

## Synthesis and Thermal Properties of Polyamide 6-*block*-Poly(cyclohexylmaleimide)

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(Received September 16, 1998)

**ABSTRACT:** Block copolymers consisting of poly(cyclohexylmaleimide) (PCHMI) and polyamide 6 (PA6) were synthesized and thermal properties were measured. Carboxyl group-terminated PCHMIs initiated by 4,4'-azobis-4-cyanopentanonic acid (ACPA) under several conditions had different  $T_g$ s, depending on the molecular weight of PCHMI. Copolymers consisting of PA6 and PCHMI were prepared by melt-polymerization of  $\epsilon$ -caprolactam, 6-aminocaproic acid and PCHMI. The copolymers contained ABA and AB judging from  $^1\text{H}$  NMR and reduced viscosity measurements.  $T_g$ s of the copolymers were independent of  $T_g$  of the original PCHMI, and increased with PCHMI content in the copolymers.

**KEY WORDS** Polyamide 6 / Poly(cyclohexylmaleimide) / Block Copolymer / Melt-Polymerization / Thermal Properties /

Polyamide 6 (PA6) has many industrial applications, and block copolymers from PA6 and other polymers, such as vinyl polymers, polyethers, polyimides, and polyesters, were synthesized to expect new properties.<sup>1</sup> However, major vinyl polymers copolymerized with PA6 are poly(styrene)<sup>2-7</sup> and rubbers such as poly(butadiene-acrylonitrile),<sup>8-11</sup> poly(styrene-butadiene),<sup>12,13</sup> poly(butadiene)<sup>6,14-16</sup> and poly(isobutylene).<sup>17</sup> There have been few studies on the synthesis and characterization of block copolymers of PA6 with vinyl polymers, except poly(styrene) and rubbers.

The polymerization of  $\epsilon$ -caprolactam (CL) has been initiated with end groups of prepolymers consisting of other polymers for prepolymers having amino or carboxyl end groups.<sup>1</sup> In the preparation of block copolymers, initiators such as dicarboxylic acids,  $\omega$ -aminocarboxylic acids, or water were often added to the system to increase the rate of copolymerization.<sup>1</sup> In general, however, the preparations were carried out above the melting points ( $T_m$ ) of copolymers.<sup>1</sup> Thus, thermal stability of the prepolymers is required.

Poly(*N*-substituted maleimide)s (poly(RMI)s) have usually good thermal stability and various properties depending on the *N*-substituents.<sup>18</sup> Since homopolymers are brittle, copolymers with other vinyl monomers were usually used. The unique thermal and optical properties, and characteristic of separation of the copolymers have been reported.<sup>18</sup>

Poly(*N*-cyclohexylmaleimide) (PCHMI) has a high softening point<sup>19</sup> and thermal decomposition temperature.<sup>20</sup> Block copolymers from PA6 and PCHMI are of great interest from the point of synthesis and thermal properties. The present paper describes the synthesis of PA6-*block*-PCHMI from CL, 6-aminocaproic acid (ACA) and carboxyl group-terminated PCHMI obtained from the radical polymerization of CHMI with 4,4'-azobis-4-cyanopentanonic acid (ACPA). Thermal properties of the copolymers were investigated by differential scanning calorimetry (DSC) and dynamic mechan-

ical spectrometry.

## EXPERIMENTAL

### Materials

CL (Ube Ind., Ltd.) was commercial-grade. CHMI (melting point; 89°C) was prepared as described earlier.<sup>19</sup> ACA, *m*-cresol, methanol, tetrahydrofuran (THF), 1,4-dioxane (DOX) and 1-methyl-2-pyrrolidinone (NMP) as extra pure grades of Kishida Chemical Co. were used without further purification. ACPA (Aldrich) was recrystallized twice from methanol.

### Polymerization

**Carboxyl-Terminated PCHMI.** The radical polymerizations of CHMI with ACPA as the initiator were carried out in THF or DOX at 60°C under nitrogen atmosphere. After a required time, the solution was cooled to r.t. and filtered to remove insoluble parts. PCHMI was precipitated by pouring the filtrate into excess of methanol-water (=85:15, weight) mixture, filtered, washed 3 times, and dried under reduced pressure at r.t. for 1 day.

