

Synthesis and Characterization of Poly(ether urethane)-Nylon 6 Block Copolymer

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SYNOPSIS

Poly(ether urethane) (PEU) prepolymer terminated with isocyanate at both ends was prepared by controlling the mol ratio of poly(tetramethylene glycol) and methane diphenyl-4,4'-diisocyanate. Using this prepolymer as an activator, the anionic polymerization of ϵ -caprolactam was carried out to obtain PEU-nylon 6 block copolymer. The phase structure of the block copolymers was characterized on the basis of molecular interaction. The results of dynamic mechanical and thermal analyses revealed that the block copolymer films prepared via melt pressing and subsequent quenching had a one-phase structure. The equilibrium melting temperatures determined by a Hoffman-Weeks plot showed that the two blocks are miscible in the melt state. *N*-Trifluoroacetylation of the block copolymer led to the conclusion that this miscible behavior is due mainly to the specific interaction between urethane groups in PEU block and amide groups in nylon 6 block through hydrogen bonding.

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INTRODUCTION

A-B-A block copolymers, consisting of nylon 6 segments as the A blocks and polyether segments as the B blocks, have drawn great attention during the past decades because the introduction of polyether segments into nylon 6 improves the elastic deformation of fibers and the impact resistance of plastics. However, it is a matter of general knowledge that most block copolymers show microphase separation due to segmental incompatibility between the blocks.¹⁻³ On the other hand, urethane and amide groups are known to have strong self-associated intermolecular interactions through hydrogen bonding.⁴⁻¹⁰ Hence, if we introduce urethane groups into the polyether-nylon 6 block copolymer, it is expected that the prepared poly(ether urethane) (PEU)-nylon 6 block copolymer will have interesting morphological properties. Nevertheless, little attention has been given to this system.

This paper describes the relationship between the composition and molecular interaction of the PEU-nylon 6 block copolymer on the basis of measurements of dynamic mechanical and thermal properties.

EXPERIMENTAL

Reagents Used

Poly(tetramethylene glycol)s (PTMG)s (DuPont) were dried in a vacuum for 12 h at 80°C. Methane diphenyl-4,4'-diisocyanate (MDI) (Nihon Polyurethane) was freshly distilled and stored in a refrigerator. ϵ -Caprolactam (Ube) was dried in a vacuum for 3 days at room temperature over phosphorus pentoxide. Sodium hydride (Wako Pure Chem.), a 60% dispersion in mineral oil, was used as received.

Synthesis of PEU-Nylon 6 Block Copolymer

All the experiments and manipulations were carried out in a dry glass flask filled with dry nitrogen.

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Prepolymer was prepared at 75°C in an oil bath. A 500 mL flask equipped with a separating funnel, a mechanical stirrer, and a nitrogen inlet was charged with $(n + 1)$ mol of MDI. After the complete melting of MDI, n mol of PTMG was added dropwise through the separating funnel over 0.5–1 h with vigorous stirring. The viscosity of the mixture gradually increased; after ca. 3 h, the stirring was stopped and the reaction was continued for 15 h.

For the preparation of block copolymer, the reactor containing the above prepolymer was thermostatted at 105°C and molten ϵ -caprolactam was introduced with continuous stirring. When the mixture of the prepolymer and ϵ -caprolactam was completely mixed, sodium hydride was added with vigorous stirring. After 3–4 h, the stirring was stopped due to the increase of viscosity and the mixture was further reacted for 24 h. The crude product was cut into pieces and crushed with a pulverizer in liquid nitrogen. The crushed polymer was extracted with tetrahydrofuran (THF) and subsequently with trifluoroethanol and dried in a vacuum for 24 h at 50°C.

Preparation of Melt Pressed Films

The block copolymer was melted at 230°C between two Mylar films pressing with a hot press and subsequently quenched in liquid nitrogen. The prepared film was clearly transparent.

N-Trifluoroacetylation of Block Copolymers

Two grams of block copolymer was added into a 200 mL flask equipped with a reflux condenser connected with a tube filled with the molecular sieves of 5 Å and was suspended in 60 mL of pure dichloromethane. Then, a 2 molar excess of trifluoroacetic anhydride was added. The reaction mixture became homogeneous within a few hours and was further reacted for 24 h at 40°C. The solution was evaporated using a rotatory evaporator and the residual solvent was evacuated in a vacuum desiccator for about 10 h.

Determination of NCO Content¹¹

The PEU prepolymer was allowed to react with an excess of di-*n*-butylamine. After the reaction had been completed, the residual di-*n*-butylamine was determined by back titration with the standard hydrochloric acid using Bromophenol blue as an indicator, and the NCO content of the prepolymer was calculated.

Thin-layer Chromatography (TLC)

Aluminum sheets coated with Kieselgel 60 (Merck) were activated by heating at 110°C for 30 min. Stock solutions of the samples for TLC were prepared by dissolving 20 mg of each sample in 10 mL of *m*-cresol, and 15–20 μ g of the sample from solution was spotted on the starting line of the TLC sheet with a microsyringe. The spotted sheet was dried for 30 min at 100°C in a vacuum, and the spots were developed in a closed chamber at room temperature by the usual method.¹² The eluents were a mixture of chloroform/methanol (70/30 by volume) for the solubility-controlled phase-separation process and phenol/THF/methanol (10.5/3.5/1 by volume) for the polarity-controlled adsorption process. When the solvent front reached 10 cm from the starting line, the development was stopped. The TLC sheets were dried in a vacuum oven at 110°C for 1 h. The positions of the samples were visualized by heating the plate in an oven after the sheet was immersed in 1% methanolic iodine solution. Nylon 6 for TLC reference was obtained from Tong Yang Nylon Co. and was used after extraction with ethanol to remove oligomers.

