

Phase Behavior of Poly(ether urethane)-Nylon 6 Block Copolymer

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SYNOPSIS

Poly(ether urethane) (PEU)-Nylon 6 block copolymer film prepared via melt pressing and subsequent quenching in liquid nitrogen exhibited a one-phase structure due to the specific interaction between urethane groups in the PEU block and the amide groups in Nylon 6 block through hydrogen bonding. Contrary to this, the solvent cast film showed a microphase separated structure which had arisen from the poor solubility characteristics of the PEU block in the solvent. However, by heat treatment, the mutual miscibility of the block copolymer increased as a result of the hydrogen bonding formation. The block copolymer and Nylon 6 binary blend showed that these two polymers are compatible over the entire composition range mainly due to the specific interactions between the urethane and the amide groups in the blend through hydrogen bonding. The block copolymer in the ternary blend which consists of polyurethane (PU), Nylon 6, and the block copolymer prepared by melt extrusion was soluble in either of the PU and Nylon 6 homopolymers, inducing a homogenizing effect. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In the previous article,¹ polyether urethane (PEU)-Nylon 6 A-B-A triblock copolymer was synthesized and the phase structure of the block copolymers was characterized on the basis of molecular interaction. Several investigators²⁻⁵ have shown that the microstructures of the usual block copolymer films cast from different solvents differ from each other and from that of the films prepared via melt pressing. Likewise, the effect of using a liquid which is a good solvent for one of the blocks and a poor solvent for the other has shown a very significant change in both the phase morphology and the physical properties of the evaporated film. On the other hand, polyblends are usually made by mixing two or more homopolymers to obtain optimal properties in the end material, which cannot be attained from any of

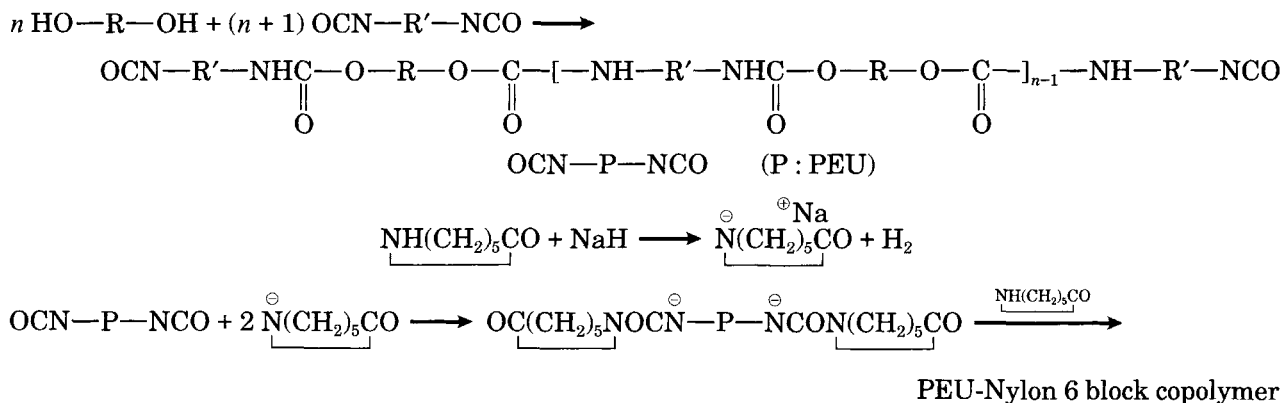
the compositions alone. Furthermore, use of the polyblend of the elastomeric block copolymer and Nylon 6 will be an attractive method to achieve the modification of Nylon 6. In this article the phase behavior of the PEU-Nylon 6 block copolymer film cast from the solvent is compared with that of the film prepared from the melt. The phase behavior of the binary blend of Nylon 6 and the block copolymer and ternary blend of polyurethane (PU), Nylon 6, and the block copolymer will also be dealt with.

EXPERIMENTAL

Synthesis of PEU-Nylon 6 Block Copolymer¹

PEU prepolymers terminated with isocyanate groups at both ends were prepared by reacting n mol of poly(tetramethylene glycol) (PTMG) and $(n + 1)$ mol of methane diphenyl-4,4'-diisocyanate (MDI). Using this prepolymer as an activator, the PEU-Nylon 6 block copolymer was synthesized via anionic polymerization of ϵ -caprolactam according to the following schemes:

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

Chemical composition and the physical properties of the block copolymers are listed in Table I. Here, PTMG mol % is identical to the mol % of urethane groups in the block copolymer, and TMG mol % is the relative block length of PEU block with respect to that of Nylon 6.

