

Study on the Shape Memory Polyamides. Synthesis and Thermomechanical Properties of Polycaprolactone– Polyamide Block Copolymer

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ABSTRACT: Poly(caprolactone)(PCL)–polyamide multiblock copolymers were synthesized by the linear chain extension of PCL diol and diamine-terminated polyamide oligomer with hexamethylene diisocyanate in dimethylformamide. The thermal and mechanical properties of these block copolymers were examined and compared with the results in our previous papers about thermoplastic polyurethane elastomers (TPEs). PCL–polyamide block copolymers showed enhanced microphase separation and lower degree of fatigue by repeated deformation in shape memory behavior, and had higher rubbery plateau modulus, compared with TPEs.

KEY WORDS Polyamide / Polycaprolactone / Multiblock Copolymer / Thermal Properties / Mechanical Properties / Shape Memory /

Thermal-responsive shape memory polymers basically consist of the fixed structure for memorizing original shape and the thermally reversible phase for maintaining transient shape.^{1,2} Crystal, glassy state, entanglement, or crosslinking can be used as a fixed structure. Thermally reversible phase is generally designed to have a large drop in elastic modulus above shape recovery temperature (T_s), *i.e.*, glass transition temperature (T_g) or melting temperature (T_m).^{3–5}

In our previous papers,^{6,7} we reported the shape memory behaviors of thermoplastic polyurethane elastomers (TPEs) from crystalline polycaprolactone (PCL) soft segment and 4,4'-methylenediphenyl diisocyanate (MDI)/1,4-butanediol (BD) based hard segment. Rubber elasticity was indicated at the temperature range between the melting temperature of soft segment (T_{ms}) and hard segment (T_{mh}) because of the free molecular motion of soft segment and fixed structure of crystalline hard segment. When they were deformed at the temperature range between T_{ms} and T_{mh} , and subsequently cooled below T_{ms} under constant strain, the deformed shape is fixed because the molecular motion of PCL segment is restricted when crystallized below T_{ms} . If they were reheated to the temperature range between T_{ms} and T_{mh} , 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_{mh} .

For TPEs, the crystallization of soft and hard segments and the role of hard segment as physical crosslink or fixed phase are enhanced when the soft–hard phase mixing is reduced.^{8,9} And lower residual strain after shape recovery was observed in our previous study on the shape memory behaviors when the soft–hard phase mixing was reduced or rubbery plateau modulus was enhanced.⁷

We observed the segmental interaction between polyester or polyether soft segment and MDI/BD based hard segment and the consequent phase mixing was re-

duced as hard segment was replaced by polyamide segment.^{10,11} So, in this study we synthesized PCL–polyamide multiblock copolymers, and their thermal and mechanical properties, including shape memory behavior, were observed and compared with those of TPEs.

EXPERIMENTAL

Materials

N,N-Dimethylformamide (DMF, Aldrich) was used after dehydration with 4 Å molecular sieve for more than a week. LiCl (Junsei) was dried at 150°C for 3 h before use. PCL diol having the number average molecular weight (M_n) 2000 (Aldrich) and 4000 (Daicel) were dried at 100°C under 10 mmHg for more than 3 h. Hexamethylene diisocyanate (HDI, Aldrich), adipic acid (AA, Aldrich), hexamethylene diamine (HA, Aldrich), ϵ -caprolactam (CA, Aldrich), phenol (Aldrich), *m*-cresol (Aldrich), chloroform (Aldrich), ethanol (James Burrough), dibutyltin dilaurate (Aldrich), formic acid (96%, Aldrich) were used as received.