Inherent Viscosity

The viscosity of 0.6% solution of the block copolymer in *m*-cresol was measured with an Ubbelohde viscometer at 25°C in *m*-cresol. Thus, the inherent viscosity of the block copolymer was obtained by determining the relative viscosity of the block copolymer solution.

IR Spectroscopy

All the IR spectra were acquired on a Bruker IFS-88 Fourier transform infrared spectrometer at a resolution of 2 cm⁻¹ at room temperature.

NMR Spectroscopy

NMR spectra were recorded at room temperature on a Bruker AC-80 (80 MHz) FT-NMR spectrometer in phenol/chloroform D (7/3 by volume) mixture with tetramethylsilane as an internal standard.

Thermal Analysis

A Perkin-Elmer Model DSC-2 differential scanning calorimeter was used. Program (a), with a heating rate of 20°C/min, was used for the melt-pressed/quenched samples to observe their melting temper-

atures. Program (b) was used for studying the isothermal crystallization of the block copolymers. Under this program, the samples were maintained at 230°C for 5 min and then cooled to the crystallization temperature (T_c) at a cooling rate of 360°C/min. The samples were maintained at T_c for 30 min and then cooled to 50°C. In succession, the samples were heated at a rate of 20°C/min.

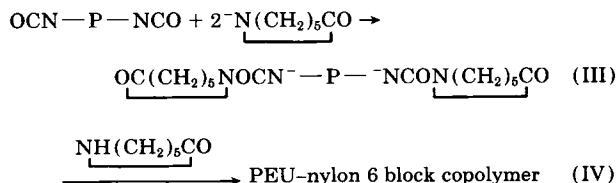
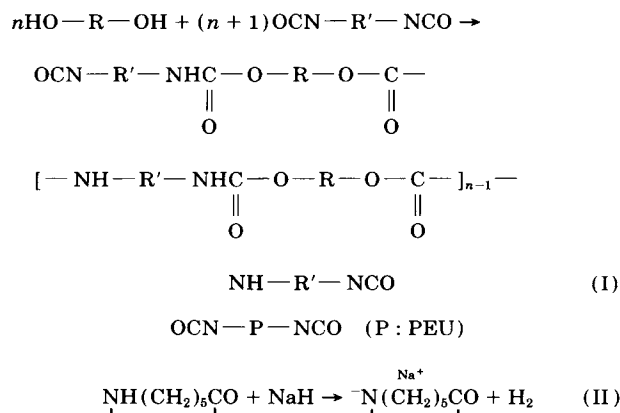
Dynamic Mechanical Measurement

The measurement was made on a Rheometrics Dynamic Spectrometer RDS II using the film/fiber attachment. The temperature range was from -120 to 180°C under a nitrogen atmosphere and the frequency employed was 2.5 Hz.

RESULTS AND DISCUSSION

Synthesis of PEU-Nylon 6 Block Copolymer

PEU-nylon 6 block copolymers were synthesized in two steps according to the following reaction schemes:



where HO-R-OH = PTMG and OCN-R'-NCO = MDI.

The PEU prepolymers terminated with the isocyanate group at both ends were prepared by controlling the mol ratios of PTMG and MDI (Scheme I). The reaction was followed by the anionic block copolymerization of ϵ -caprolactam (Schemes II, III, and IV). Anionic lactam polymerization essentially requires anhydrous conditions,¹³ since the presence of water can make the catalyst inactive. Furthermore, the water can react with the isocyanate in the prepolymer. Hence, all experiments were carried out in a flash-dried glass flask filled with dry nitrogen and all the reagents were sufficiently dried.

In the IR spectrum of PEU prepolymer, the absorption at 3600 cm^{-1} , assignable as the terminal hydroxyl group of PTMG, disappeared completely. On the other hand, the absorption at 2270 cm^{-1} assigned to the isocyanate groups and the absorptions due to the urethane groups at 3300 cm^{-1} and around 1530 cm^{-1} (NH) and 1734 cm^{-1} (ester carbonyl), as well as the aromatic ring absorptions at 1600 cm^{-1} and 1500 cm^{-1} , appeared. These results strongly suggest that chain extension occurred, forming urethane groups, and the chain ends are terminated with isocyanate groups. The preparation conditions of PEU prepolymer are summarized in Table I. Measured NCO content was a little bit higher than the theoretical value based on a PTMG/MDI molar ratio in the feed. This was probably due to the high viscosity of the reactant, resulting in unreacted MDI in the prepolymer.

Table I PEU Prepolymers

Sample code	MW of PTMG	Materials in the Feed			NCO%	
		PTMG (g)	MDI (g)	PTMG/MDI mol ratio	Theoretical	Measured
1000A	1000	100	30.03	5/6	1.29	1.40
1000B	1000	100	28.60	7/8	0.93	1.00
1000C	1000	100	27.80	10/11	0.73	0.96
1000D	1000	100	26.81	14/15	0.47	0.52
650A	650	65	26.81	14/15	0.65	0.76
1400	1400	100	20.86	6/7	0.87	1.02
2000A	2000	70	10.50	5/6	0.73	0.95
3000	3000	100	11.20	3/4	0.84	0.97

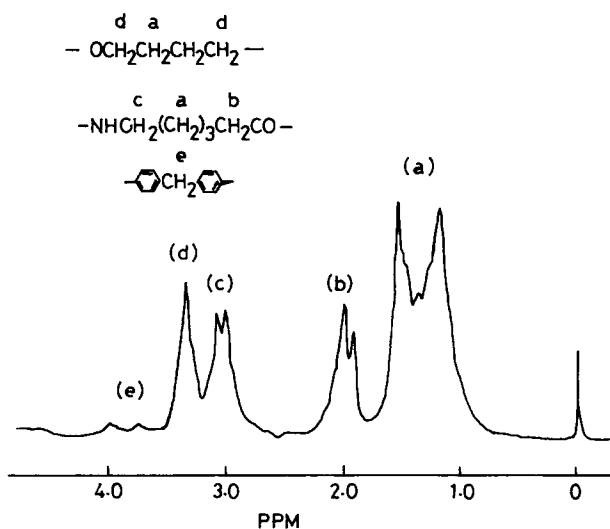


Figure 1 A typical NMR spectrum of PEU-nylon 6 block copolymer.