Preparation of the 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.

Preparation of the Solution Cast Films

The block copolymer was cast from 10 wt % solution in formic acid onto glass plates, and then dried in a vacuum for 24 h at 60°C.

Preparation of the Binary Blend Samples

Nylon 6 and the block copolymer were dissolved in *m*-cresol followed by casting on a glass plate, and then dried in a vacuum for 48 h at 80°C.

Preparation of the Ternary Blend Samples

Commercial PU, made from MDI, PTMG (M.W. 1000), and 1,4-butanediol according to the usual analytical methods,^{6,7} was obtained from Nihon Polyurethane Co., its molecular weight being 180,000. Nylon 6 was obtained from Tong Yang Nylon Co., its molecular weight being 20,000. Ternary polymer blends (Nylon 6/PU/the block copolymer with small amount of thermal stabilizer) were prepared by melt

extrusion, using a Brabender Plasticorder. The extruder barrel had three zones with a mixing head attached in front of the barrel. Its temperature was set to 230°C. The extrudate was cut into pellets and dried in a vacuum at 80°C for 24 h, followed by feeding into an injection molding machine (Toshiba IS-60B). The temperature setting was 230°C for the melting zone and 50°C for the mold.

Thermal Analysis

A Perkin-Elmer Model DSC-2 differential scanning calorimeter was used for measurement of thermal behavior. To observe the glass transition, crystallization, and melting behaviors, samples were

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

Sample code	PTMG mol (%)	TMG mol (%)	T_g^a (°C)	T_m^b (°C)	T_c^c (°C)
1000A-N	2.42	25.3	47	202	157
1000B-N	4.76	40.5	36	193	154
1000C-N	6.69	49.4	33	182	124
1000D-N	7.78	53.4	28	180	119
650A-N	9.23	47.2	25	176	116
1400-N	4.27	46.1	38	198	150
2000A-N	2.97	45.7	43	199	153
3000-N	1.55	39.5	—	207	157
Nylon 6				59	218
650				-22	
1000				-38	
2000				-56	

^a T_g : glass transition temperature measured by RDS.

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

^c T_c : nonisothermal crystallization temperature measured by DSC (cooling rate -10°C/min).

quenched in liquid nitrogen after melting at 230°C for 5 min. After complete quenching, the samples were transferred to a DSC pan maintained at -70°C and heated to 250°C at a rate of 20°C/min. For the measurement of nonisothermal crystallization temperature, the samples were heated to 230°C with a heating rate of 80°C and maintained for 5 min at this temperature, followed by cooling at a rate of 10°C/min.

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. A minimum of 200 scan signals were averaged.

Dynamic Mechanical Measurement

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

Wide Angle X-Ray Diffraction (WAXD)

WAXD measurements were made on a Rigaku Denki wide-angle x-ray diffractometer DMaxIIIa with Ni-filtered CuK α radiation at 35 KV and 20 mA in the transmission mode.

Small Angle X-Ray Scattering (SAXS)

The SAXS intensity distribution was measured with a Rigaku Denki DMax IIIA operated at 40 KV and 35 mA. The x-ray source was monochromatized to CuK α radiation with a four slit system with solar slits between the third and fourth. The intensity data were corrected for sample absorption and background scattering, and normalized for sample thickness.

Electron Microscopy

Transmission electron micrographs of the block copolymer were taken on a Jeol 100 CX II at an acceleration voltage of 80 KV, with the magnification of 100,000–200,000. The samples were stained by immersion for 30 min in 1% phosphotungstic acid (PTA) in methanol/water (1/1 by volume), followed by washing and drying.