A thermoplastic polyurethane elastomer, 4TPE73 (Run No, 4–70 in our previous paper⁶), was synthesized from PCLdiol ($M_n = 4000$), MDI, and BD. The content of PCL segment in 4TPE73 was 70 wt%, and the detailed synthetic method was described in our previous paper.⁶

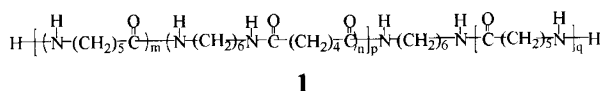
Synthesis and Characterization of Polyamide Oligomer

The diamine-terminated nylon 6/6,6 copolyamide oligomer (CPA) 1, having the M_n shown in Table I were synthesized by the melt polycondensation reaction of CA, AA, and HA.^{10,11} An excess of HA over AA was used to obtain CPA with terminal amine groups and the molecular weight was controlled by a stoichiometric imbalance of reactants, *i.e.*, by varying the AA/HA feed mole ratio at fixed CA/AA feed mole ratio (Table I). CA, AA, and HA were completely melted at 200°C for

Table I. Characteristics of polyamide oligomers

| Designation | Feed mole ratio of CA/AA/HA | M_n | | T_m °C | ΔH_m at T_m J g ⁻¹ |
|-------------|-----------------------------|-------|-----------|-------------|---|
| | | NMR | Titration | | |
| CPA1 | 2.00/1.00/2.60 | 1180 | 1320 | 177 | 81 |
| CPA2 | 2.00/1.00/1.49 | 2150 | 2500 | 168 | 53 |
| CPA3 | 2.00/1.00/1.30 | — | 3760 | 174 | 55 |
| HPA1 | 2.00/—/0.29 | — | 1340 | 181 | 111 |

45 min in the reaction vessel and reacted at 220°C for 2 h under N₂ atmosphere with stirring. The solid product was crushed mechanically after cooling to room temperature, dissolved in hot ethanol to 17% (w/w) solution, and precipitated into ten times volume of water. The precipitate was filtered and dried under vacuum at 45°C for 48 h. This purification process was repeated three times. The diamine-terminated nylon 6 homopolyamide oligomer (HPA) was similarly synthesized in the absence of AA (Table I).



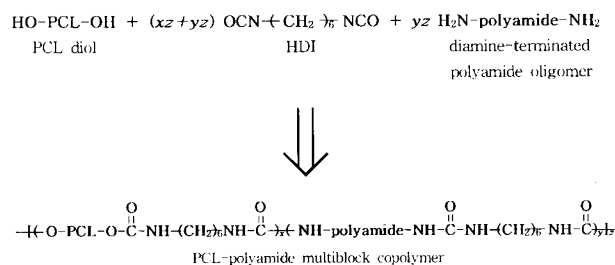
M_n of the polyamide oligomer was determined by NMR and titration measurements (Table I). In NMR method the peak intensity of methylene protons adjacent to unreacted terminal amine group at 3.5 ppm was compared with that of methylene protons adjacent to reacted amine group at 3.8 ppm. In a typical titration procedure, 0.1 g of polyamide oligomer was dissolved with 50 mL of phenol and 20 mL of chloroform, and the terminal amine group was titrated with 0.01 M HClO₄ solution in ethanol.

Synthesis of PCL–Polyamide Block Copolymer

PCL–polyamide multiblock copolymers were synthesized by the linear chain extension of PCL diol and diamine-terminated polyamide oligomer with HDI in DMF (Figure 1). That is, PCL diol was reacted with HDI at 60°C for 30 min and another 2 h at 80°C in the presence of dibutyltin dilaurate (0.03 wt% on solid base) as a catalyst. DMF was added to the reactor occasionally when the viscosity of the reaction mixture became too high. After cooling to room temperature a 20% (w/v) solution of polyamide oligomer in LiCl-DMF (10% (w/v)), being divided into three parts, was added into the reactor successively. After feeding, the reaction mixture was agitated for 30 min. Formic acid (0.1 wt% on solid base) used to inhibit gelation was added into the reactor before the feeding of polyamide oligomer.

Intrinsic viscosity, $[\eta]$ and the compositions of PCL–polyamide block copolymers are shown in Table II.