The IR spectrum of PEU-nylon 6 block copolymer showed absorption at around 1640 cm^{-1} assigned to the amide I band of nylon 6. However, amide II bands at 3300 cm^{-1} and ca. 1540 cm^{-1} were overlapped with the absorbance of urethane groups. A typical NMR spectrum and assignments are given in Figure 1. This spectrum could be analyzed by superposing the spectrum on that found for the corresponding homopolymer. Based on these peak assignments, the composition of PTMG and TMG for

the PEU-nylon 6 block copolymer synthesized was determined by comparing the relative areas of peak c and peak d (Table II). Here, PTMG mol % is identical to the mol % of urethane groups in the block copolymer and TMG mol % means the relative block length of PEU block with respect to that of nylon 6.

The purity of block copolymers was tested by TLC. Figure 2 shows typical thin-layer chromatograms of PEU-nylon 6 block copolymer, nylon 6, and PEU prepolymer obtained with chloroform/methanol (70/30 by volume) by the solubility-controlled phase-separation process. The PEU prepolymer migrated up to the solvent front, while the PEU-nylon 6 block copolymer and nylon 6 remained on the starting level due to the insoluble property of block copolymer and nylon 6 in the developer. A preliminary TLC test for MDI showed that MDI moved up to near the solvent front, showing a horizontally spread spot without tailing. Considering these results, it is evident that the block copolymer contains neither the homo PEU prepolymer nor MDI. Figure 3 shows typical thin-layer chromatograms of nylon 6 and PEU-nylon 6 block copolymer obtained with phenol/THF/methanol (10.5/3.5/1 by volume) according to the polarity-controlled adsorption process. Here, first, we should consider the occupation of the active site on silica gel by methanol molecules. Then, the interaction between the polymer and the developer is stronger than that between the polymer and the adsorbant, and this induces the

Table II Chemical Composition and Physical Properties of PEU-Nylon 6 Block Copolymers

Sample Code	PTMG (mol %)		TMG (mol %)	η_{inh}^b	T_g^c (°C)	T_m^d (°C)
	In Feed	Measured ^a				
1000A-N	2.69	2.42	25.3	0.75	47	202
1000B-N	3.86	4.76	40.5	0.84	36	193
1000C-N	5.55	6.69	49.4	0.89	33	182
1000D-N	6.90	7.78	53.4	0.98	28	180
650A-N	7.31	9.23	47.2	1.01	25	176
1400-N	3.19	4.27	46.1	1.21	38	198
2000A-N	2.69	2.97	45.7	1.47	43	199
3000-N	1.64	1.55	39.5	1.41	—	207
Nylon 6					59	218
650					-22	
1000					-38	
2000					-56	

^a Measured by NMR (phenol/ CDCl_3).

^b Inherent viscosity, $\ln \eta_{r/c}$ (η_r : relative viscosity; c: 0.6% in *m*-cresol at 25°C).

^c T_g : glass transition temperature measured by RDS.

^d T_m : melting temperature measured by DSC (20°C/min).

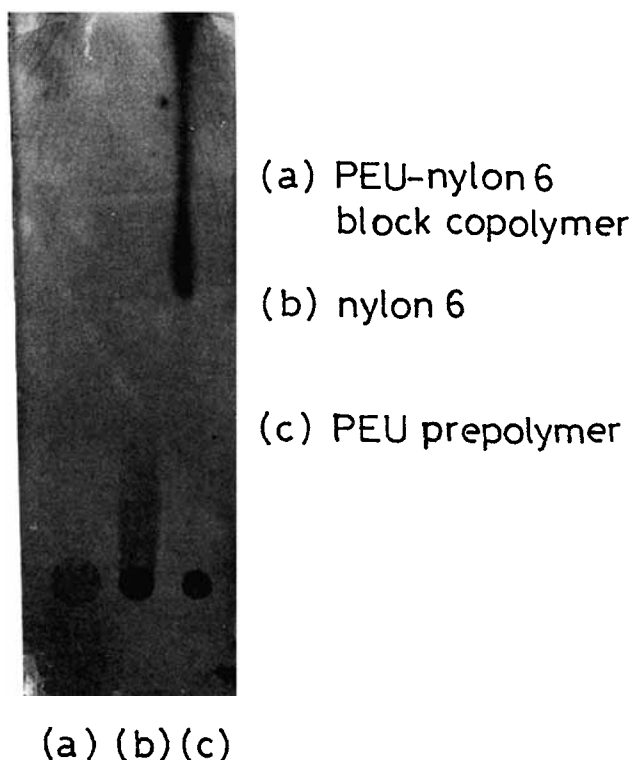


Figure 2 Typical thin-layer chromatograms developed with chloroform/methanol mixture (7/3 by volume).

polymers to migrate. On the other hand, the interaction between the developer and the PEU-nylon 6 block copolymer is stronger than that between the developer and nylon 6. Thus, the PEU-nylon 6 block copolymer migrates up to the solvent front, while the migration of nylon 6 homopolymer is retarded due to the polarity difference. The above consideration is a possible explanation for the results shown in Figure 3 and it is suggested that there is no nylon 6 homopolymer in the PEU-nylon 6 block copolymer synthesized. The presence of diblock copolymer, which might be formed due to the prepolymer terminated with the isocyanate at one end, would be expected. However, the amount was thought to be negligible.

