

Crystallinity and Morphology of Segmented Polyurethanes with Different Soft-Segment Length

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SYNOPSIS

A series of polycaprolactone/4,4'-diphenylmethane diisocyanate/1,4-butanediol (PCL/MDI/BDO) segmented polyurethanes of different compositions was synthesized by solution polymerization. The molecular weight of PCL diols used was in the range of 1600–7000. The crystallinity and morphology of these polymers were studied by using DSC, dynamic mechanical analysis, WAXD, and polarizing microscopy methods. It was found that the crystallinity of PCL prepolymers was depressed in segmented polyurethanes. A lower limit of PCL molecular weight was found, below which the PCL segments were not able to crystallize at the usual processing conditions. This limit of molecular weight is in the range of 2000–3000 and exhibits a slight increase with increasing hard-segment content of polyurethanes. The glass transition temperature related to the PCL segment regions in polyurethane specimens deviated from that of pure amorphous PCL prepolymer to a higher temperature. The deviation resulted from the crystallization of PCL segments and also the influence of hard segments. The formation of hard-segment domains becomes very difficult for polyurethanes having low hard-segment content and short hard-segment length. There is a lower limit of hard-segment content and segment length. Only above that limit do the polyurethanes have enough hard-segment domains acting as physical crosslinks at temperatures above the melting point of the PCL crystals. The structural characteristics of segmented polyurethanes which may exhibit a shape memory effect are also discussed.

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INTRODUCTION

Segmented polyurethanes are multiblock copolymers of the —(H—S)— type. The chain structure of their molecules is characterized by the alternating sequence of two chemically different segments. The two segments are different in molecular motion; usually, the hard segments H have a glass transition temperature T_g higher than room temperature, while the soft segments S are in a rubbery state. Hard and soft segments are usually thermodynamically immiscible, so microphase separation of the segments occurs in these specimens.

The hard-segment domains may serve as physical crosslinks for the rubbery soft-segment matrix, imparting high elasticity of the material. Since the crosslinks are physical in nature, they can be processed as thermoplastics.

Much work has been done studying the morphology and properties, and their relationship with chemical structure, of the segmented copolymers. The microphase-separated morphology was first suggested by Cooper and Tobolsky¹ on the basis of the glass transition temperature data from dynamic mechanical measurements of segmented polyurethanes. For specimens having low interactions between the hard and soft segments, clear glass transitions for domains of both segments can be easily detected by dynamic mechanical or DSC studies.^{2–4} X-ray scattering^{5–7} and electron microscopy^{7–10} were

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used for direct observation of the micro-two-phase morphology, giving information about the size and shape of the domains. It was found that in most cases the segregation of segments was not complete, depending on the chemical structure and length of the hard and soft segments and also on the thermal history and processing conditions. This can be evidenced, e.g., by variations of the temperature and other parameters of transitions ascribed to soft- or hard-segment regions¹¹⁻¹³ and by the amount of hydrogen bonding between hard and soft segments.¹⁴ The morphology of segmented polymers is even more complicated because of the fact that the macromolecules of a segmented copolymer sample can vary greatly in their chemical composition and average hard-segment length due to the heterogeneity of the reaction system. This means that there might be a superposition of the microphase separation of different segments and the macrophase separation of molecules of different composition or different hard-segment length. This phenomenon has been presented clearly for polybutadiene/TDI-based polyurethanes.^{4,7,15}

Recently, we prepared some polycaprolactone (PCL)-based polyurethanes which may exhibit a clear thermally stimulated shape-memory effect with high values of recoverable deformation and recovery rate.¹⁶ The advantage of using segmented copolymers as shape-memory materials is the possibility of controlling the critical recovery temperature to meet the needs of different applications. In addition, the thermoplastic nature makes them quite convenient in processing. According to the mechanism of this effect, the crystallization of the PCL segment in polyurethanes at room temperature and the formation of hard-segment domains which are stable under strain are the necessary conditions for their shape-memory effect. It is expected that the crystallinity and morphology of the polymers will have significant influence on their shape-memory behavior. However, in previous studies of segmented copolymers, only a very few samples, which show soft-segment crystallinity, were used, and the research interest was limited to how to obtain samples without soft-segment crystallization. Therefore, the structure and properties of segmented copolymers with crystallizable soft segments were not the main topic of research in the literature. In this work, the crystallinity and morphology of PCL-based segmented polyurethanes and the influence of the molecular weight of PCL segments and composition of copolymers were investigated. The shape-memory behavior of these segmented polyurethanes and its relationship with the crystallization behavior and