**PA6-*block*-PCHMI and PA6 Homopolymer.** The copolymers were prepared by melt-polymerizations under nitrogen atmosphere. PCHMI was dissolved in CL and ACA at 180°C for 30 min. The mixture solution was heated at 250°C for the desired time. The products were crushed and washed with methanol and THF by Soxhlet apparatus for 5 h to remove the monomers, oligomers and unreacted PCHMI. The products were dried under reduced pressure at r.t. for 1 day.

PA6 homopolymer was obtained by the hydrolytic polymerization of CL in the presence of stearylamine (SA) as terminator. CL, water and SA were heated in a stainless steel reactor under nitrogen atmosphere at 250°C. PA6 was washed with methanol by Soxhlet apparatus for 20 h and dried under reduced pressure at 60°C for 1 day.

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### Characterization

**<sup>1</sup>H NMR Spectroscopy.** PCHMI was dissolved in CDCl<sub>3</sub>. PA6 and PA6-*block*-PCHMI were dissolved in D<sub>2</sub>SO<sub>4</sub> (97%). <sup>1</sup>H NMR spectra were measured using a JEOL JNM-EX400WB FT-NMR (400 MHz) spectrometer at r.t. Tetramethylsilane (TMS) was used as the internal standard.

**End Group.** The concentrations of carboxyl groups in PCHMI were measured by potentiometric titration in NMP at r.t. with 0.1 N sodium methoxide in pyridine. The concentrations of amino groups in PA6 were measured by titration in phenol/methanol (90/10<sub>volume</sub>) at r.t. with 0.05 N sodium hydroxide.

**Molecular Weight.** Number-average ( $M_n$ ) and weight-average ( $M_w$ ) molecular weights of PCHMI were measured by GPC using a Shimadzu Chromatopac C-E4A, SPD-10A UV detector and LC-10A pump with columns of HSG-10H, 15H, 20H, and 40H. THF was used as solvent; column temperature = 50°C, and flow rate = 0.8 ml min<sup>-1</sup>.  $M_n$  and  $M_w$  were calibrated with a polystyrene standard.

$M_n$  of PCHMI were measured by vapor pressure osmometry (VPO), performed using a CORONA Molecular Weight Apparatus 114 at 30°C. THF was used as solvent.

$M_n$  of PA6 was calculated from concentrations of amino groups.

**Solution Viscosity.** Reduced viscosity ( $\eta_{red}$ ) of 0.5 g dl<sup>-1</sup> PCHMI and PA6-*block*-PCHMI solution in *m*-cresol were measured using an Ostwald viscometer at 25°C.

**Thermal Properties.** DSC was used for thermal measurement with a Perkin-Elmer Model DSC-7. PCHMI was first heated to 320°C, cooled to 0°C, and scanned at 10°C min<sup>-1</sup>. Copolymers were first heated to 260°C, cooled to -40°C at 10°C min<sup>-1</sup> and scanned at 10°C min<sup>-1</sup>.

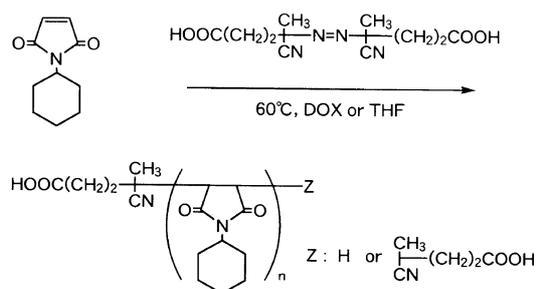
Dynamic mechanical spectrometry was performed using a Rheometrics RSA II at 10 Hz. The specimen was prepared from *m*-cresol solution (15 wt%) poured on to a glass plate and the solvent was evaporated at 70°C for 24 h. The film (about 25 μm in thickness) was washed with methanol by Soxhlet apparatus for 5 h to remove remaining solvent and dried under reduced pressure at r.t. for 1 day.