RESULTS AND DISCUSSION

Phase Behavior of the Melt Pressed Block Copolymer Film

To get evidence of specific interaction between the polymer blocks, FTIR spectroscopy was employed. Nylon 6 is strongly self-associated through extensive intermolecular hydrogen bonding between the amide groups.⁸⁻¹⁰ To mix one segment with another, intermolecular interaction in the pure constituent polymer should be broken or a new one between the two different segments should be formed. In the block copolymer, the amide and urethane groups are expected to give specific interaction through hydrogen bonding. The amide I band of the Nylon 6 block at around 1640 cm⁻¹ was chosen to ascertain if hydrogen bond formation is occurring, since the amide II bands of the Nylon 6 block at around 3300 cm⁻¹ and 1540 cm⁻¹ overlap with those of the urethane groups. The amide I region of the spectrum of nylon 6 is sensitive to conformation change through dipole-dipole interaction. Accordingly, infrared bands attributed to the ordered and disordered hydrogen bonded amide groups are readily discerned.^{8,9} If intermolecular hydrogen bonding between the amide groups is completely destroyed, the amide I band shifts to higher frequency at 1680 cm⁻¹.¹⁰ Figure 1 shows the scale expanded FTIR spectra in the amide I region of the melt pressed block copolymers, and the frequencies are plotted against PTMG mol % in the block copolymer as illustrated in Figure 2. The amide I mode of the Nylon 6 homopolymer at room temperature is centered at 1637 cm⁻¹. With increasing PTMG mol %, the amide I mode is shifted progressively to a higher frequency from 1637 cm⁻¹ to 1645 cm⁻¹. After the interaction of the amide groups in Nylon 6 block with the urethane groups in PEU block, intermolecular interaction between the amide groups in the pure Nylon 6 block is supposed to be broken or weakened, resulting in a shift to higher frequency and the occurrence of compatible mixing.

For direct observation of the block copolymer domains in the amorphous phase, transmission electron microscopy (TEM) was employed. Unfortunately, TEM showed no distinct domain structure even at a magnification of 280,000. Again the SAXS technique was used to study the domain structure. This technique provided an excellent means for characterizing the bulk sample morphology and determining microphase structure of the order of 20 to 1000 Å in size in the polymeric materials, if suf-

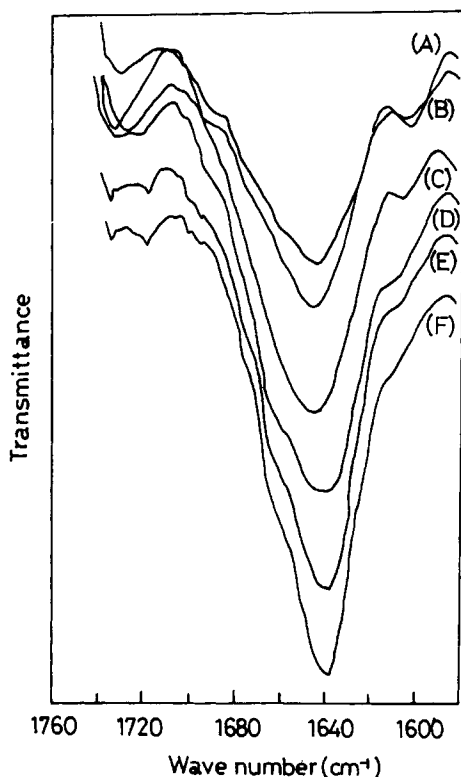


Figure 1 FTIR spectra of the amide I region of melt-pressed block copolymer films; (A), 650A-N; (B), 1,000D-N; (C), 1000C-N; (D), 1400-N; (E), 2000A-N; (F), 3000-N.

ficient contrast scattering power existed. The intensity of the SAXS is proportional to the mean square fluctuation of the electron density, $(\sigma - \bar{\sigma})^2$, which may be defined by the scattering power of the system. If we assume a heterogeneous system of electron densities, σ_1 and σ_2 of each domain and a sharp boundary between the domains, then the following relation holds:

$$(\sigma - \bar{\sigma})^2 = (\sigma_2 - \sigma_1)^2 V_1 V_2 = \Delta\sigma^2 V_1 V_2$$

where V_1 and V_2 are volume fractions of the domains. Therefore, if the block copolymer shows microphase separation, the electron density difference exists between the blocks, and the SAXS intensity pattern will exhibit a peak representing interdomain spacing as in the case of most block copolymers. The simplest SAXS analysis involves the determination of the maxima occurring in the scattering profile. The scattering vector s , can be related to an estimate of the interdomain spacing, d , through Bragg's equation:

$$|s| = 2 \sin \theta / \lambda = 1/d$$

where θ is the scattering angle and λ is the wavelength of x-ray. Bragg's law assumes a regular placement in one direction. If a one-dimensional analog of the interdomain spacing is to be determined, then the Lorentz correction is necessary to determine the d spacing.^{11,12} This requires a plot of $s^2 I(s)$ versus s and then determining the position of the maximum on these curves.¹³ The WAXD patterns for the block copolymer, prepared by the melt pressing and subsequent quenching in liquid nitrogen, showed only the presence of an amorphous halo as shown in Figure 3. The SAXS pattern of a typical block copolymer is presented in Figure 4. No scattering maximum was observed in the melt pressed samples (dotted line in Fig. 4), even when using a Rigaku Denki Rotaflex operated at 40 KV and 200 mA, which indicates a homogeneous system. This was probably due to the fact that the two blocks might be intermixed in the amorphous state showing homogeneous structure, as previously discussed.¹

To improve the electron density difference between the blocks, the block copolymer film was immersed in PTA, which preferentially stains the PEU block,¹⁴ as shown in Figure 5. Returning to Figure 4, the PTA-stained block copolymer shows a distinct scattering maximum. Since the domains are supposed to have random orientation, it is obvious that it is not a representative of a one-dimensional array. For this reason, a Lorentz correction was performed on the scattered intensity (solid line in Fig. 4). Figure 6 illustrates the SAXS patterns of the PTA-stained block copolymer after the Lorentz correction. From the scattering patterns, interdomain spacing be-

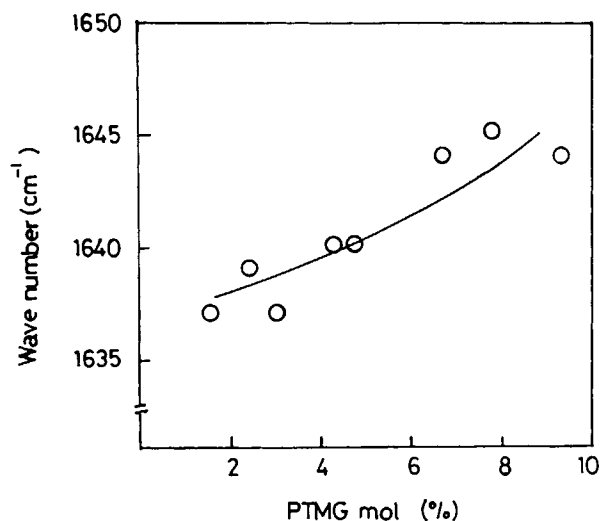


Figure 2 Frequency shifts of amide I band vs. PTMG mol % in the block copolymers.

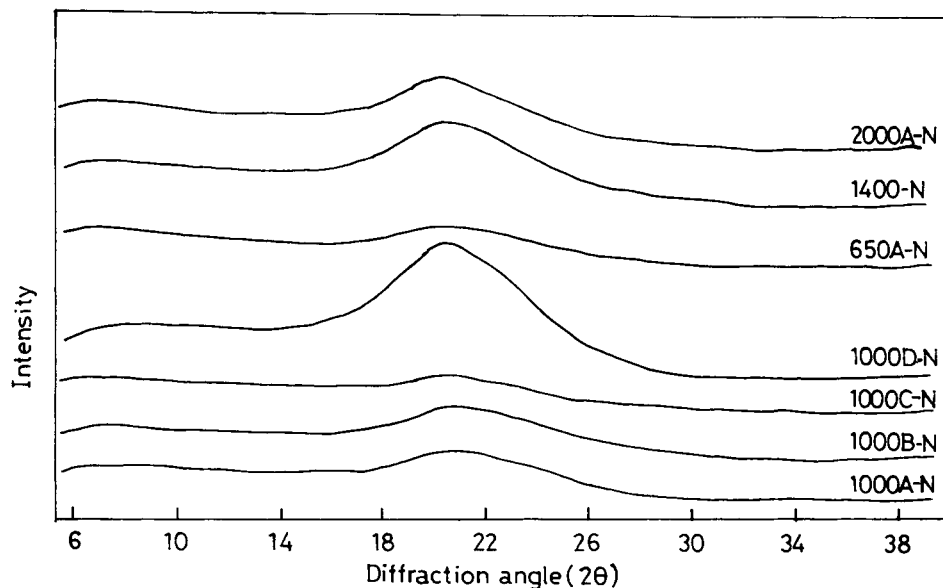


Figure 3 Wide-angle x-ray diffraction curves for melt pressed block copolymers.