morphology of these samples will be given in a subsequent article.¹⁷

EXPERIMENTAL

Segmented polyurethanes were synthesized by a two-step method involving endcapping the hydroxy-terminated PCL with 4,4'-diphenylmethane diisocyanate (MDI) followed by reaction in solution with the chain extender, 1,4-butanediol (BDO). Six hydroxy-terminated PCL samples of different molecular weights ranging from 1600 to 7000 were used. The polyurethanes have a wide composition range with hard-segment content from about 6 to 45% by weight. The composition and intrinsic viscosity of the polyurethanes are listed in Table I. The intrinsic viscosity of a sample was measured in *N,N'*-dimethylformamide at 30°C.

DSC thermographs of the samples were recorded over the temperature range from -70 to 240°C using a Perkin-Elmer DSC-4 purged with nitrogen. Runs were conducted at a heating or cooling rate of 20°C/min. Indium was used as the standard for temperature calibration. The glass transition temperature was taken to be the temperature corresponding to one-half the increase in heat capacity accompanying the transition.

WAXD profiles were measured at room temperature on a Rigaku D/MAX- γ B X-ray unit with CuK α radiation. Intensities were counted in the Bragg angle (2θ) of 5-45°.

Dynamic mechanical data were obtained at 10 Hz using a dynamic mechanical thermal analyzer Mk III of Rheometric Scientific Ltd. The specimens were solution-cast and then vacuum-dried for 100 h before use. Thin sheet specimens of 20 mm length and 3 mm width were used, and their thickness was around 0.3 mm. The measurements were carried out at a heating rate of 2°C/min.

RESULTS AND DISCUSSION

Segmented copolymers exhibiting a thermal recovery effect can be characterized by the microphase separation and the ability of soft segments to crystallize at room temperature. So, the crystallization of PCL prepolymers of different molecular weights and the corresponding segmented polyurethanes were studied. Figure 1 shows the thermographs of PCL prepolymers with different molecular weights in cooling and subsequent heating processes. They were all crystallizable. The crystallization temper-

Table I Parameters and DSC Results for Segmented Polyurethanes

Sample	Mol Ratio PCL/MDI/BDO	M_n of PCL Prepolymer	Hard Segment (wt %)	$[\eta]$ (dL/g)	T_c (°C)	ΔH_c (cal/g-soft)	Crystallinity (%)	T_m (°C)
M-121-1.6	1/2/1	1600	26.97	0.30	—	0	0	—
M-132-1.6	1/3/2	1600	36.79	0.20	—	0	0	—
M-143-1.6	1/4/3	1600	44.28	0.40	—	0	0	—
M-121-2.0	1/2/1	2000	22.80	—	—	0	0	—
M-132-2.0	1/3/2	2000	31.70	—	—	0	0	—
M-143-2.0	1/4/3	2000	38.81	—	—	0	0	—
M-154-2.0	1/5/4	2000	44.60	—	—	0	0	—
M-121-4.0	1/2/1	4000	12.95	0.41	8.7	13.52	41.7	50.3
M-132-4.0	1/3/2	4000	18.99	0.36	-0.8	9.89	30.5	47.8
M-143-4.0	1/4/3	4000	24.25	0.40	-4.3	3.62	11.2	45.2
M-121-5.0	1/2/1	5000	10.56	0.60	11.9	12.74	39.3	50.3
M-132-5.0	1/3/2	5000	15.68	1.04	-0.8	9.78	30.2	48.0
M-143-5.0	1/4/3	5000	20.26	0.95	-4.0	6.48	20.0	44.9
M-121-7.0	1/2/1	7000	7.77	1.11	15.3	12.99	40.1	50.7
M-132-7.0	1/3/2	7000	11.73	0.77	12.9	12.70	39.2	50.7
M-143-7.0	1/4/3	7000	15.36	0.97	7.3	11.02	34.0	50.7
M-154-7.0	1/5/4	7000	18.70	0.98	8.4	9.98	30.8	49.5