## RESULTS AND DISCUSSION

### Synthesis of Carboxyl Group-Terminated PCHMI

According to Scheme 1, carboxyl group-terminated PCHMI was synthesized by radical polymerization of CHMI with ACPA. Figure 1 shows <sup>1</sup>H NMR spectra of PCHMI. Assignments of signals based on CHMI unit are presented elsewhere.<sup>21</sup> Signals of methyl protons (A) coalesced with those of methylene protons of cyclohexyl groups (a) which appeared at the same range (0.9–2.2 ppm). The intensity of signals at 2.60–2.95 ppm increased with decrease of the molecular weight and thus were assigned to two methylene protons of ACPA unit (B) in PCHMI.

The results of the synthesis of PCHMI are summarized in Table I. Polymerization with ACPA proceeded first



Scheme 1. Synthesis of carboxyl group-terminated PCHMI.

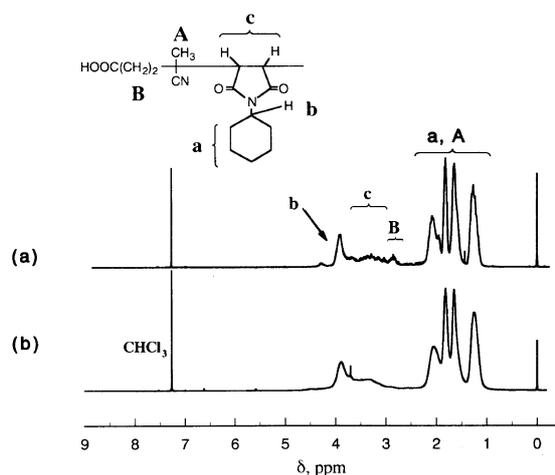


Figure 1. <sup>1</sup>H NMR spectra of PCHMI in CDCl<sub>3</sub>: (a) Run T6 and (b) Run D7 (in Table I).

homogeneously in THF and DOX and heterogeneously as well as that of CHMI with 2,2'-azobis(isobutyronitrile) (AIBN) in THF.<sup>19</sup> In this study, only the dissolved component in the solvent was used.  $M_n$  and  $M_w$  of PCHMI, except at lower concentration of ACPA (Run D1 and T1), slightly decreased with increasing molar ratio of ACPA to CHMI.  $M_n$  and  $M_w$  of PCHMI obtained in DOX were higher than in THF.

Otsu *et al.* reported that the polymerization of styrene with ACPA gave telekelic polymers with carboxyl groups at chain-ends, but the telekelic polymer was not obtained for the polymerization of methyl acrylate.<sup>22</sup> As shown in Table I, the number of carboxyl groups per polymer chain ( $N_c$ ) calculated from the concentration of carboxyl group and  $M_n$  measured by GPC, except for D1, were smaller than 2.0.  $M_n$  of D1, D3, and T2 measured by VPO ( $M_{n,VPO}$ ) were  $3.1 \times 10^3$ ,  $1.4 \times 10^3$ , and  $1.0 \times 10^3$ , respectively. These values were similar to those by GPC, and  $N_c$  calculated from the  $M_{n,VPO}$  were smaller than 2.0. This suggests that the radical polymerization of CHMI with ACPA is not terminated only by the recombination reaction. Thus, copolymerization using PCHMI is expected to form copolymers having ABA and AB structures (A, PA6 segment; B, PCHMI).

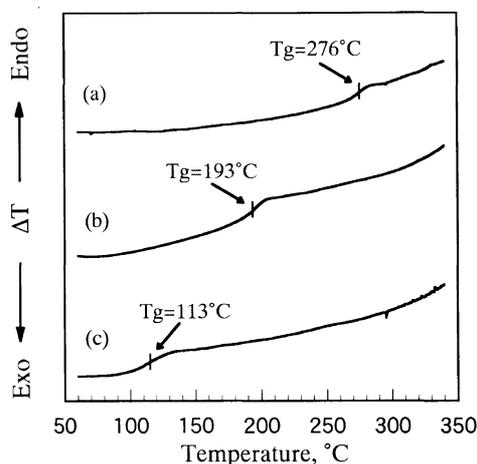
Figure 2 shows DSC curves of PCHMI. Melting was not observed. The glass transition temperature ( $T_g$ ) increased with  $M_n$ , as shown in Figure 3. In general,  $M_n$  dependence on  $T_g$  is expressed by Fox and Flory<sup>23</sup> as,

$$T_g = T_{g\infty} - \frac{K}{M_n} \quad (1)$$

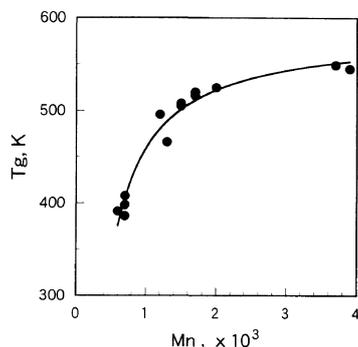
**Table I.** Radical polymerization of CHMI with ACPA at 60°C