The PEU prepolymer was soluble in molten ϵ -caprolactam and the reaction system was thought to be homogeneous. Hence, polymerization in the absence of solvent was possible. The differences between PTMG mol % in the feed and that found in the block copolymer (Table II) can be explained as follows: One explanation is the sublimation of ϵ -caprolactam due to the flow of dry nitrogen gas throughout the reaction. Another one may be the limited mobility of monomers due to high viscosity

of the mixture, which was almost solidified after 5–6 h, thus resulting in residual unreacted monomer. Homopolymerization may also have occurred due to free MDI in the prepolymer. A polymer cleavage reaction, which may occur by an attack of an activated monomer anion to an amide linkage of a polymer chain, seemed not to be dominant under this mild condition used (105°C). In fact, monomers and homopolymers found in the purification process amounted to less than 15%, which verifies that the block copolymerization was successfully accomplished. It was not possible to assign a molecular weight to the block copolymer owing to the lack of a suitable molecular weight/viscosity relationship.

Most block copolymer systems related to the anionic polymerization of ϵ -caprolactam such as polystyrene-*b*-nylon 6^{14–18} or polybutadiene-*b*-nylon 6^{16,18,19} have an inevitable condition of heterogeneous reaction due to the low solubility of ϵ -caprolactam in corresponding prepolymers. This may make the active chain ends of prepolymer less accessible to the monomer or monomer anion. Hence, it is note-

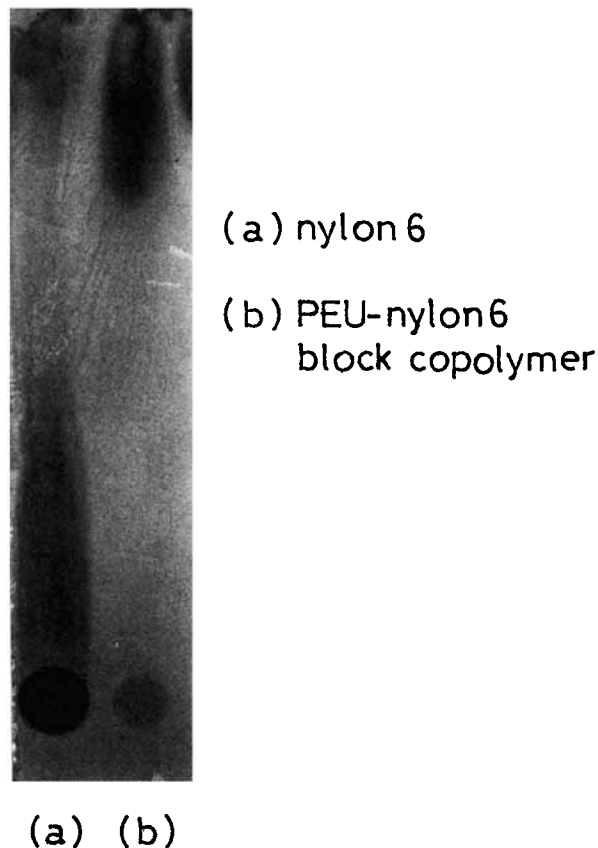


Figure 3 Typical thin-layer chromatograms developed with phenol/THF/methanol mixture (10.5/3.5/1 by volume).

worthy that the block copolymerization yield was found to be higher than 80%.

Phase Behavior of Block Copolymer Films Prepared via Melt Pressing and Subsequent Quenching

Dynamic Mechanical and Thermal Analyses

It is well known that most block copolymers show microphase separation as a consequence of the positive free energy of mixing between the polymer blocks. Dynamic mechanical measurements have been extensively used for the elucidation of phase structure of the block copolymers. In the microphase-separated block copolymers, two distinct loss tangent peaks appear at temperatures corresponding to the maxima for each respective homopolymer. In contrast, a single intermediate loss tangent peak

would be expected from a single-phase system of mixed composition.

Figure 4 shows the typical temperature dependence of the dynamic Young's modulus E' and the loss factor $\tan \delta$ for films of the block copolymer 1000C—N, as well as the prepolymer 1000 and nylon 6. The maxima of the loss curves for the prepolymer 1000 and nylon 6 are located at -38 and 59°C , respectively, which give an indication of the onset of their glass transition process at these frequencies. On the other hand, the block copolymer 1000C—N exhibited only a single peak and the temperature at the peak was between -38 and 59°C . The $\tan \delta$ peak at around -60°C , which appeared also in nylon 6 homopolymer, can be attributed to the effect of moisture²⁰ or crank-shaft-type motion involving an unbonded amide group and several methylene carbon groups.²¹ The main loss tangent