ature T_c and melting temperature T_m of the crystals are given in Table II. The sample of molecular weight 1600 has lower T_c and T_m . For the other samples of higher molecular weight, the variation in T_c and T_m is very small. The T_m values of these samples, 53–55°C, are lower than the value 63–65°C for higher molecular weight PCL.^{18,19} The enthalpy of crystallization ΔH_c in cooling is used to characterize the crystallizability of the samples. It decreases slightly with increasing molecular weight. The enthalpy of fusion of 100% crystalline PCL, 32.4 cal/g, evaluated from the melting-point depression of PCL by ethylbenzoate,¹⁸ was used to calculate the crystallinity of the samples, which is in the range of 56–60%.

The crystallization ability of PCL segments in segmented polyurethanes is significantly depressed due to the connection with the hard segments. Figures 2 and 3 are the DSC thermographs of polyurethanes with different lengths of soft or hard segments. The results are summarized in Table I. It is clear that the molecular weight of the soft segments is the main factor determining the crystallizability. No crystallinity was observed for polyurethanes with PCL segments of molecular weights 1600 and 2000. For PCL segments of higher molecular weight, the influence of copolymerization on the crystallization behavior was found in the lowering of the T_c and the decrease of crystallinity. The higher the molecular weight, the less the influence. For polyurethanes

of the same soft-segment length, the crystallinity of PCL segments decreases with increasing hard-segment content of the samples. Figure 4 gives the WAXD patterns for a PCL prepolymer of molecular weight 7000 and the corresponding polyurethanes in the 2θ range of 5°–45°. It indicates that the hard segments only decrease the crystallizability of the PCL segments, but do not result in a change of crystal structure.

Figure 5 shows the dependence of PCL crystallinity on the molecular weight of soft segments. No crystallinity was observed for samples with soft segments of low molecular weights. The crystallinity of PCL segments increases abruptly after a critical molecular weight value, then it approaches a constant. This critical molecular weight is in the range of 2000–3000 and slightly increases with increasing hard-segment length, and it might be the lower limit for molecular weight of PCL segments which can be used for preparing segmented polyurethanes having a shape-memory effect. It should be noted that the crystallinity of PCL segments is dependent on the crystallization condition or the thermal history of the polyurethane samples. All the data given in Figure 5 were obtained for specimens in a cooling process from the melt state at a constant rate of 20°C/min. It is supposed that these conditions may, more or less, simulate the usual processing conditions of polyurethanes used as shape-memory materials.

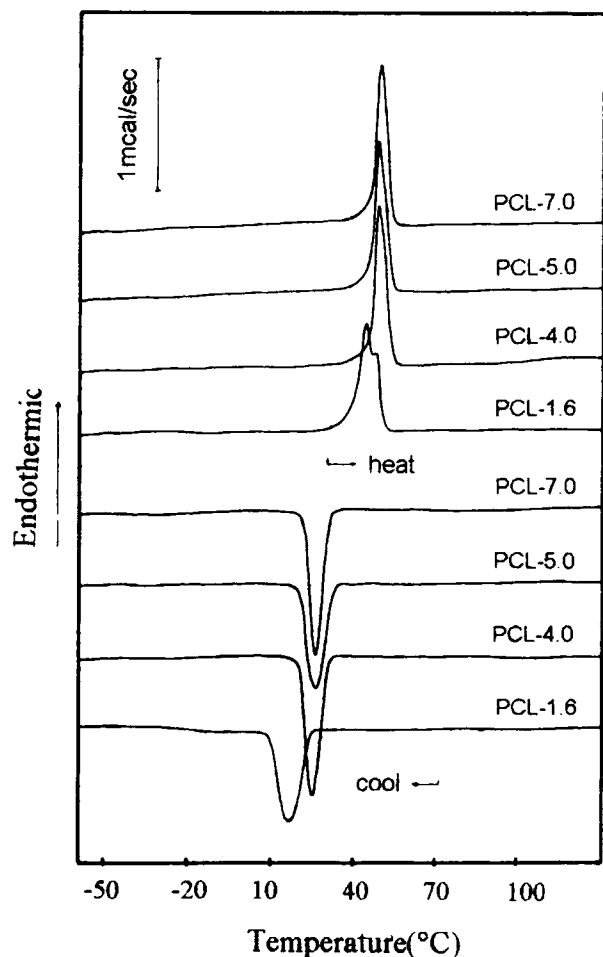


Figure 1 DSC thermographs of PCL prepolymers with different molecular weight in cooling and subsequent heating processes.

