memory polymers basically consist of two phases, a frozen phase and a reversible phase. Mitsubishi Heavy Industries, Ltd. has commercialized some kinds of shape memory polyurethanes, where the amorphous and crystalline phases were designed to be the reversible phase and the frozen phase respectively [1, 2]. They were designed to have a large change in elastic modulus above and below the glass transition temperature (T_g) of the amorphous phase. Micro-Brownian movement of a polymer chain can be performed at temperatures above T_g. However, rubber elasticity will be indicated at the temperature range between T_g and the melting temperature (T_m) of the crystalline phase because of the restricted molecular motion due to the frozen or crystalline phase. When they are deformed within the temperature range between T_g and T_m, and subsequently cooled below T_g, under constant strain, the deformed shape is fixed because the micro-Brownian movement will be frozen. If they are reheated to the temperature range between T_g and T_m, the original shape is recovered again. The driving force of shape recovery is the elastic force generated during the deformation. These polyurethanes are thermoplastic because they can flow above T_m.

In the segmented thermoplastic polyurethanes (TPUs), the T_m of the soft segment can also be used as the shape recovery temperature (T_s) instead of T_g, because the TPU can be designed to have a large change in elastic modulus above and below T_m of the soft segment, and the crystalline hard segment can perform the role as the fixed phase. In our previous article [3], we examined the shape memory effect of TPUs from diol-terminated poly(caprolactone) (PCL diol), 1,4-butanediol (BD), and 4,4′-diphenylmethane diisocyanate (MDI), where the T_m of the soft PCL segment was designed as a T_s and the hard segment from BD and MDI was designed as a frozen phase.

It has been reported that TPUs with mesogenic moiety in the hard segment have a higher value of modulus compared with TPUs from conventional nonmesogenic chain extenders [4, 5], even at low content of hard segment where the liquid crystallinity of the hard segment cannot be manifested [6]. The shape memory effect of PCL diol/MDI/BD based TPUs were manifested at reversible phase (PCL phase) rich composition [3]. In the present study, we used mesogenic 4,4′-bis-(2-hydroxyethoxy)biphenyl (BEBP) or 4,4′-bis-(6-hydroxyhexoxy)biphenyl (BHBP) as chain extenders, and the mechanical and thermal properties, including the shape memory effect for these PCL diol/MDI/BEBP or PCL diol/MDI/BHBP based TPUs at PCL phase rich compositions were examined and compared with those reported on PCL diol/MDI/BD based TPUs [3].

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. Dimethylacetamide (DMAc) was used after dehydration with a 0.4 nm molecular sieve for 2 days. MDI (from Tokyo Kasei, Japan) was melted at 45 °C and MDI dimer or impurities precipitated in the melt were removed before use. BEBP or BHBP were

synthesized by the reaction of 4,4′-dihydroxy biphenyl (from Tokyo Kasei, Japan) with 2-chloroethanol (from Fluka) or 6-chlorohexanol (from Fluka) [7].

2.2. Synthesis of TPUs

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. TPUs were synthesized by solution polymerization in DMAc under dry N_2 by a prepolymer method. That is, PCL diol was reacted with MDI in the presence of DMAc for 2 h at 80 °C, to prepare a prepolymer with terminal NCO group. The prepolymer was subsequently chain extended with BEBP or BHBP for 3 h at 80 °C. DMAc 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 MDI/(PCL diol + BEBP or BHBP) was kept at 1.01/1.00 to yield a linear polymer.

The intrinsic viscosity, $[\eta]$ and the hard segment contents of TPUs are shown in Table I, where the TPU2 series were synthesized with BEBP and PTU6 series with BHBP.

2.3. Characterization

The viscosity of TPU solution (2 kg/m^3) in dimethyl sulfoxide was measured with Cannon-Fenske Routine Viscometer at 30 °C. The intrinsic viscosity was calculated by the equation of Solomon and Ciuta using the measured viscosity value [8].

^{1}H n.m.r. spectra were obtained in DMF-d$_6$ on a Varian Gemini-2000.