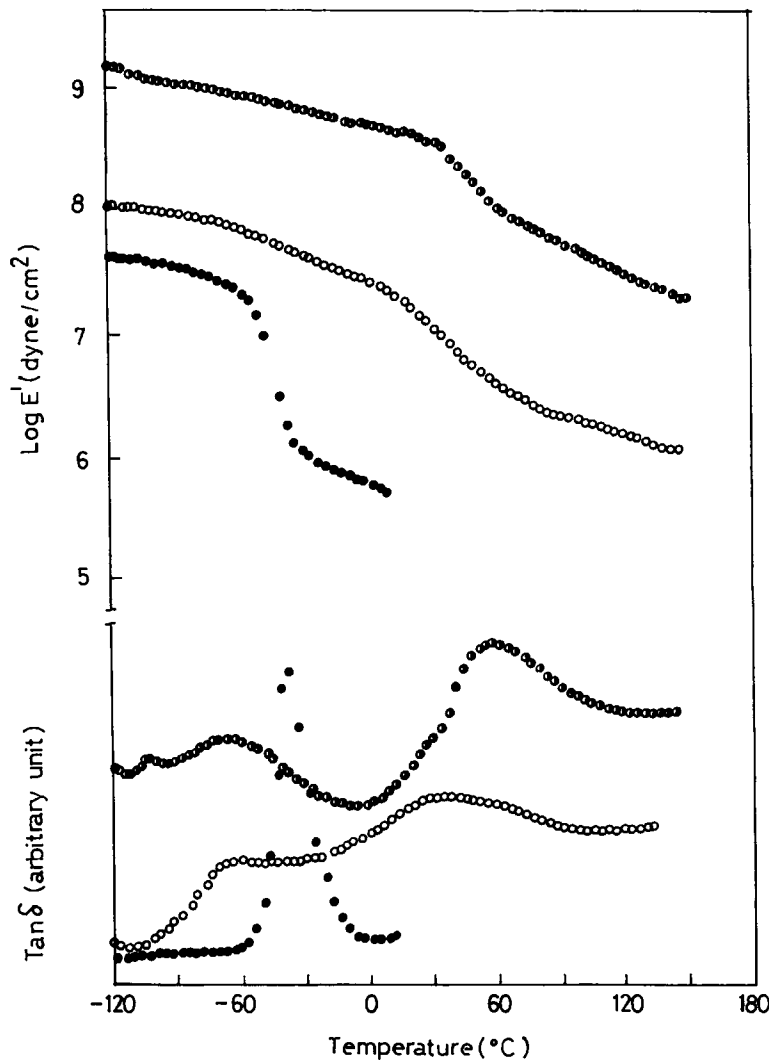


Figure 4 Dynamic mechanical spectra of (●) nylon 6, (○) 1000C—N, and (●) 1000.

peaks of all the block copolymers shifted down in comparison with that of the nylon 6 homopolymer, and no peaks corresponding to the glass transition of the PEU prepolymer were observed. The fact that the PEU-nylon 6 block copolymers exhibited only a single loss tangent peak is indicative of the absence of microphase separation, suggesting that some interactions exist between the PEU and nylon 6 blocks.

The glass transition temperatures (T_g) and melting temperatures (T_m) of block copolymers are listed in Table II. The melting temperatures of the block copolymers were lowered in comparison with that of the nylon 6 homopolymer. This phenomenon bears a close similarity to the melting temperature depression in the crystalline polymer-diluent system, which will be discussed later.

The T_g and T_m of the block copolymers were plot-

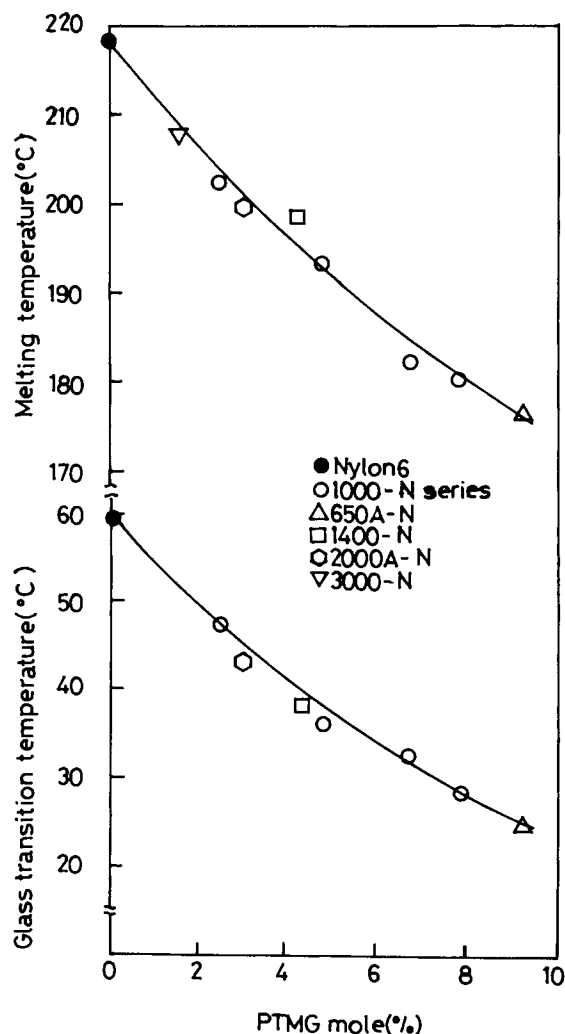


Figure 5 Plots of glass transition and melting temperatures vs. PTMG mol % in the block copolymers.

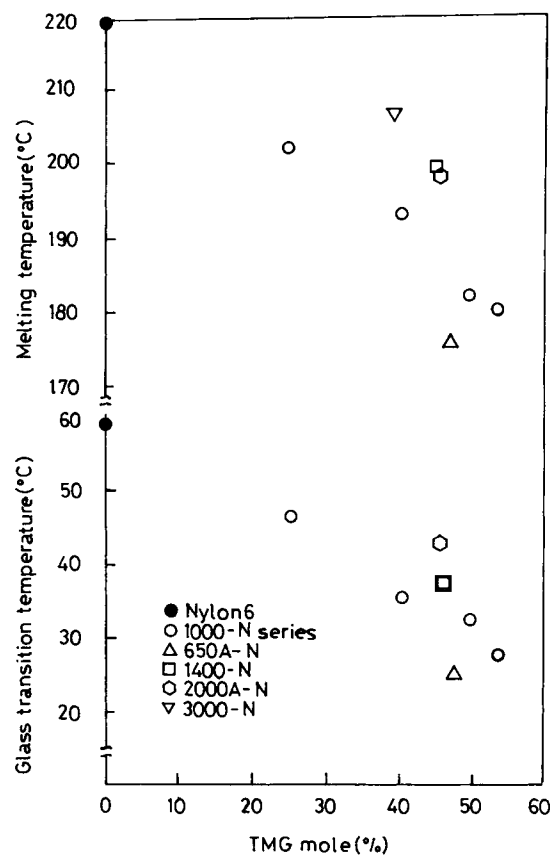


Figure 6 Plots of glass transition and melting temperatures vs. TMG mol % in the block copolymers.

ted against PTMG mol % and TMG mol % to clarify what factors affect the miscibility behavior, i.e., the interactions between the blocks. As Figure 5 shows, it is remarkably interesting that the T_g and T_m of the block copolymers are closely related to PTMG mol %. With increasing PTMG mol %, i.e., mol % of urethane groups, T_g 's were systematically depressed. However, as illustrated in Figure 6, the T_g and T_m of the block copolymers were scattered when these were plotted against TMG mol %. (Even if the block copolymers had a similar TMG content, T_g 's were different.)