Run	Solvent <sup>a</sup>	Feed		Time h	Yield %	$M_n^b$ $\times 10^{-3}$	$M_w^b$ $\times 10^{-3}$	[COOH] <sup>c</sup> mmol g <sup>-1</sup>	$N_C^d$	$T_g^e$ °C
		[CHMI]	[ACPA]							
		mol L <sup>-1</sup>	$\times 10^2$ /mol L <sup>-1</sup>							
D1	DOX	0.46	0.12	24	54.6	3.7	7.0	0.58	2.1	276
D2	DOX	0.46	0.46	16	83.1	2.0	4.4			252
D3	DOX	0.42	2.10	16	82.5	1.7	3.9	0.94	1.6	247
D4	DOX	0.42	4.20	16	82.3	1.7	3.9			243
D5	DOX	0.42	8.40	16	78.8	1.5	3.3			235
D6	DOX	0.42	16.80	16	74.4	1.2	2.9			223
D7	DOX	0.28	11.20	16	72.3	1.5	3.0	1.01	1.5	232
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T1	THF	0.46	0.05	24	37.3	3.9	7.8	0.36	1.4	272
T2	THF	0.46	0.46	16	88.1	0.7	1.0	1.53	1.1	113
T3	THF	0.28	0.56	16	58.1	1.3	2.5			193
T4	THF	0.28	0.70	16	75.4	0.7	1.0	2.48	1.7	135
T5	THF	0.28	2.80	16	59.2	0.6	0.7			118
T6	THF	0.28	5.60	16	72.8	0.7	0.9			126

<sup>a</sup> DOX, 1,4-dioxane; THF, tetrahydrofuran. <sup>b</sup> Measured by GPC based on standard polystyrene. <sup>c</sup> Measured by titration. <sup>d</sup> Number of COOH per PCHMI chain calculated from [COOH] and  $M_n$ . <sup>e</sup> Measured by DSC, rate = 10°C min<sup>-1</sup>.

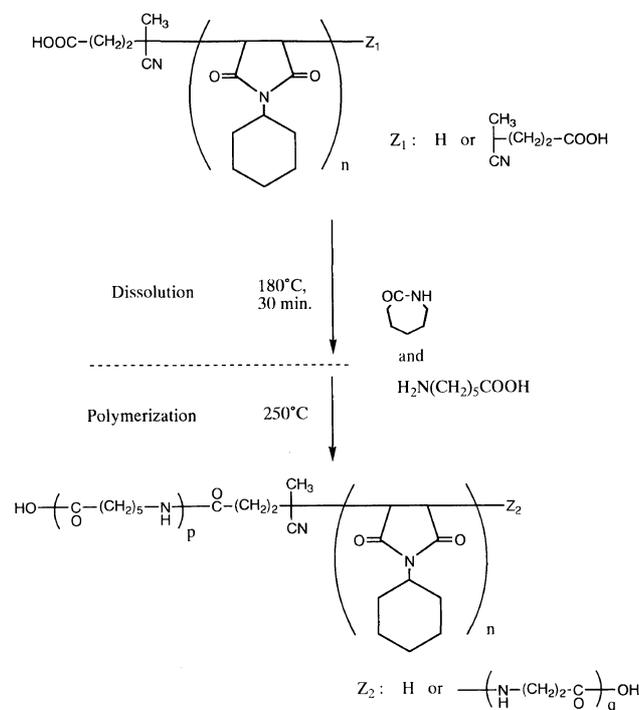


**Figure 2.** DSC curves of PCHMI having different molecular weight: (a) Run D1 ( $M_n=3700$ ), (b) Run T3 ( $M_n=1300$ ) and (c) Run T2 ( $M_n=700$ ).