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 2 Hz.

Films for the measurement of tensile properties were prepared by the casting of TPU solution in DMAc on a glass plate. After the evaporation of DMAc at 120 °C for 24 h, films were further dried at 25 °C under vacuum for the next 4 days. Tensile tests were done using a tensile tester (Tinius Olsen Series 1000), attaching a constant temperature heating chamber. The microten-

sile test specimens had the dimensions of 30 mm length, 5 mm width, and 0.5 mm thickness.

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

3. Results and discussion

The changes of tensile storage modulus, E' in TPUs on heating are shown in Fig. 1. Gradual decrease of E' in the temperature range between the glass transition temperature of PCL phase (T_{gs}, −30 to −10 °C) and the melting temperature of PCL phase (T_{ms}), and a sudden drop of E' at T_{ms} can be observed. The minute drop of E' at T_{gs} (−20 °C) of TPU 620 is more evident and located at a somewhat higher temperature than that of TPU 220. The higher T_{gs} suggests the enhanced dissolution of hard segment into the soft segment phase [9, 10] and the reduced crystallinity of the PCL phase by this enhanced phase mixing seems to be the cause of the relatively larger E' drop at T_{gs}.

In Table II, we can see that the T_{ms} values of the TPU2 series are higher than those of the TPU6 series

TABLE I Characteristics of TPUs prepared

Sample designation	Hard segment content (MDI+BEBP (or BHBP)) (wt %)		MDI+BEBP (or BHBP)/ PCL diol (mole ratio in feed)	$[\eta]$ (m^3/kg)
	In feed	In polymer[a]		
TPU2 series				
TPU 220	20.0	20.1	3.66	7.2
TPU 230	30.0	28.6	6.30	7.6
TPU 240	40.0	42.8	9.94	6.3
TPU6 series				
TPU 620	20.0	21.3	3.26	8.9
TPU 630	30.0	30.2	5.50	8.1
TPU 640	40.0	41.3	8.36	7.8

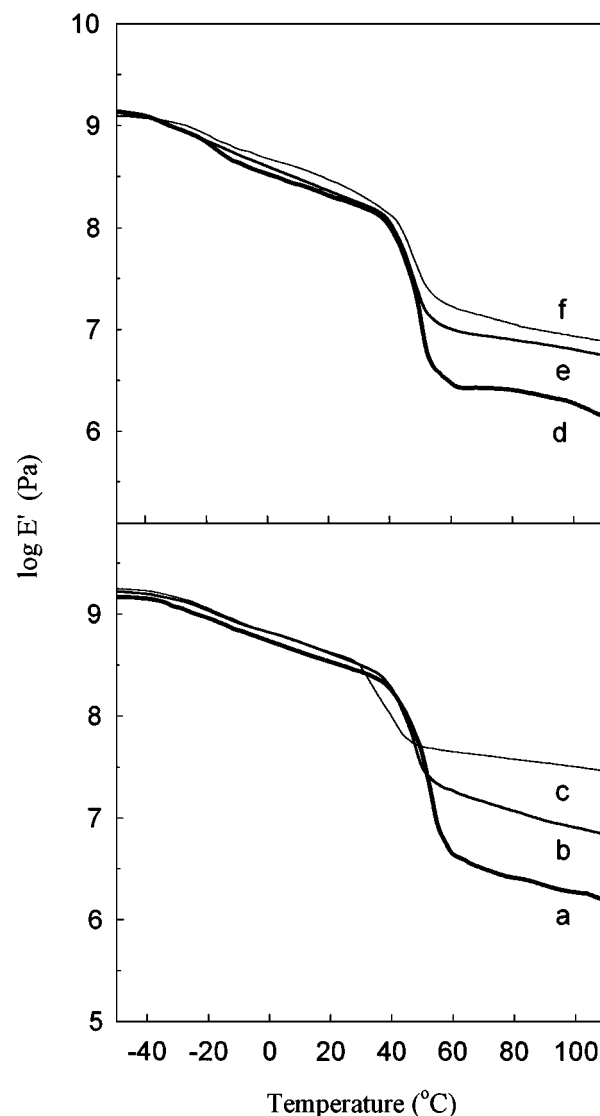[a]Determined by ^{1}H n.m.r. analysis.