tween the blocks could be calculated. These results are shown in Figure 7. The interdomain spacing is in the range of 40–50 Å and is reasonably small in

size as compared to the case of PVC/polycaprolactone amorphous miscible blend system calculated by the Debye-Bueche plot of SAXS patterns.¹⁵

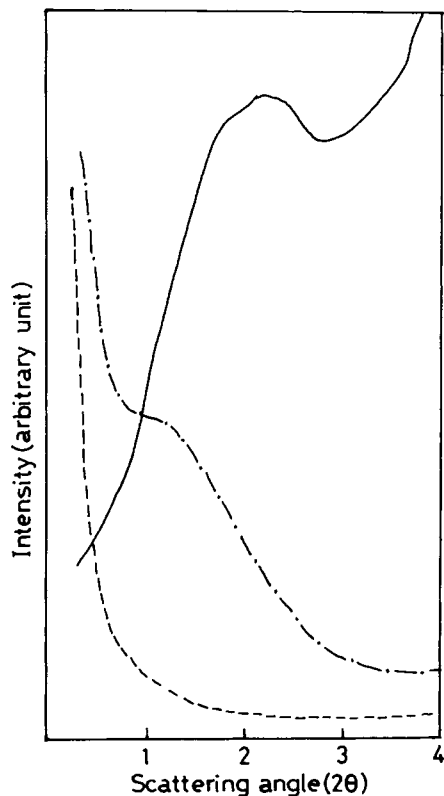


Figure 4 Small-angle x-ray scattering curves for block copolymer 1000A-N; (---), melt pressed; (-.-), PTA stained; (—), Lorentz-corrected.

Phase Behavior of the Solvent-Cast Films

Formic acid is a good solvent for Nylon 6, but a poor solvent for PEU. Therefore, as-cast film from formic acid might exhibit an appreciably different morphology from that prepared by the melt press. The

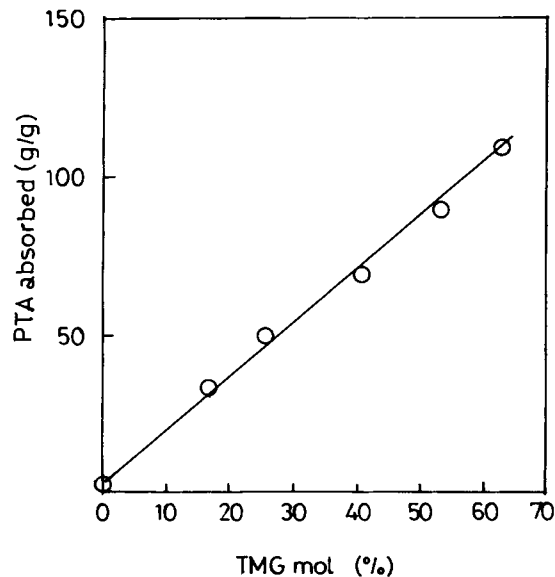


Figure 5 Plot of absorbed PTA vs. TMG mol % in the block copolymer 1000-N series.

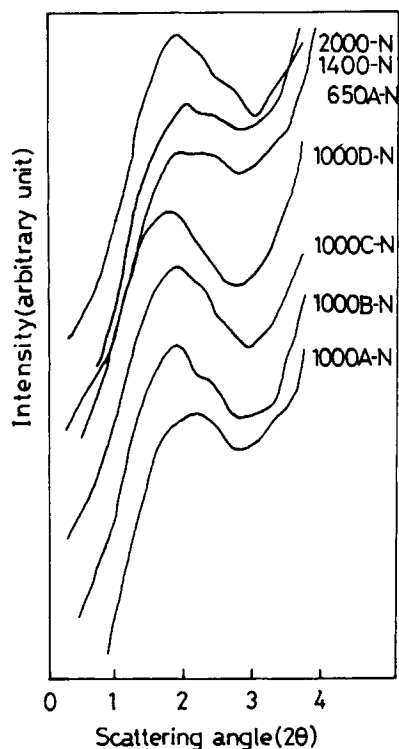


Figure 6 Lorentz-corrected small-angle x-ray scattering curves for PTA stained block copolymers.