**Figure 3.** Effects of  $M_n$  on  $T_g$  of PCHMI; experimental data (●) and curve fitting (—) with eq:  $T_g = T_{g\infty} - K/M_n$  ( $T_{g\infty} = 586$  K; and  $K = 1.26 \times 10^5$ ).  $M_n$  was measured by GPC based on standard polystyrene, and  $T_g$  by DSC (10°C min<sup>-1</sup>).

where  $T_{g\infty}$  is the limiting  $T_g$  at high molecular weight and  $K$  is a polymer specific constant. Fit of eq 1 was in fair agreement with the experimental data.  $T_{g\infty}$  and  $K$  were 586K (313°C) and  $1.26 \times 10^5$ , respectively.



**Scheme 2.** Synthesis of PA6-block-PCHMI.

#### Syntheses of PA 6-block-PCHMI

Several block copolymers have been prepared by the hydrolytic polymerization of CL with carboxyl group-terminated prepolymers.<sup>1</sup> In this study, it was presumed that imide rings of PCHMI are hydrolyzed as well as CL. Yumoto *et al.*<sup>24</sup> and Kruissink *et al.*<sup>25</sup> reported the polymerization of CL to be initiated with ACA in the absence of water. To avoid hydrolysis of imide rings, PA6-block-PCHMI were prepared using ACA, as shown in Scheme 2. PCHMI was dissolved in molten CL and thus copolymers were synthesized by the dissolution of PCHMI in molten CL at 180°C for 30 min, followed by heating at 250°C for a desired time. When PCHMI was dissolved in basic solvents such as *N,N*-dimethylformamide and dimethylsulfoxide, the solution turned red.<sup>19</sup>

The same was observed when PCHMI was dissolved in molten CL. When the reaction was complete, the solution and product turned brown. The  $^1\text{H}$  NMR spectrum of PA6-*block*-PCHMI is shown in Figure 4. Some signals based on PA6 and PCHMI were observed.

The polymerization of CL and ACA on addition of 4 wt% PCHMI (T1 in Table I) is summarized in Table II. Solution viscosity increased with reaction time, and became approximately constant after 4 h. As shown in Figure 5, the intensity of the signal (F) at 2.69 ppm, assigned to methylene protons of PA6 segments adjacent to amino groups, decreased with reaction time, compared with that (E) of methylene protons of PA6 segments adjacent to carboxyl groups. Hallden-Abberton reported

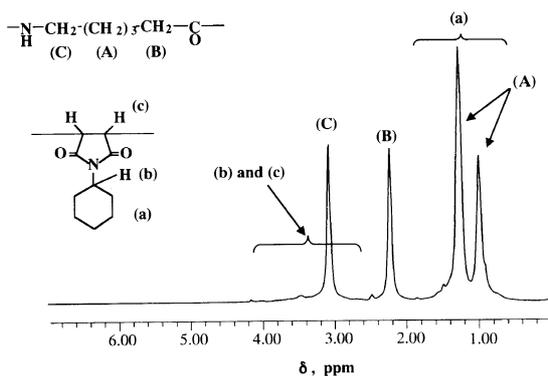


Figure 4.  $^1\text{H}$  NMR spectrum of PA 6-*block*-PCHMI (Run CP14) in  $\text{D}_2\text{SO}_4$ .

no grafting when polyamide and polyglutarimide, which has little acid and/or anhydride sites, are mixed at  $275^\circ\text{C}$  in an extruder.<sup>26</sup> This suggests that no reaction between amino groups of polyamide and imide groups of polyglutarimide occurs. Reaction between amino groups of PA6 and imide groups of PCHMI prevents the polymerization of PA6 segments, but the average number of repeating units for PA6 segments increases with reaction times. It is presumed, therefore, that reaction between amino groups of PA6 and imide rings little occurs as well as results of Hallden-Abberton's study. The decrease of amino groups of PA6 segments may be caused by reaction *via* carboxyl end groups of PCHMI. Since PA6 segments connecting PCHMI have no amino groups and all PA6 segments have carboxyl end groups, the molar fraction of PA6 segments not bonded to PCHMI,  $R_0$ , may be calculated as,