Figure 1 Tensile storage modulus of (a) TPU 220, (b) TPU 230, (c) TPU 240, (d) TPU 620, (e) TPU 630, and (f) TPU 640.

TABLE II Thermal properties of TPUs

		TPU 220	TPU 230	TPU 240	TPU 620	TPU 630	TPU 640
Original specimens	T_{ms}	49.8	46.6	39.9	46.7	41.9	41.3
	ΔH_{ms}	63.0	62.0	44.9	59.6	50.7	51.7
	T_{mh}	255.3	264.5	268.1	—	163.1	181.4
	ΔH_{mh}	9.6	26.9	79.1	—	23.6	44.0
	T_{mc}	3.9	0.1	−9.8	1.5	−2.2	1.7
Cooled after 100% elongation	T_{ms}	47.9	44.5	40.4	46.2	42.9	43.2
	ΔH_{ms}	59.3	54.9	30.6	51.7	46.5	48.6
	T_{mh}	254.1	262.8	268.8	—	159.4	177.8
	ΔH_{mh}	18.0	32.7	86.3	—	22.5	40.3
Cooled after 300% elongation	T_{ms}	—	—	39.2	45.3	38.0	42.7
	ΔH_{ms}	—	—	43.7	56.0	53.0	52.0
	T_{mh}	—	—	269.5	—	158.0	181.6
	ΔH_{mh}	—	—	81.2	—	24.9	37.4
Recovered after 300% elongation	T_{ms}	—	—	35.5	46.2	43.0	43.5
	ΔH_{ms}	—	—	22.8	54.2	43.7	42.8
	T_{mh}	—	—	269.0	—	157.5	180.8
	ΔH_{mh}	—	—	94.5	—	26.2	39.2

T_{ms} (°C): melting temperature of soft segment.
T_{mh} (°C): melting temperature of hard segment.
T_{mc} (°C): crystallization temperature of soft segment.
ΔH_{ms} (J/g$_{soft\ segment}$): melting enthalpy of soft segment.
ΔH_{mh} (J/g$_{hard\ segment}$): melting enthalpy of hard segment.

when the content of hard segment is 20 or 30 wt %. This also supports the view that the dissolution of the hard segment into the PCL phase is greater in the TPU6 series, because the melting temperature generally decreases as the concentration of the crystallizable component in the melt is reduced by molecular mixing [11]. The lower ΔH_{ms} of the TPU6 series compared with the TPU2 series (Table II), when the hard segment content is 20 or 30 wt %, can also be explained by this enhanced phase mixing. However, when the hard segment content is 40 wt %, the TPU 640 has higher T_{ms} and ΔH_{ms} than those of TPU 240. This seems to be due to kinetic factors rather than phase mixing or thermodynamic factors. That is, because BEBP based hard segment is more rigid than BHBP based hard segment, and the MDI+BEBP/PCL diol mole ratio is higher than the MDI+BHBP/PCL diol mole ratio at the same weight content of hard segment (see Table I), the crystallization of the PCL segment in TPU 240 seems to be more severly hindered at high content of hard segment. The relatively lower crystallization temperature (T_{mc}) of soft segment on cooling from the melt and the larger supercooling for crystallization ($T_{ms} - T_{mc}$) of TPU 240 compared with TPU640 also support this explanation [12].

The T_{gs}s of BEBP or BHBP based TPUs in the present study are generally higher than those of BD based TPUs in our previous report [3] whose T_{gs}s were near −50 °C. This suggests the higher dissolution of hard segment into the PCL phase in BEBP or BHBP based TPUs.