$\tan \delta$ curve of block copolymer 650A-N film prepared by casting from the formic acid exhibited two distinct maxima, as illustrated in Figure 8B. Existence of two distinct maxima in $\tan \delta$, which are not even located at temperatures close to those of the homopolymers, is evidence that the block copolymer was microphase separated between the blocks in the as-cast film state. The temperature shift of the first maximum located at about 0°C as compared with the maximum of PEU prepolymer at -22°C (Fig. 8D), might be ascribed to incomplete phase separation between the blocks. However, the melting temperature of the as-cast film was almost the same as that of the melt-pressed sample. The melting temperature depression phenomenon is an indication of miscible behavior, as previously discussed.¹ To solve the question of these two conflicting data, a second measurement for dynamic mechanical analysis was carried out with the sample of the first run. Interestingly, the maximum loss peak at 0°C completely disappeared (Fig. 8C). Similar trends were also found in other PEU-Nylon 6 block copolymers. This phenomenon can be interpreted as follows: as the temperature rises, the two phases gradually intermix with each other and form a homogeneous phase. The loss tangent maximum of Nylon

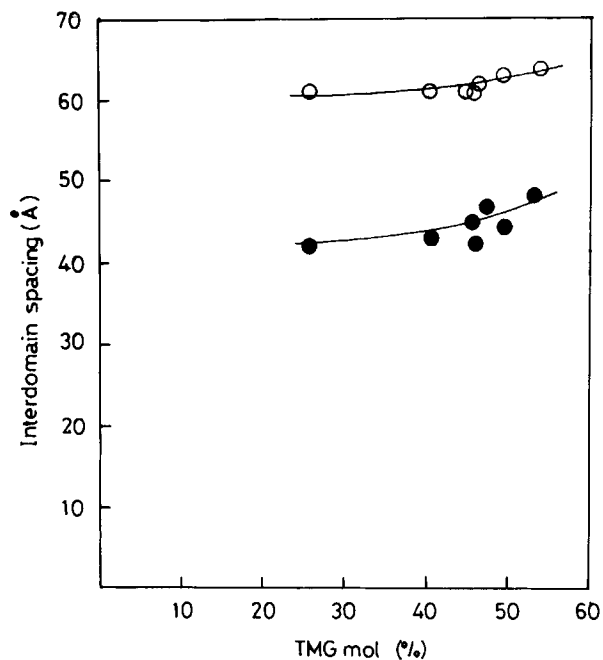


Figure 7 Plots of interdomain spacing vs. TMG mol % in the block copolymers; \circ , original; \bullet , Lorentz-corrected.

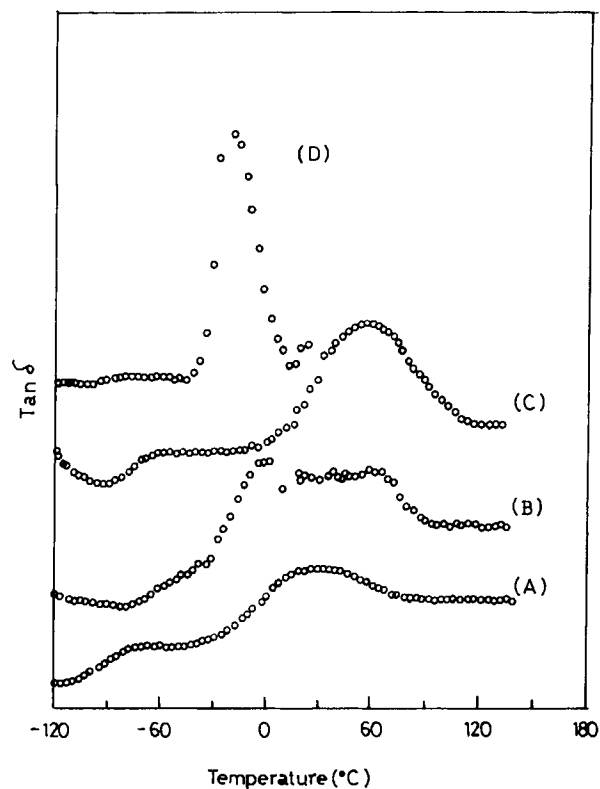


Figure 8 $\tan \delta$ curves for block copolymer 650A-N; (A), melt-pressed; (B), formic acid cast film (1st run); (C), formic acid cast film (2nd run); (D) PEU prepolymer.