The sample designation code in Table II indicates the molecular weight and the content of PCL block, and the kind of polyamide block in PCL–polyamide block copolymer. For example, 4P1HN73 indicates that this PCL–polyamide block copolymer was synthesized with PCL diol whose M_n is 4000 and HPA1 (Table I), and the content of PCL segment is about 70 wt%.

**Figure 1.** Reaction scheme of PCL diol, diamine-terminated polyamide oligomer, and HDI to give PCL–polyamide multiblock copolymer.

Characterization

PCL–polyamide block copolymers were characterized after LiCl was removed. That is, film was made by spreading polymerized solution on a polyethylene plate and evaporating DMF in a convection oven at 80°C for 5 h. This film was further dried for 24 h in a vacuum oven at 80°C and immersed in distilled water for 3 days to remove LiCl, and dried again in a vacuum oven at 80°C for 12 h. This film was redissolved in *m*-cresol to give 10% (w/w) solution and final cast film was obtained on a polyethylene plate by evaporating *m*-cresol in a vacuum oven for 24 h at 90°C.

The viscosity of PCL–polyamide block copolymer solution in *m*-cresol was measured with Ostwald viscometer at 25°C.

¹H NMR spectra were obtained in CF₃COOD on a Varian Unity Plus 300.

Differential scanning calorimetry (DSC) was carried out with TA Instruments DSC-2910 at a heating rate and a cooling rate of 10°C min⁻¹. All runs were carried out with a sample of *ca.* 5 mg. The DSC thermograms in Figure 2 and the thermal properties in Table III were determined as follows. After melting for 3 min at 20°C above the melting temperature (T_{mh}) of polyamide segment in DSC device, the crystallization temperature (T_{mch}) and the heat of crystallization (ΔH_{mch}) of polyamide segment, and the crystallization temperature (T_{mcs}) and the heat of crystallization (ΔH_{mcs}) of PCL segment were measured on cooling scan to -140°C. On the subsequent heating scan after staying 1 min at -140°C, the glass transition temperature (T_{gs}), the melting temperature (T_{ms}), and the heat of fusion (ΔH_{ms}) of PCL segment, the crystallization temperature of polyamide segment (T_{mhh}), and T_{mh} and the heat of fusion (ΔH_{mh}) of polyamide segment were measured. The thermal properties in Table I were measured on heating the scan from -5°C to 220°C.

Dynamic mechanical properties of cast film were determined using a dynamic mechanical thermal analyzer (Rheometric Scientific, PL-DMTA MK III) at 1 Hz and at a heating rate of 3°C min⁻¹.

Tensile tests were done at a strain rate of 500 mm min⁻¹ using a tensile tester (Tinius Olsen Series 1000), attaching a constant temperature heating chamber. Microtensile specimen for test has the dimensions of 40 mm length, 10 mm width, and 0.2 mm thickness.

Table II. Characteristics of PCL-polyamide block copolymers

| Sample designation | M_n of PCL diol | Polyamide oligomer | Composition in feed/wt% | | | Composition in polymer ^a /wt% | | | $[\eta]$ dL g ⁻¹ |
|--------------------|-------------------|--------------------|-------------------------|--------------------|------|--|--------------------|------|--------------------------------|
| | | | PCL diol | Polyamide oligomer | HDI | PCL diol | Polyamide oligomer | HDI | |
| 4P1HN73 | 4000 | HPA1 | 70.00 | 23.54 | 6.46 | 71.2 | 20.8 | 8.0 | 0.89 |
| 4P1CN73 | 4000 | CPA1 | 70.00 | 23.30 | 6.70 | 72.1 | 20.7 | 7.2 | 1.02 |
| 4P2CN73 | 4000 | CPA2 | 70.00 | 25.15 | 4.85 | 70.3 | 24.0 | 5.7 | 1.71 |
| 4P3CN73 | 4000 | CPA3 | 70.00 | 25.71 | 4.29 | 72.0 | 22.8 | 5.2 | 1.39 |
| 4P1CN64 | 4000 | CPA1 | 60.00 | 32.61 | 7.39 | 62.7 | 28.5 | 8.8 | 1.02 |
| 4P1CN82 | 4000 | CPA1 | 80.00 | 14.47 | 5.53 | 81.7 | 11.3 | 7.0 | 1.19 |
| 2P1CN73 | 2000 | CPA1 | 70.00 | 20.98 | 9.02 | 69.2 | 19.3 | 11.5 | 1.35 |

^a Determined by ¹H NMR analysis.