$$R_0 = \frac{[\text{NH}_2]_{\text{PA6}}}{[\text{COOH}]_{\text{PA6}}} = \frac{S_F}{S_E} \quad (2)$$

where  $[\text{NH}_2]_{\text{PA6}}$  and  $[\text{COOH}]_{\text{PA6}}$  are concentrations of amino and carboxyl end groups of PA6 segments,  $S_E$  and  $S_F$  are intensity of the signal (E) and signal (F).  $R_0$  decreased with reaction time and  $R_0$  for the copolymer CP5 in Table II could not be determined. More than 90% of PA6 segments may thus be bonded to PCHMI after 4 h at  $250^\circ\text{C}$  because  $R_0$  was below 0.1 in this measurement.

The average number of repeating units for PA6 seg-

Table II. Copolymerization of CL and ACA with PCHMI<sup>a</sup>

Run	Reaction time		Resulting				
	180–250°C <sup>b</sup>	250°C	Polymer <sup>c</sup>	$\eta_{\text{red}}^{\text{d}}$	Ln <sup>e</sup>	$R_0^{\text{f}}$	PCHMI <sup>g</sup>
	h	h					
CP1	0.8	0.0	39	0.28			
CP2	0.8	0.5	56	0.42	29	0.65	8
CP3	0.8	1.0	66	0.50	42	0.38	9
CP4	0.8	2.0	73	0.54	50	0.14	10
CP5	0.8	4.0	78	0.56	51	(<0.1)	10
CP6	0.8	6.0	80	0.58			

<sup>a</sup> CL/ACA/PCHMI (T1) = (0.85/0.11/0.04)<sub>weight</sub>. <sup>b</sup> Heated at  $180^\circ\text{C}$  for 30 min and raised to  $250^\circ\text{C}$  for about 20 min. <sup>c</sup> Insoluble part in methanol and THF. <sup>d</sup> Measured in *m*-cresol at  $25^\circ\text{C}$ ,  $c = 0.5 \text{ g dl}^{-1}$ . <sup>e</sup> Average number of repeating units for Nylon 6 block; calculated from  $^1\text{H}$  NMR data. <sup>f</sup> Molar fraction of PA6 segments which was not bonded to PCHMI. <sup>g</sup> Calculated from  $^1\text{H}$  NMR data.

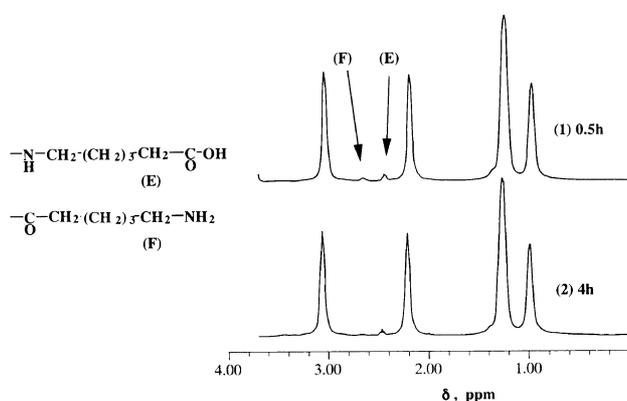


Figure 5.  $^1\text{H}$  NMR spectra of Nylon 6-*block*-PCHMI in  $\text{D}_2\text{SO}_4$ : (1) Run CP2 ( $250^\circ\text{C} \times 0.5 \text{ h}$ ); (2) Run CP5 ( $250^\circ\text{C} \times 4 \text{ h}$ ).