In our previous report of PCL diol/MDI/BD based TPUs [3], E' at 20 °C increased from 100 to 200 MPa as the content of PCL soft segment in TPU was increased from 60 to 80 wt %. Whereas in our PCL diol/MDI/BHBP based TPUs (Fig. 1), E' at 20 °C decreased from 300 to 200 MPa as the content of PCL soft segment was increased from 60 to 80 wt %.
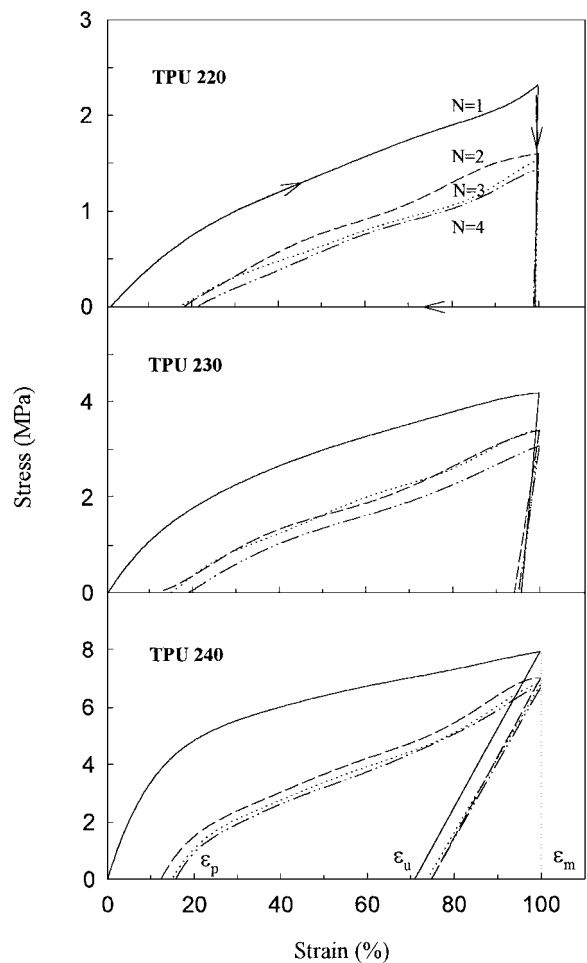

Figure 2 Cyclic tensile behaviour of TPU2 series with 100% maximum strain.

The PCL diol/MDI/BEBP based TPUs have E' values near 400 MPa at 20 °C (Fig. 1). It also slightly decreased as the content of PCL soft segment in PCL diol/MDI/BEBP based TPUs was increased. The

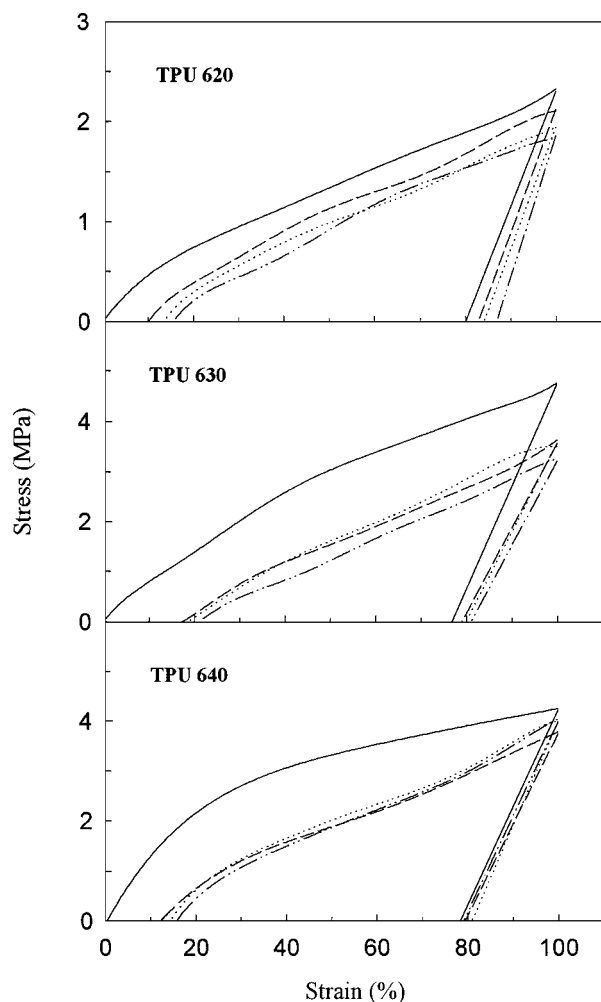*Figure 3* Cyclic tensile behaviour of TPU6 series with 100% maximum strain.