RESULTS AND DISCUSSION

Thermal Properties

DSC thermograms of some typical PCL-polyamide block copolymers are shown in Figure 2. All the thermograms obtained on cooling from the melt state show a sharp exothermic crystallization peak (T_{mcs}) of PCL segment, and that of 4P3CN73 exceptionally has the crystallization peak (T_{mch}) of polyamide segment also. This result suggests that the relatively longer polyamide segment in 4P3CN73 can relatively easily crystallize on cooling scan. The thermograms of 4P1CN73 and 4P2CN73, obtained on subsequent heating scan, show T_{gs} , T_{ms} , the small crystallization peak of polyamide segment (T_{mhh}), and T_{mh} . However, 4P3CN73, whose polyamide segment was crystallized on cooling scan, does not have the peak of T_{mhh} . The T_{mhh} placed just above T_{ms} suggests the possibility that the glass transition of polyamide segment is masked by the melting peak of PCL segment, because the crystallization on heating can occur above the glass transition temperature. The thermal properties measured by DSC are summarized in Table III. All the T_{gs} shown in Table III lies in the temperature range -63°C — 56°C . In TPEs, T_g of soft segment generally increases as some of hard segment is dissolved into soft segment domain due to phase mixing.^{12,13} As the T_g of pure PCL is about -60°C ,¹⁴ the results of T_{gs} in Table III suggest that the dissolution of polyamide segment into PCL domain is not so much. Compared with other PCL-polyamide block copolymers, 4P3CN73 and 4P1CN82 generally have lower T_{gs} , higher ΔH_{ms} and ΔH_{mcs} , and smaller supercooling necessary for crystallization on cooling ($T_{ms} - T_{mcs}$). These results show that in these two polymers the dissolution of polyamide segment into PCL domain is relatively smaller and the crystallization of PCL segment is relatively easier than other PCL-polyamide block copolymers,^{10,11,15} because of higher molecular weight or lower content of polyamide segment. Whereas, 2P1CN73 generally has higher T_{gs} , lower ΔH_{ms} and ΔH_{mcs} , and larger value of $T_{ms} - T_{mcs}$ than other block copolymers. These results show that the dissolution of polyamide segment into PCL domain, *i.e.*, phase mixing is enhanced when the molecular weight of PCL segment is small.^{10,11,15} In our previous papers,^{6,7} we compared the properties of PCL diol/MDI/BD based TPE nonionomers with those of PCL diol/MDI/BD/dimethylol propionic acid (DMPA) based TPE ionomers. And we observed lower residual strain