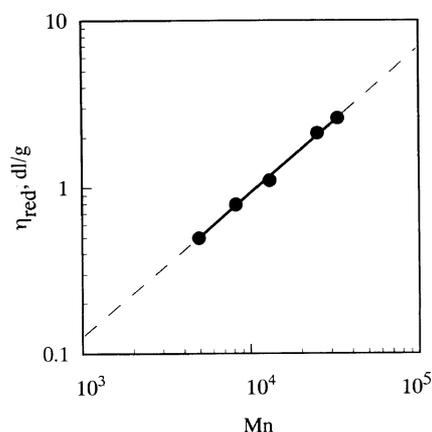
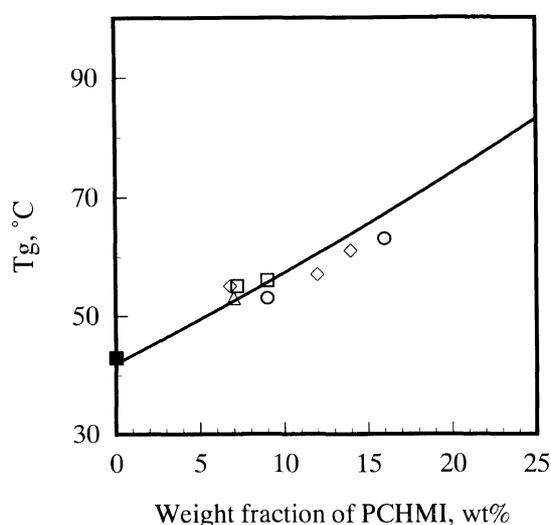


Figure 6. Relationship between  $\eta_{\text{red}}$  and  $M_n$  of PA6 homopolymer.  $\eta_{\text{red}}$  was measured in *m*-cresol at  $25^\circ\text{C}$ ,  $c = 0.5 \text{ g dl}^{-1}$ .  $M_n$  was calculated from end group concentration.

**Table III.** Syntheses of PA6-*block*-PCHMI and their thermal properties

Run	Feed <sup>a</sup>		Copolymers			Thermal properties		
	PCHMI <sup>c</sup>		PCHMI <sup>d</sup>	$\eta_{red}$ <sup>e</sup>	Ln <sup>f</sup>	$T_{gRSA}$ <sup>g</sup>	$T_{gDSC}$ <sup>h</sup>	$T_m$ <sup>h</sup>
	Run No.	wt%	wt%	dl g <sup>-1</sup>		°C	°C	°C
PA6 <sup>b</sup>						79	42	221
CP11	T1	15	14	0.38	44		61	214
CP12	T1	9	12	0.48	51		57	216
CP13	T1	5	7	0.60	68	98	55	218
CP14	T3	10	16	0.43	46		63	216
CP15	T3	5	9	0.60	62		53	219
CP16	T6	5	7	0.72	66	94	52	220
CP17	D7	10	9	0.48	58	94	56	218
CP18	D7	5	7	0.60	75	91	55	220

<sup>a</sup> Polymerization at 250°C for 5 h. <sup>b</sup>  $M_n = 1.3 \times 10^4$ . <sup>c</sup> See Table I,  $T_g = T1(272^\circ\text{C})$ ,  $T3(193^\circ\text{C})$ ,  $T6(126^\circ\text{C})$ , and  $D7(232^\circ\text{C})$ . <sup>d</sup> Calculated from <sup>1</sup>H NMR data. <sup>e</sup> Measured in *m*-cresol at 25°C,  $c = 0.5 \text{ g dl}^{-1}$ . <sup>f</sup> Average number of repeating units for PA6 segments; calculated from <sup>1</sup>H NMR data. <sup>g</sup> Measured by a dynamic mechanical spectrometer, temperature of maximum  $E''$ . <sup>h</sup> Measured by DSC, rate  $10^\circ\text{C min}^{-1}$ .



**Figure 7.** Effects of PCHMI content on  $T_g$  of PA6-*block*-PCHMI obtained from Run T1 ( $T_g = 272^\circ\text{C}$ ) ( $\diamond$ ), Run T3 ( $T_g = 193^\circ\text{C}$ ) ( $\circ$ ), Run T6 ( $T_g = 126^\circ\text{C}$ ) ( $\triangle$ ), and Run D7 ( $T_g = 232^\circ\text{C}$ ) ( $\square$ ): PA6 homopolymer ( $M_n = 1.3 \times 10^4$ ;  $T_g = 43^\circ\text{C}$ ) ( $\blacksquare$ ) and calculated data (—) by Fox equation.