Taking into account the fact that poly(propylene oxide)-segmented nylon 610 (Refs. 22 and 23) and poly(tetramethylene oxide)-segmented nylon 610 (Ref. 24) multiblock copolymers, composed of poly(ether and nylon segments but not containing urethane groups, show microphase-separated structure, it is suggested that the miscibility behavior of each block in the present block copolymer system can be attributed to the interaction between the urethane groups in PEU block and the amide groups in nylon 6 block, probably due to hydrogen bonding.

Isothermal Crystallization

The present block copolymer system shows a melting temperature depression. Equilibrium melting temperatures were determined to clarify if the melting temperature depression is due to a diluent effect or to a morphological one.

The depression in the melting temperature of a semicrystalline polymer in a mixture is due to a decrease of the chemical potential of the amorphous (and miscible) phase of the sample that is composed of the two polymers. In this case, it has been shown that^{25,26}

$$1/T_m - 1/T_m^0 = \frac{RV_{2u}}{H_{2u}V_{1u}} \chi_{12}V_1^2 \quad (1)$$

where T_m and T_m^0 are the equilibrium melting temperatures of the semicrystalline polymer in the blend (in this case, the block copolymer) and in the pure form (in this case, nylon 6 homopolymer), respectively; R , the gas constant; H_{2u} , the enthalpy of fusion per mole of repeating unit of component 2; V_{iu} , the molar volume of component i ; and χ_{12} , the thermodynamic interaction parameter. For the present block copolymer system, component 1 is the PEU block and component 2 is the nylon 6 block. In a more suitable form, eq. (1) may be written as

$$\Delta T_m = T_m^0 - T_m = T_m^0(V_{2u}/H_{2u})BV_1^2 \quad (2)$$

with $B = RT_m\chi_{12}/V_{iu}$, where B is the interaction energy density characteristic of the polymer pair. Equation (1) is only valid if the melting temperatures used are equilibrium values, since this equation does not take into account kinetic contributions to the melting temperature. The kinetic contributions to the melting temperature arise because polymer crystals are formed at temperatures below their equilibrium melting temperatures. Perfect crystals can, in principle, be grown at T_m (or T_m^0), but it takes an infinitely long time. At lower temperatures, thinner lamellae develop, the melting points of which are below T_m (or T_m^0). To get rid of this kinetic contribution to the melting point without measuring lamellar thickness, it is sufficient to determine the equilibrium melting temperatures by the Hoffman-Weeks extrapolation method²⁷:

$$T'_m = T_m^0(1 - 1/n) + T_c/n \quad (3)$$

where n is the ratio of the lamellar thickness to the thickness of the initial nucleus at the crystallization temperature, T_c , and T'_m is the experimental melting temperature.

Let $1/n = \phi$; then, eq. (3) becomes

$$T_m^0 - T'_m = \phi(T_m^0 - T_c) \quad (4)$$

where ϕ is a stability parameter depending on the crystal thickness and assumes a value between 0 and 1. $\phi = 0$ implies $T'_m = T_m^0$. Therefore, the crystals are stable at $\phi = 0$ and inherently unstable at $\phi = 1$.

Nylon 6 isothermally crystallized at various temperatures exhibited characteristic multiple endotherms as shown in Figure 7. The peak at the lowest temperature (T_{m0}), which was always observed at a temperature of about 10°C higher than the isothermal crystallization temperature (T_c), is due to the melting of small and unstable crystals formed during annealing. The peak at the middle temperature (T_{m1}) is the main one, corresponding to the melting of lamellar crystals. T_{m1} is highly dependent on the T_c and increases linearly with T_c . The peak at the highest temperature (T_{m2}), corresponding to the melting of crystals formed by the rearrangement of lamellar crystals during heating, was almost constant.²⁸ Figure 8 shows the Hoffman-Weeks plots of the melting endotherms, T_{m0} , T_{m1} , and T_{m2} for the isothermally crystallized nylon 6. The main endotherms, T_{m1} , increased with T_c and a straight line could be reasonably drawn up to the reference $T'_m = T_c$ line [eq. (3)]. The equilibrium melting temperature of nylon 6 was then calculated by extrapolation with a least-square analysis and was found to be 231.5°C, which is slightly lower than the literature value.²⁹

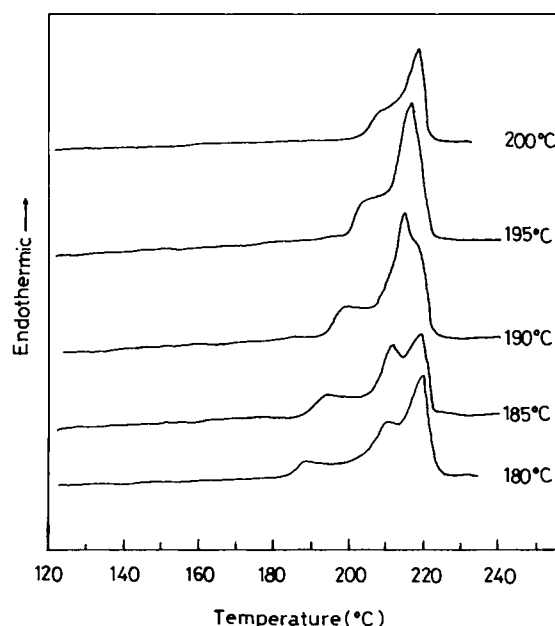


Figure 7 DSC melting endotherms for isothermally crystallized nylon 6 at various temperatures.