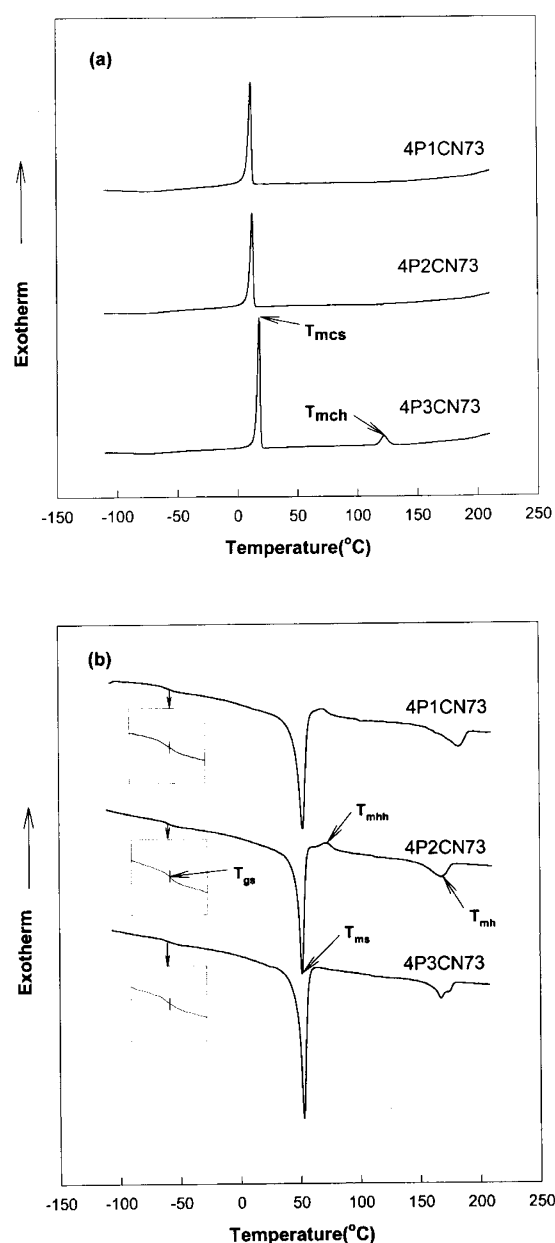


Figure 2. DSC thermograms obtained (a) on cooling and (b) on heating.

after shape recovery with TPE ionomers due to the enhanced microphase separation between soft and hard segments and due to higher rubbery plateau modulus. When the molecular weight and the content of PCL

Table III. Thermal properties of PCL–polyamide block copolymer

| Sample | Thermal properties | | | | | | | | |
|---------|--------------------|----------|--------------------------------|-----------|--------------------------------|----------|--------------------------------------|-----------|--------------------------------------|
| | T_{gs} | T_{ms} | ΔH_{ms} | T_{mcs} | ΔH_{mcs} | T_{mh} | ΔH_{mh} | T_{mch} | ΔH_{mch} |
| | °C | °C | J g ⁻¹ -PCL segment | °C | J g ⁻¹ -PCL segment | °C | J g ⁻¹ -polyamide segment | °C | J g ⁻¹ -polyamide segment |
| 4P1HN73 | -58.5 | 52.8 | 68.7 | 11.5 | 61.2 | 181.6 | 77.2 | — | — |
| 4P1CN73 | -58.8 | 52.8 | 65.0 | 11.8 | 59.1 | 183.2 | 57.8 | — | — |
| 4P2CN73 | -59.0 | 51.8 | 65.2 | 12.4 | 58.7 | 167.7 | 43.0 | — | — |
| 4P3CN73 | -62.4 | 52.9 | 70.7 | 18.1 | 63.7 | 167.5 | 38.4 | 122.2 | 31.5 |
| 4P1CN64 | -58.8 | 51.9 | 54.7 | 9.2 | 45.2 | 182.3 | 63.7 | — | — |
| 4P1CN82 | -60.1 | 52.5 | 68.6 | 16.2 | 60.4 | 181.4 | 62.8 | — | — |
| 2P1CN73 | -56.8 | 42.3 | 47.4 | -3.8 | 44.0 | 181.5 | 61.6 | — | — |

segment was 4000 and 70 wt%, ΔH_{ms} of TPE ionomer and TPE nonionomer were 64 J g⁻¹-PCL segment and 57 J g⁻¹-PCL segment, and somewhat higher value of ΔH_{ms} in TPE ionomer compared with nonionomer was explained to be due to enhanced microphase separation. In Table III, we can see that ΔH_{ms} is higher than 64 J g⁻¹-PCL segment when the molecular weight and the content of PCL segment is 4000 and 70 wt%, and this suggests that the microphase separation is enhanced as MDI/BD based polyurethane hard segment is replaced by polyamide segment. About ΔH_{mh} , we can see in Table III that HPA1 segment with intrinsic regular chemical structure has the highest value. The broad or multiple endothermic melting peaks of copolyamide blocks (Figure 2) and copolyamide oligomers (not shown in this paper) show the presence of heterogeneity in the copolyamide crystal region, probably due to copolymeric chemical structures.