Polyurethanes with PCL segments of molecular weight 2000 may exhibit a very low crystallinity of soft segments after lengthy annealing, e.g., of several days at the proper temperatures. However, such crystallization behavior is impractical for the particular application.

The PCL segments of polyurethanes are only partially crystallized, and their degree of crystallinity is usually less than 50%, so most of the PCL segments are in the amorphous state and the corre-

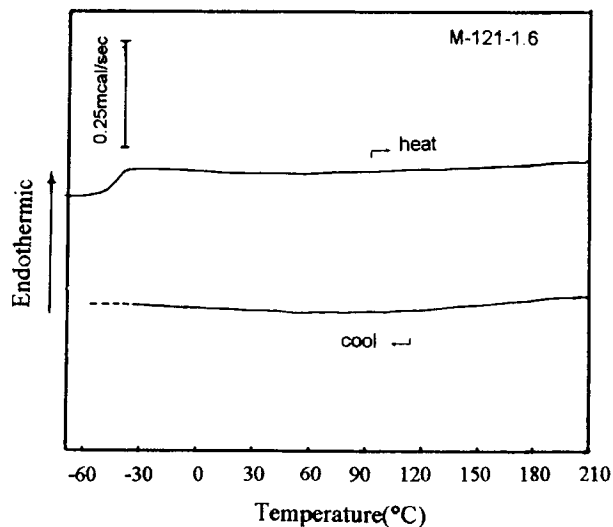


Figure 2 DSC thermographs of sample M-132-1.6 in cooling and subsequent heating processes.

sponding glass transition temperature T_g can be detected, e.g., by DSC measurements. The glass transition temperature T_g and the width of the transition range ΔT for some samples are given in Table III. In column 1 are data from specimens prepared by cooling from the melt state at a rate of $20^\circ\text{C}/\text{min}$. The T_g for PCL prepolymers was found to be around -60°C and almost independent of their molecular weight. The T_g of PCL segments in polyurethanes is always higher than that of the PCL prepolymers. The T_g moves to higher temperature with increasing hard-segment content or with decreasing molecular weight of the PCL segments, and the ΔT value increases at the same time.

There are two main factors which may influence the T_g of PCL segments: the crystallization of PCL segments and the hard segments in the molecules. Both have the effect of shifting the T_g of the PCL segments to higher temperatures. To get some idea about the influence of the two factors separately, data for quenched specimens are also listed in column 2 of Table III. The glass transition temperatures T_g^0 of these uncrystallized specimens were always lower than those of the corresponding crys-

Table II DSC Results of PCL Prepolymers of Different Molecular Weight

Sample	$M_n \times 1000$	T_c ($^\circ\text{C}$)	ΔH_c (cal/g-soft)	Crystallinity (%)	T_m ($^\circ\text{C}$)
PCL-1.6	1.6	17.00	19.50	60.2	46.33
PCL-4.0	4.0	26.34	19.53	60.3	53.53
PCL-5.0	5.0	26.70	18.86	58.2	53.49
PCL-7.0	7.0	28.19	18.40	56.8	55.86