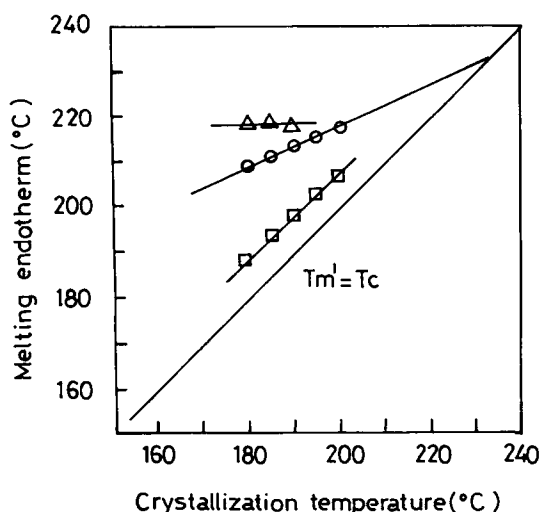


Figure 8 Hoffman-Weeks plots of melting endotherms for isothermally crystallized nylon 6: (\square) T_{m_0} ; (\circ) T_{m_1} ; (\triangle) T_{m_2} .

Figure 9 illustrates the Hoffman-Weeks plots for isothermally crystallized block copolymers including nylon 6 homopolymer and calculated data are summarized in Table III. The equilibrium melting temperatures obtained were also plotted against PTMG mol % in the block copolymer (Fig. 10).

The following considerations may be made, if the trend of the curve $T'_m - T_c$ is examined in detail:

- (i) At the same T_c , the melting temperature of T_{m_1} of the block copolymer is lower than that of pure nylon 6.

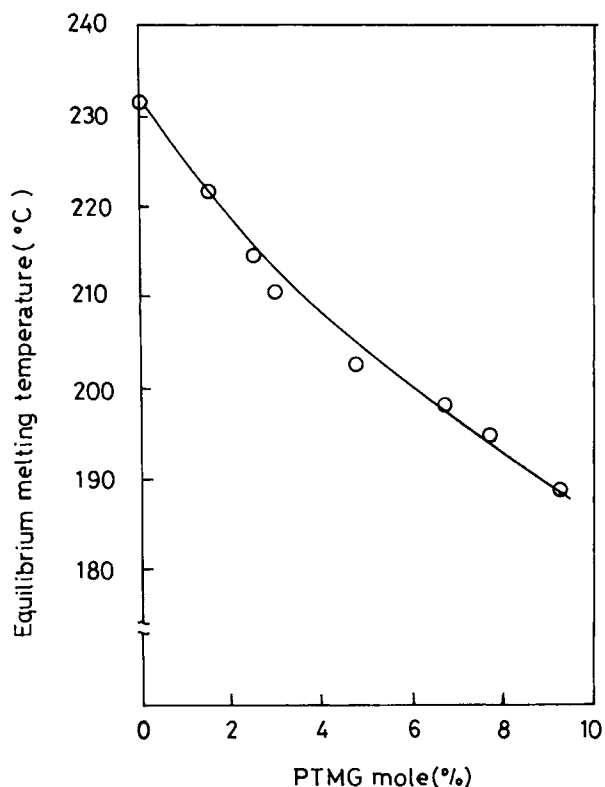


Figure 10 Plots of equilibrium melting temperature (T_{m_0}) vs. PTMG mol % in the block copolymers.

- (ii) The Hoffman-Weeks plots extrapolate to different equilibrium melting temperatures.
- (iii) The values of the slope are independent of

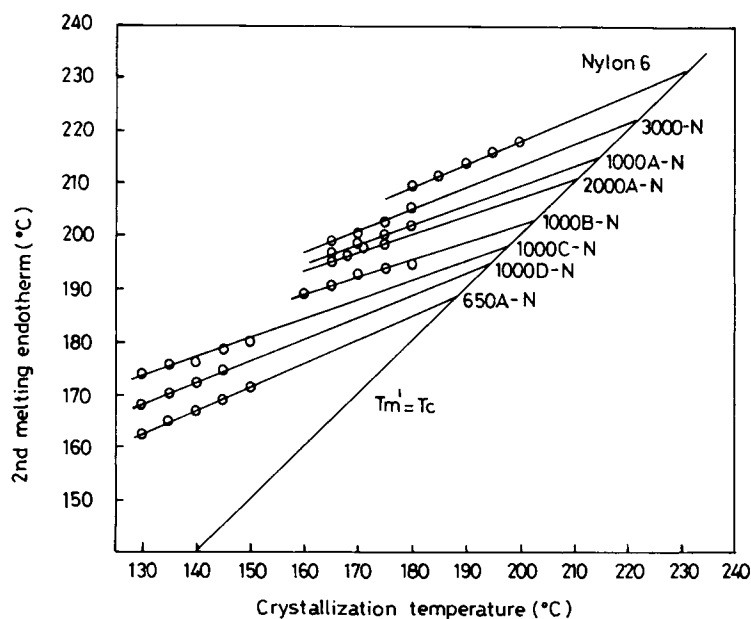


Figure 9 Hoffman-Weeks plots of second melting endotherm, T_{m_1} , for isothermally crystallized block copolymers.

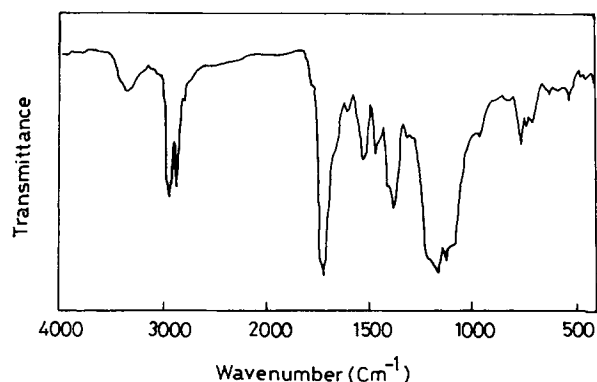


Figure 11 A typical IR spectrum of *N*-trifluoroacetylated block copolymer.

the block copolymer composition, i.e., ϕ is almost constant ($\phi = 0.3\text{--}0.4$).