Dynamic Mechanical Properties

The change of tensile storage modulus, E' in PCL–polyamide block copolymers and 4TPE73 on heating are shown in Figure 3. Gradual decrease of E' at the temperature range between T_{gs} and T_{ms} , and a sudden drop of E' at T_{ms} can be observed. The rubbery plateau above T_{ms} of PCL–polyamide block copolymer extends upto 160–190°C, and the abnormal slight increase of E' above 90°C in 4P1CN73 and 2P1CN73 seems to be due to the additional crystallization of polyamide segment which was not crystallized during the casting at 90°C.

The tensile storage moduli (E') of 4P1CN73 have larger values than those of 4TPE73. It can also be observed in Figure 3 that the E' values at rubbery plateaus of PCL–polyamide block copolymer do not decrease so much on heating upto T_{mh} , compared with TPES in our previous paper.^{6,7} These high rubbery moduli suggest that these PCL–polyamide block copolymers will have high elastic recovery at high temperature, because the driving force of shape recovery is the elastic force generated during the deformation, when the deformation is less than the yield value.

When compared with 4P1CN73, 2P1CN73 has smaller E' value below T_{ms} and larger rubbery plateau modulus. This smaller E' value below T_{ms} and earlier crystal–rubber transition might be due to lower crystallinity and larger T_{ms} depression (Table III) of PCL phase respectively, caused by enhanced PCL–polyamide phase mixing at lower molecular weight of PCL segment. The higher

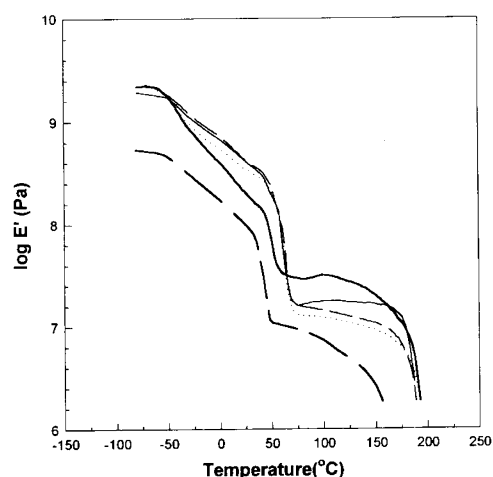


Figure 3. Dynamic mechanical properties of (—) 4P1CN73, (---) 4P3CN73, (-·-·-) 4P1CN82, (—) 2P1CN73, and (- - -) 4TPE73.

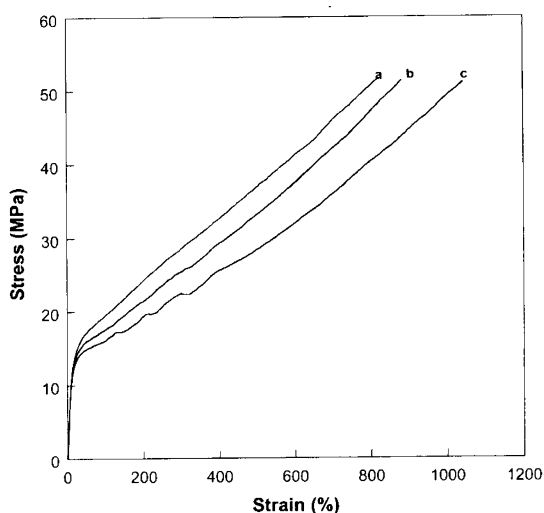
rubbery plateau modulus of 2P1CN73 suggests that well distributed polyamide segment can do its role as a fixed phase in the rubbery PCL phase more effectively. Similar result was also observed in PCL–poly(butylene terephthalate) (PBT) multiblock copolymer.³ That is, lower modulus below T_{ms} and larger rubbery modulus above T_{ms} were observed when the phase mixing was enhanced by the reduced molecular weight of PCL and PBT blocks. And those results were explained by the reduced crystallization of PCL phase and finer distribution of PBT segment in rubbery PCL phase, respectively.