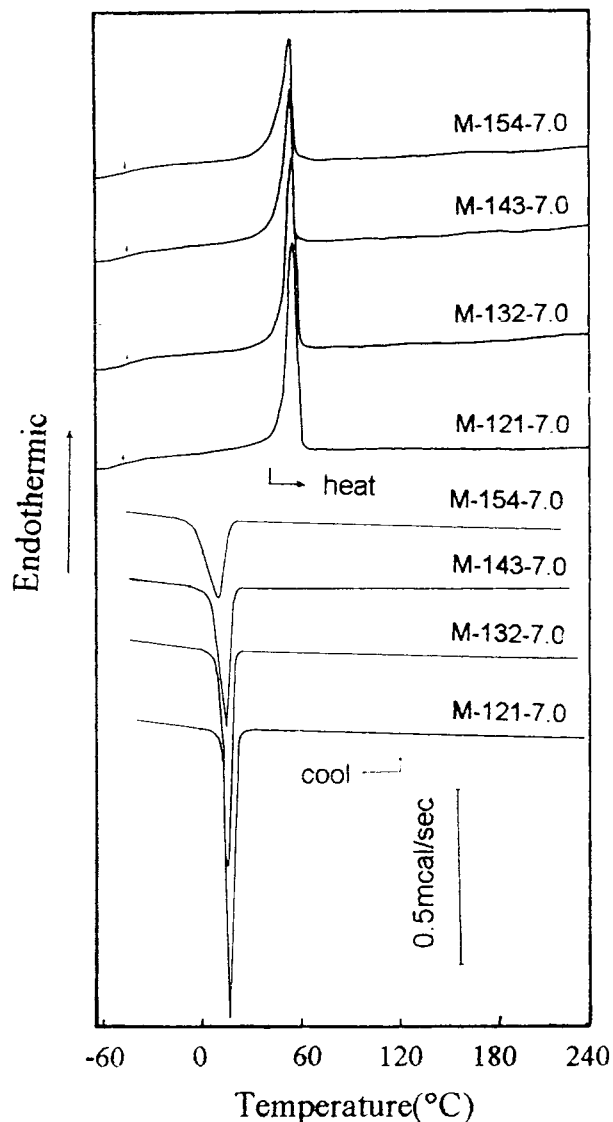


Figure 3 DSC thermographs of polyurethanes with different hard-segment length in cooling and subsequent heating processes.

talline specimens. Figure 6 gives the dependence of T_g and T_g^0 on the hard-segment content for polyurethanes with the soft segment of the same molecular weight 7000. Experimental data for crystalline specimens group around a straight line: Its extrapolation to zero hard-segment content gives a $T_g(0)$ value of about -60°C , which is quite consistent with the experimental value directly measured for the PCL prepolymer. The T_g^0 data locate very well on a straight line. The glass transition temperature of the uncrystallized PCL prepolymer $T_g^0(0)$ can be estimated by extrapolation to zero hard-segment content and is found to be -61.5°C . It is only 1.5°C lower than $T_g(0)$. Polycaprolactone crystallizes so

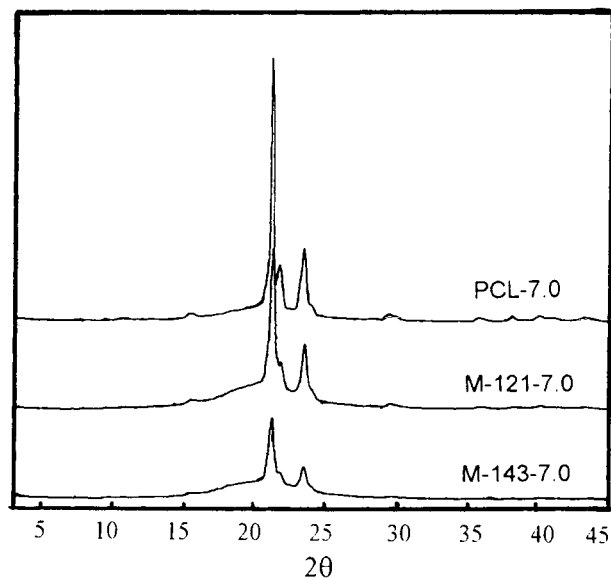


Figure 4 WAXD patterns for PCL prepolymer of molecular weight 7000 and the corresponding polyurethanes.

easily that it is impossible to obtain the glass transition temperature of uncrystalline specimens from direct experimental measurements. Koleske and Lundberg²⁰ determined this value from data of miscible blends of PCL with poly(vinyl chloride). They used a PCL sample of molecular weight 40,000, and the T_g of the blends was measured by the dynamic mechanical method. A T_g of -71°C was obtained,