Figure 4 Cyclic tensile behaviour of TPU6 series with 300% maximum strain.

predominant contribution of PCL crystallinity in PCL diol/MDI/BD based TPUs on E' seems to be the cause of the increase of E' as the content of the PCL soft segment was increased. In the BEBP or BHBP based TPUs, the decrease of E' with PCL soft segment content, shows the predominant contribution of the rigid hard segment on E' compared to that of PCL crystallinity.

E' values at 100 °C, of these PCL diol/MDI/BHBP based or PCL diol/MDI /BEBP based TPUs, are similar to those of PCL diol/MDI/BD based TPUs, except for TPU240 [3]. They increase in the range of 1–10 MPa as the hard segment content is increased from 20 to 40 wt %. However TPU 240 has an exceptionally high value of E', about 30 MPa. These results show that enhanced E' at the rubbery plateau can be achieved evidently only by some more rigid structure and at a higher hard segment content.

The results of cyclic tests to examine the shape memory effect of TPUs are shown in Figs 2–4. Samples were elongated at 65 °C to 100 or 300% maximum strain (ε_m) at a constant elongation rate of 10 mm/min. While maintaining the strain at ε_m, the sample was cooled to 25 °C and unloaded. Upon removing the constraint at 25 °C a small recovery of strain to ε_u occurred. The sample was subsequently heated to 65 °C in 5 min, and held at that temperature for the next 10 min, al-
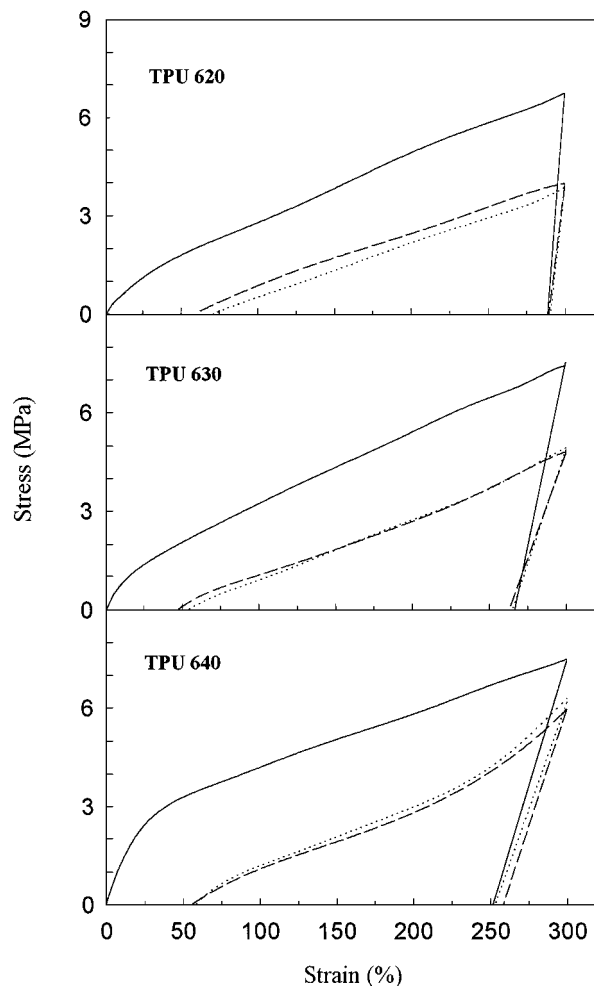
lowing recovery of strain. This completes one thermomechanical cycle ($N = 1$) leaving a residual strain, ε_p, where the next cycle ($N = 2$) starts. Compared with PCL diol/MDI/BD based TPUs [3], the stress for elongation at 65 °C is somewhat higher in Figs 2–4, when the molecular weight and the content of PCL soft segment is the same. For example, TPU 230 has the value of stress at 100% strain around 3 MPa (Fig. 2), whereas the corresponding values of PCL diol/MDI/BD based TPU were around 2 MPa. This may be due to the more rigid structure of BEBP or BHBP compared with BD. This result suggests that the recovery stress at 65 °C can be enhanced by the more rigid structure of the hard segment. However ε_p values are similar to those of PCL diol/MDI/BD based TPUs. In Figs 2 and 3, and Table II, we can see that the shape fixity, $\varepsilon_u/\varepsilon_m$ is related to the ΔH_{ms} value of the specimen cooled in the elongated state. That is, as the ΔH_{ms} of the specimen cooled in the elongated state is increased, shape fixity increases up to near 1. The shape fixity of the TPU6 series with 300% maximum strain (Fig. 3) is better than with 100% maximum strain (Fig. 4). The higher value of ΔH_{ms} in the elongated state with higher strain (Table II) seems to be due to strain induced crystallization [13]. The ΔH_{ms} values of specimens recovered after 300% elongation are smaller than those of the original specimens (Table II). The reduced crystallinity, indicated by this decreased ΔH_{ms}, seems to be a cause of generally