The 4P3CN73 and the 4P1CN73 have similar values of E' below T_{ms} , however, 4P1CN73 has somewhat higher value of rubbery plateau modulus than that of 4P3CN73. This also supports that finer distribution of polyamide segment at low molecular weight is positive for its role as a fixed phase at rubbery state.

In Figure 3, both tensile storage moduli below and above T_{ms} of 4P1CN82 are smaller when compared with 4P1CN73, as expected from smaller amount of polyamide segment which acts as a fixed phase. However, in our previous papers, the tensile moduli of both TPE ionomer and nonionomer were increased as the weight ratio of PCL soft segment/polyurethane hard segment was increased due to the predominant contribution by crystalline PCL phase on E' below T_{ms} , compared with the contribution by higher amount of hard segment having more rigid structure. These results show that the contribution of polyamide segment on E' is larger than

Table IV. Tensile properties of PCL-polyamide block copolymers

| | 3% secant modulus | Tensile strength | Elongation at break |
|---------|-------------------|------------------|---------------------|
| | MPa | MPa | % |
| 4P1HN73 | 156 | 30 | 620 |
| 4P1CN73 | 124 | 51 | 890 |
| 4P2CN73 | 138 | 71 | 970 |
| 4P3CH73 | 178 | 55 | 880 |
| 4P1CN64 | 126 | 51 | 820 |
| 4P1CN82 | 101 | 51 | 1040 |
| 2P1CN73 | 50 | 55 | 960 |


Figure 4. Stress-strain curves of (a) 4P1CN64, (b) 4P1CN73, and (c) 4P1CN82 at room temperature.

that of polyurethane hard segment.

The earlier crystal-rubber transition of 4TPE73 compared with 4P1CN73 and 4P3CN73, shows the larger T_{ms} depression of PCL phase due to larger phase mixing in 4TPE73.

Tensile Properties

The tensile properties measured at room temperature are summarized in Table IV, and three typical stress-strain curves are shown in Figure 4. The properties are similar with those of TPEs in our previous papers,^{6,7} when the molecular weight and the content of PCL segment are the same. The 3% secant modulus generally increases as the molecular weight and the content of polyamide segment are increased.

Shape Memory Behavior

Typical results of cyclic tensile test to examine the shape memory effect of PCL-polyamide block copolymers and 4TPE73 are shown in Figure 5.^{6,7,16,17} Sample was elongated at 65°C to 100% strain (ϵ_m) at a constant elongation rate of 500 mm min⁻¹. 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