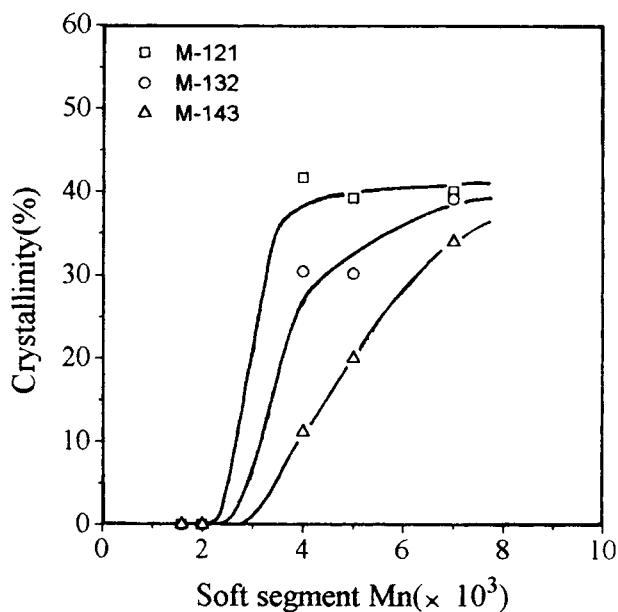


Figure 5 Dependence of PCL crystallinity of polyurethanes on molecular weight of soft segments.

which was about 10°C lower than the T_g of the crystalline specimens.

These results are similar to ours; however, it is not meaningful to make a detailed comparison because of the difference in the molecular weight of the samples, thermal history, and also the measuring techniques used. It is clear that the deviation in the glass transition temperature from pure amorphous PCL to PCL-based polyurethanes $T_g - T_g^0(0)$ is composed of two parts, $T_g - T_g^0$ and $T_g^0 - T_g^0(0)$:

$$T_g - T_g^0(0) = (T_g - T_g^0) + [T_g^0 - T_g^0(0)]$$

which can be ascribed to the effects of the PCL crystallization and hard-segment content, respectively. Results for polyurethanes with a PCL segment of molecular weight 7000 are given in the third column of Table III. It was found that in this case the two effects have the same order of magnitude, and they both increase with increasing hard-segment content.

It is usually accepted that microphase separation of hard and soft segments in polyurethanes is far from complete. Infrared spectroscopic studies of a PCL/MDI/BDO polymer with a PCL molecular weight of 1000 and hard-segment content of 37.1% have indicated that only about 30% of the hard-segment segregates in the domains.¹⁴ The samples used in this work have less hard-segment content and much longer soft-segment length. It is very interesting to learn whether the hard segments are still able to aggregate and form individual domains at such low contents and when they are separated far away by long soft segments of several thousands of molecular weight. The formation of hard-segment domains is especially important, because it is a necessary structural characteristic for shape-memorable segmented copolymers. The glass transition temperature of MDI/BDO hard-segment domains has

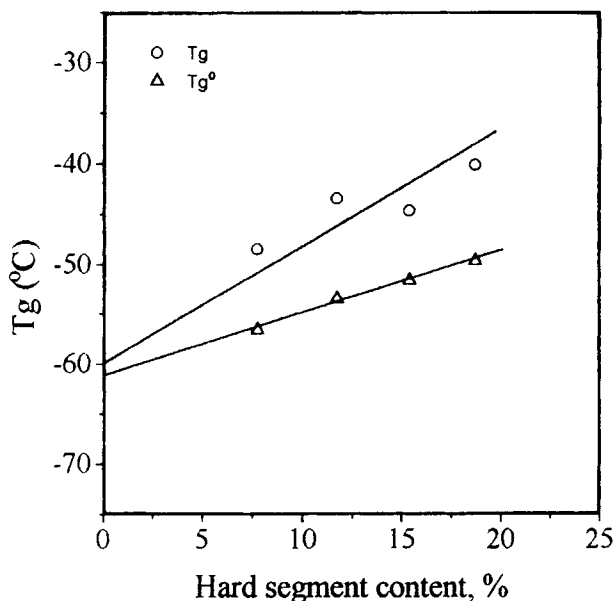


Figure 6 The dependence of soft-segment T_g on hard-segment contents for polyurethanes with PCL segments of molecular weight 7000.

been reported to be around 125°C,²¹ and the melting point of MDI/BDO hard-segment crystals is in the range of 200–240°C.²² However, no hard-segment T_g transition and melting were observed for the as-cast polyurethane specimens.