- (iv) The equilibrium melting temperatures of the block copolymer decrease with the increase in PTMG mol %.

According to Nishi and Wang,²⁵ the first, second, and third of the above explanations indicate that the melting temperature depression is primarily ascribed to the diluent effect of the noncrystallizable polymer on the chemical potential of the crystalliz-

Table III Data Obtained from Hoffman–Weeks Plots for PEU–Nylon 6 Block Copolymers

Sample Code	T_m^0 (°C)	ΔT_m^a (°C)	ϕ^b
1000A-N	214.5	17.0	0.36
1000B-N	202.5	29.0	0.32
1000C-N	198.5	33.0	0.37
1000D-N	195.0	36.5	0.42
650A-N	188.5	43.0	0.44
2000A-N	210.5	21.0	0.34
3000-N	221.5	10.0	0.40
Nylon 6	231.5		0.40

^a ΔT_m : T_m^0 of nylon 6 – T_m^0 of block copolymer.

^b ϕ : stability parameter.

able component, as the two components are compatible in the melt. In addition, from the fact that the equilibrium melting temperature depression is due mainly to the increase of PTMG mol % in the block copolymer, it is suggested again that the melting temperature depression of the block copolymer can be ascribed to the interaction between the urethane groups in PEU block and the amide groups in nylon 6 block through hydrogen bonding. If the depression is due mainly to morphological effects such as reduction in crystal size or lamellar thick-

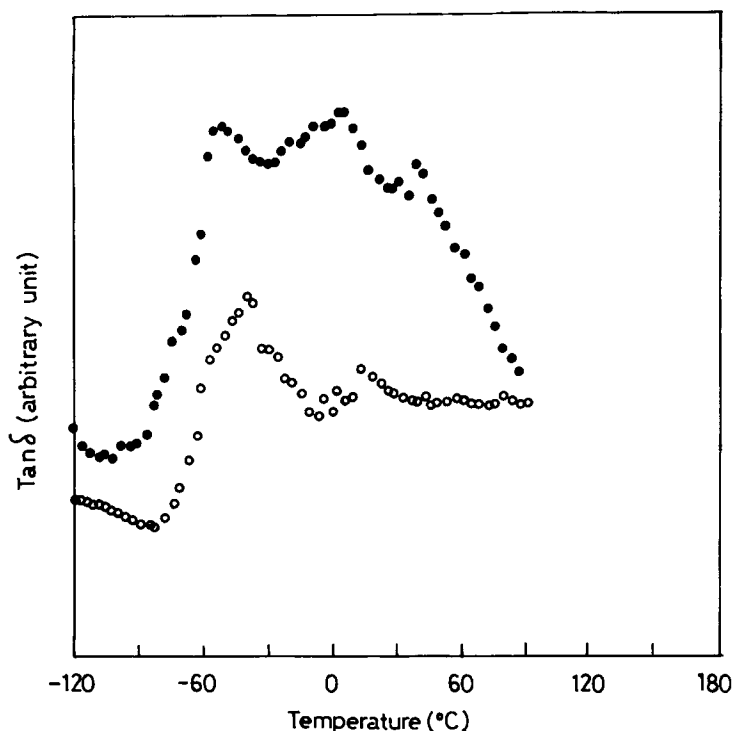
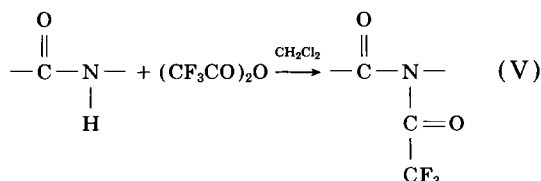


Figure 12 Tan δ curves of *N*-trifluoroacetylated PEU-nylon 6 block copolymers: (●) 1000C–N; (○) 1000B–N.

ness, then ϕ would be dependent upon the composition and the plots of $T'_m - T_c$ would have different slopes, extrapolating to a single equilibrium melting temperature.

N-Trifluoroacetylation of Block Copolymer

To eliminate the effect of the hydrogen bonding between the urethane and amide groups in the block copolymer, *N*-trifluoroacetylation of the amide groups in the nylon 6 block was carried out according to the following reaction scheme:



This reaction leads to nearly quantitative conversion without polymer degradation.³⁰ A typical IR spectrum of *N*-trifluoroacetylated block copolymer is shown in Figure 11.

The absorption at around 1640 cm^{-1} assigned to the hydrogen-bonded amide I band reduced as a shoulder and shifted to a higher frequency of 1730 cm^{-1} , which is overlapped with the absorption band of urethane carbonyl groups. The *N*-trifluoroacetylation of urethane groups is reported to be difficult in practice,³⁰ and it seemed to occur preferentially in the amide groups of nylon 6 block.

In Figure 12, the *N*-trifluoroacetylated block copolymers show a distinct loss tangent maximum at about -38°C , corresponding to that of PEU prepolymer, which could not be observed in the original block copolymer (Fig. 4). Other additional loss tangent maxima are ascribed to the unreacted amide groups in the block copolymer. The new appearance of the loss tangent maximum that corresponds to that of prepolymer seems to suggest that the microphase separation occurred between the PEU block and *N*-trifluoroacetylated nylon 6 block due to the breakage of hydrogen bonding. Hence, in conclusion, we can safely say that hydrogen bonding between urethane and amide groups plays an important role in the miscibility between the two blocks of the present block copolymer.

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