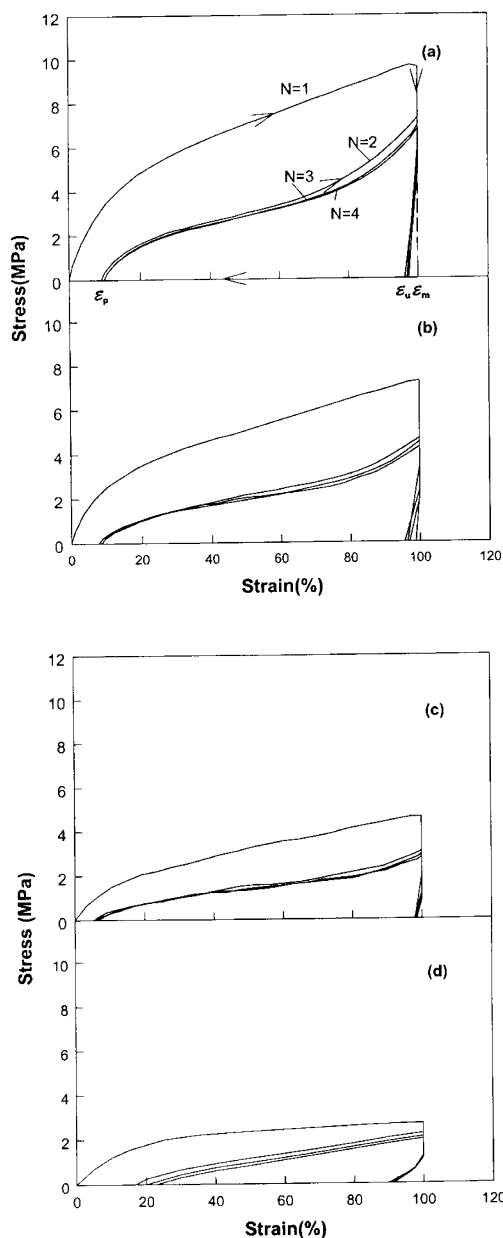

Figure 5. Cyclic tensile behavior of (a) 4P1CN64, (b) 4P1CN73, (c) 4P1CN82, and (d) 4TPE73.

Table V. Residual strain after thermomechanical cycle of PCL-polyamide block copolymers and 4TPE73

| | ϵ_p /% | | |
|---------|-----------------|-------|-------|
| | $N=1$ | $N=2$ | $N=3$ |
| 4P1HN73 | 7.3 | 8.4 | 8.5 |
| 4P1CN73 | 7.8 | 8.6 | 8.6 |
| 4P2CN73 | 8.1 | 9.2 | 10.6 |
| 4P3CN73 | 9.4 | 11.1 | 11.4 |
| 4P1CN64 | 9.1 | 10.0 | 9.9 |
| 4P1CN82 | 5.6 | 6.4 | 6.3 |
| 2P1CN73 | 6.5 | 7.1 | 7.3 |
| 4TPE73 | 17.0 | 20.0 | 23.0 |

residual strain ϵ_p , where the next cycle ($N=2$) starts.

In Figure 5, we can see that cyclic tensile test curves of PCL-polyamide block copolymers maintain their shapes almost identically after first tempering cycle. And Table V shows that ϵ_p values does not vary so much

upon repeated thermomechanical cycle and their values lies around 10%. When we carried out twenty thermo-mechanical cycles with 4P1CN73 and 4P1CN82, the results were almost the same. These results are somewhat different from those of TPEs,^{6,7,16,17} where the shape of curves were changed and ϵ_p increased from about 20% remarkably by the repeated thermo-mechanical cycles (one example is Figure 5(d)). Because fatigue by repeated deformations in TPEs comes from soft-hard phase mixing and orientation,^{18,19} these results show that changes in phase mixing or segmental orientation by repeated deformations are not so much in PCL-polyamide block copolymers.

The variation of ϵ_p in Table V according to the kind of PCL-polyamide block copolymer show the following orders: 4P1CN64 > 4P1CN73 > 4P1CN82 by the content of PCL block, 4P1CN73 > 2P1CN73 by the length of PCL block, and 4P3CN73 > 4P2CN73 > 4P1CN73 by the length of polyamide block. The reduction of ϵ_p at higher content of PCL segment was also observed in TPE's², however, the reduction of ϵ_p at shorter block length of reversible (PCL) or fixed (polyamide) segment is somewhat different from those of TPE's.

As anticipated from higher rubbery modulus (Figure 3), stress necessary for deformation of 4P1CN73 is higher, in Figure 5, than that of 4TPE73.^{6,7} This suggests that PCL-polyamide block copolymer will have higher recovery stress which is necessary for practical application as shape memory materials.

CONCLUSIONS

Compared with TPEs, PCL-polyamide block copolymers,

1. showed enhanced microphase separation
2. had higher rubbery plateau modulus which persists stably upto T_{mh}
3. needed higher stress for deformation at 65°C

4. showed lower degree of fatigue by repeated deformation in shape memory behavior.

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