Indirect evidence of the formation of hard-segment domains was obtained in the temperature dependence of dynamic modulus. Figures 7 and 8 give this dependence for polyurethanes with PCL segments of molecular weight 7000 and 5000, respectively. The dynamic modulus of these samples at room temperature is about $1-2 \times 10^8$ Pa. It is almost unchanged with temperature until the melting of PCL crystals at around 60°C. Then, the curves may

Table III T_g Results of Soft Segment in Polyurethanes with Different Compositions

Sample	1		2		3	
	ΔT_g	T_g	ΔT_g^0	T_g^0	$T_g - T_g^0$	$T_g^0 - T_g^0(0)$
M-121-1.6			22.91	-39.65		
M-121-2.0	30.11	-34.47				
M-121-4.0			14.89	-53.12		
M-121-5.0	27.87	-46.42	14.51	-53.58		
M-121-7.0	27.48	-48.50	10.28	-56.60		
M-121-7.0	27.48	-48.50	10.28	-56.60	8.10	4.90
M-132-7.0	28.80	-43.50	16.35	-53.51	10.01	7.99
M-143-7.0	35.58	-44.69	19.80	-51.63	6.94	9.87
M-154-7.0	34.65	-40.18	27.35	-49.65	9.47	11.85

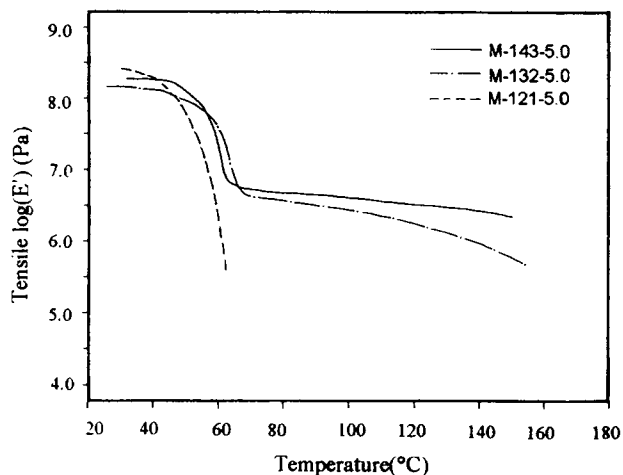


Figure 7 The temperature dependence of dynamic modulus for polyurethanes with PCL segments of molecular weight 5000.

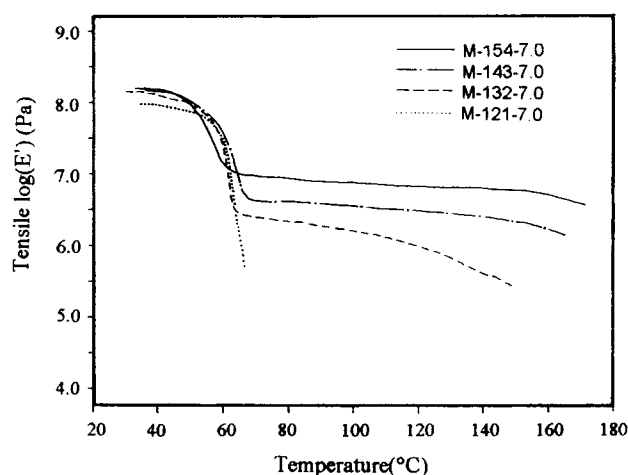


Figure 8 The temperature dependence of dynamic modulus for polyurethanes with PCL segments of molecular weight 7000.