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reduced 2nd cycle initial modulus compared with 1st cycle.

4. Conclusions

When compared with PCL diol/MDI/BD based TPUs, PCL diol/MDI/BEBP or PCL diol/MDI/ BHBP based TPUs;

1. showed enhanced dissolution of the hard segment into PCL phase

2. had somewhat higher E' at 20 °C

3. had similar rubbery plateau E' values, except for a PCL diol/MDI/BEBP based TPU with 40 wt % hard segment which showed higher E' value

4. had higher values of stress at the same strain at 65 °C, suggesting higher recovery stress

5. had similar values of ε_p at soft PCL segment rich compositions.

The shape fixity was related to the crystallinity of the PCL phase of specimens cooled in the elongated state.

References

1. S. HAYASHI, *Int. Prog. Urethanes* **6** (1993) 90.
2. H. TOBUSHI, S. HAYASHI and S. KOJIMA, *JSME Intern. J.* **35** (1992) 296.
3. B. K. KIM, S. Y. LEE and M. XU, *Polymer* **37** (1996) 5781.
4. K. MAEJIMA and A. NIKI, *Kobunshi* **41** (1992) 582.
5. Y. ONOUCHI, S. INAGAKI, H. OKAMOTO and J. FURUKAWA, *Cell. Poly.* **15** (1996) 30.
6. S. MORIYUKI, *Polymer Digest (Japan)* **44** (1992) 52.
7. P. PENCZEK, B. SZCZEPANIAK, K. C. FRISCH and A. WOLINSKA-GRABCZYK, *Adv. Urethane Sci Technol.* **13** (1996) 167.
8. G. ALLEN and J. C. BEVINGTON (eds), "Comprehensive Polymer Science" (Pergamon Press, Oxford, 1989) Vol. 1, p. 185.
9. J. W. C. VAN BOGART, P. E. GIBSON and S. L. COOPER, *J. Polym. Sci., Polym. Phys.* **21** (1983) 65.
10. T. O. AHN, S. U. JUNG, H. M. JEONG and S. W. LEE, *J. Appl. Polym. Sci.* **51** (1994) 43.
11. T. NISHI and T. T. WANG, *Macromolecules* **8** (1975) 909.
12. T. O. AHN, S. Y. LEE, S. W. LEE and H. M. JEONG, *Polymer (Korea)* **14** (1990) 497.
13. C. B. WANG and S. L. COOPER, *Macromolecules* **16** (1983) 775.