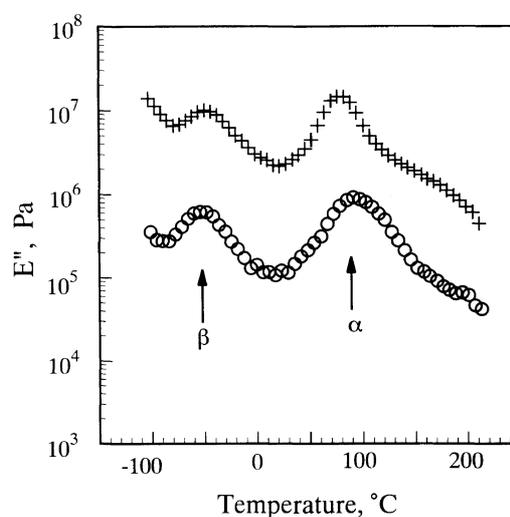
ments, Ln, of the copolymer obtained for 4 h was 51 (CP5 in Table II). This indicates that a chain of the copolymer has 102 units of ACA corresponding to  $1.2 \times 10^4 \text{ g mol}^{-1}$ , if the copolymer is a complete ABA type. Figure 6 gives the relationship between  $M_n$  and  $\eta_{red}$  for the PA6 homopolymer expressed by,

$$\eta_{red} = 3.08 \times 10^{-4} \cdot M_n^{0.87} \quad (3)$$

between  $M_n = 4000$  and  $30000$ .  $\eta_{red}$  for the copolymer (0.56; CP5) was much smaller than that (1.09) calculated by eq 3 when  $M_n$  was  $1.2 \times 10^4$ . This is because PA6-*block*-PCHMI contains ABA and AB.

#### Thermal Properties of PA6-*block*-PCHMI

The thermal properties of PA6-*block*-PCHMI prepared from PCHMI having different  $T_g$  are summarized in Table III.  $T_m$  of PA6 slightly decreased with PCHMI content.  $T_g$  of copolymers measured by DSC increased with the weight fraction of PCHMI and did not depend on  $T_g$  of the original PCHMI, as shown in Figure 7. The relationship between the  $T_g$  and composition of co-



**Figure 8.** Relationship between loss modulus  $E''$  and temperature of PA6-*block*-PCHMI: Run CP18 ( $\circ$ ) and PA6 homopolymer ( $+$ ). Run CP 18 ( $\circ$ ): shifted vertically ( $\times 0.1$ ) for clarity.

polymer is generally expressed by the Fox equation,<sup>27</sup>

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \quad (4)$$

where  $W_x$  is the weight fraction of  $x$  component. Change in  $T_g$  depending on  $M_n$  is attributed to the ends of the polymer chains having more free volume than the same number of atoms in the middle of the chain.<sup>28</sup> Since the end groups, COOH, in the original PCHMI little exist in the copolymer,  $T_g$ s of copolymers were calculated by eq 4, using  $313^\circ\text{C}$  ( $T_{g\infty}$  of eq 1) as  $T_g$  of PCHMI and  $42^\circ\text{C}$  as that of PA6. The experimental results were consistent with the solid line calculated by eq 4, as shown in Figure 7.

Figure 8 shows the relationship between loss modulus  $E''$  and temperature for PA6-*block*-PCHMI and PA6 homopolymer. The alpha transition ( $T_{gRSA}$ ) of the copolymer became higher than that of PA6, as shown in Table III. Only one  $T_g$  of the block copolymer was obtained by DSC and dynamic mechanical measurements. PA6 and PCHMI segments in the PA6-*block*-PCHMI would thus appear to form a homogeneous phase.

## CONCLUSIONS

1. Carboxyl group-terminated PCHMIs were obtained by the radical polymerization of CHMI with ACPA as initiator under several conditions. The number of carboxyl groups per polymer chain was smaller than 2.0.

2. PCHMI had different  $T_g$ , depending on the molecular weight.  $M_n$  dependence on  $T_g$  could be expressed by the description of Fox and Flory;  $T_{g\infty}$  and  $K$  were 313°C and  $1.26 \times 10^5$ , respectively.

3. Block copolymers consisting of PA6 and PCHMI were prepared by melt-polymerization of CL, ACA, and PCHMI.  $\eta_{red}$  of the copolymer became approximately constant after 4 h polymerization. The copolymers consisted of ABA and AB.

4.  $T_g$ s of the copolymers were independent of  $T_g$  of the original PCHMI, and increased with PCHMI content in the copolymer. The relationship between the  $T_g$  and composition could be expressed by the Fox equation.

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