have a plateau which indicates the existence of physical crosslinks in these specimens. The length of the plateau increases with increasing the hard-segment content of the samples. For specimens having low hard-segment molecular weight (samples M-121-5.0 and M-121-7.0) the modulus drops abruptly and no plateau is observed. This means that there is a lower limit to the hard-segment content level for polyurethanes with crystallizable soft segments, about 10% by weight, below which the hard segments are not able to segregate and form individual domains or, at least, not able to form a sufficient amount of individual domains stable under strain as physical crosslinks and the polyurethanes might not exhibit a shape-memory effect. The plateaus shown in Figures 7 and 8 extend to about 100°C for samples of low hard-segment content and to about 140°C and more in the case of high hard-segment content. This may imply that the hard-segment domains can be amorphous or partly crystalline. For well-crystallized specimens, some endo peaks appear in DSC thermograms above 200°C (Fig. 9). In some cases, even spherulites of hard segment crystals can be formed. Figure 10 shows the polarizing micrographs of a specimen of M-154-7.0 before and after melting of PCL crystals. The spherulites of MDI/BDO segments in Figure 10 (b) are about 10 microns in diameter and they disappear at about 196°C.

CONCLUSIONS

The crystallinity of PCL prepolymers is depressed in segmented polyurethanes. A lower limit of PCL

molecular weight was found, below which the PCL segments were not able to crystallize under the usual conditions of processing. This limit of molecular weight is in the range of 2000–3000 and exhibits a slight increase with increasing the hard-segment content of polyurethanes. The formation of hard-segment domains becomes very difficult for polyurethanes having low hard-segment content and short hard-segment length. There is a lower limit of hard-segment content and segment length. Only above this limit do the polyurethanes have enough hard-segment domains acting as physical crosslinks at temperatures above the melting point of PCL crystals. The above two limits should be important structural characteristics for segmented copolymers with a shape-memory effect.

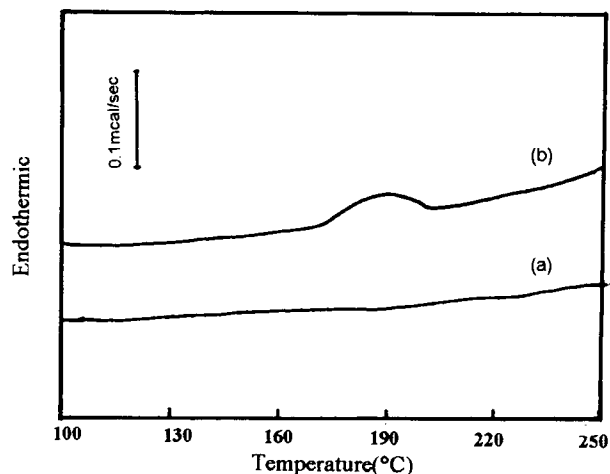


Figure 9 DSC thermographs of polyurethane M-154-7.0 specimens (a) as-cast and (b) well annealed.

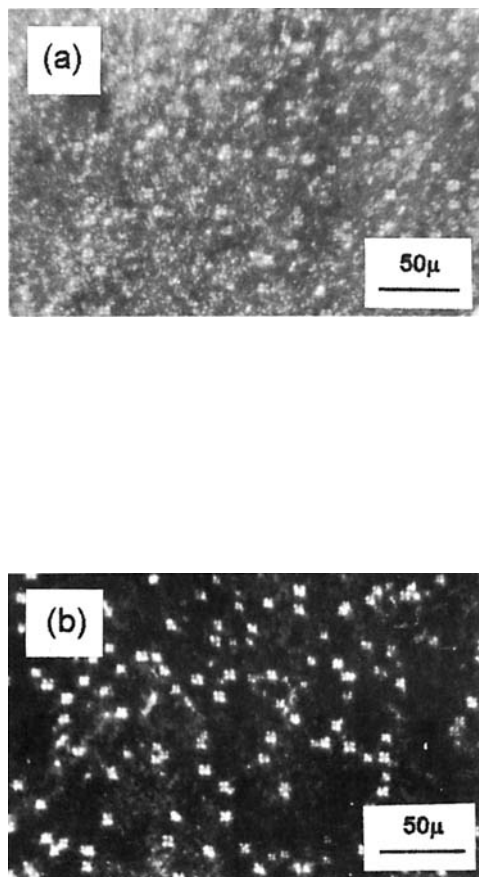


Figure 10 Polarizing micrographs of a well-crystallized M-154-7.0 specimen (a) before and (b) after melting of PCL crystals.

We are grateful to the National Natural Science Foundation of China and the Korean Science and Engineering Foundation for supporting this work.

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Received November 21, 1995

Accepted May 10, 1996