6 is known to be dependent on the crystallinity of this polymer. As with the crystallinity, the loss tangent maximum shifts to higher temperature, thus it is not an indication of phase separation. To provide further evidence for such phase behavior, FTIR measurement was also carried out. As shown in Figure 9B, the amide I mode of as-cast block copolymer is centered at 1637 cm^{-1} . Contrary to this, in the case of the heat treated sample at 160°C for 10 min, the amide I mode shifts up to higher frequency (Figure 9C), which is an indication of intermolecular interaction between the amide and urethane groups in the block copolymer, resulting in the formation of a homogeneous phase at higher temperature.

The morphology of the solvent cast block copolymer was investigated by transmission electron microscopy. In the melt-pressed samples, a distinct domain structure could not be found. However, the transmission electron micrographs of the formic acid cast samples revealed the presence of microphase separation as shown in Figure 10. The dark regions in these micrographs correspond to the PEU domain stained with the PTA. Figure 11 shows also the micrographs of the block copolymers cast from *m*-cre-

sol which is a rather better solvent for the PEU than formic acid. The domain size of the block copolymer samples cast from *m*-cresol is smaller than for those cast from formic acid, indicating a lower degree of phase separation. The degree of phase continuity of the PEU block cast from *m*-cresol is also larger than that cast from the formic acid. Such differences in morphology, particularly in the degree of phase separation and phase continuity, are ascribed to the differences in the solubility of the PEU block with the solvents. The solvents with low solvation power tend to cause agglomeration of the one constituent block, thus forming a microphase separation of the block copolymer.¹⁶

It is obvious that the solvent cast film shows a microphase-separated domain structure that arises from poor solubility of the PEU block in the solvent. However, as the temperature rises, the mutual miscibility between the PEU and Nylon 6 blocks will increase due to the interaction between urethane and amide groups through hydrogen bonding, resulting in the formation of a thermodynamically homogeneous phase.

Block Copolymer/Nylon 6 Binary Blend

The polymer incompatibility rises from the very small entropy gained by mixing the different kinds of long chains. Therefore, when two polymers are mixed together, the blend components are readily separated into the component phases. In fact, for the limit of high molecular weight, only polymer pairs with zero or negative heat of mixing form one phase. Although two polymers form an immiscible system, it may be possible to modify the system to improve miscibility. One of the direct methods of achieving miscibility is to modify the structure of one or both components. The introduction of specific interactions between the constituent of the individual chains is one method, and block or graft formation is another method for enhancing the miscibility. Experimental studies of the copolymer blocked with one of the corresponding homopolymers generally indicate that the homopolymers whose molecular weight is equal to or less than that of the corresponding block in the block copolymers are solubilized into the microphase comprised of the corresponding block copolymer.¹⁷ However, if specific interactions such as hydrogen bonding or dipolar interaction exist between the block copolymer and the corresponding homopolymer, mutual solubility can be achieved regardless of their molecular weight. When the homopolymer is solubilized into the corresponding microphase in a block copolymer,

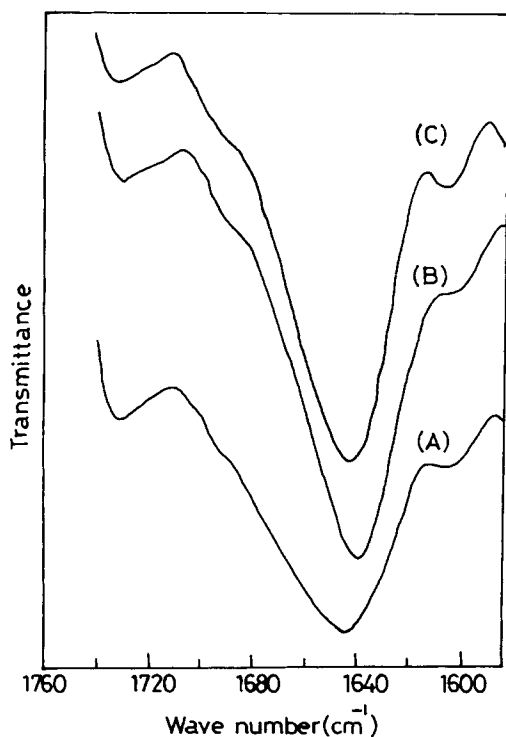


Figure 9 FTIR spectra of the amide I region for block copolymer 650A-N; (A), melt pressed; (B), formic acid cast; (C), formic acid cast, and thereafter heat treated at 160°C for 10 min.

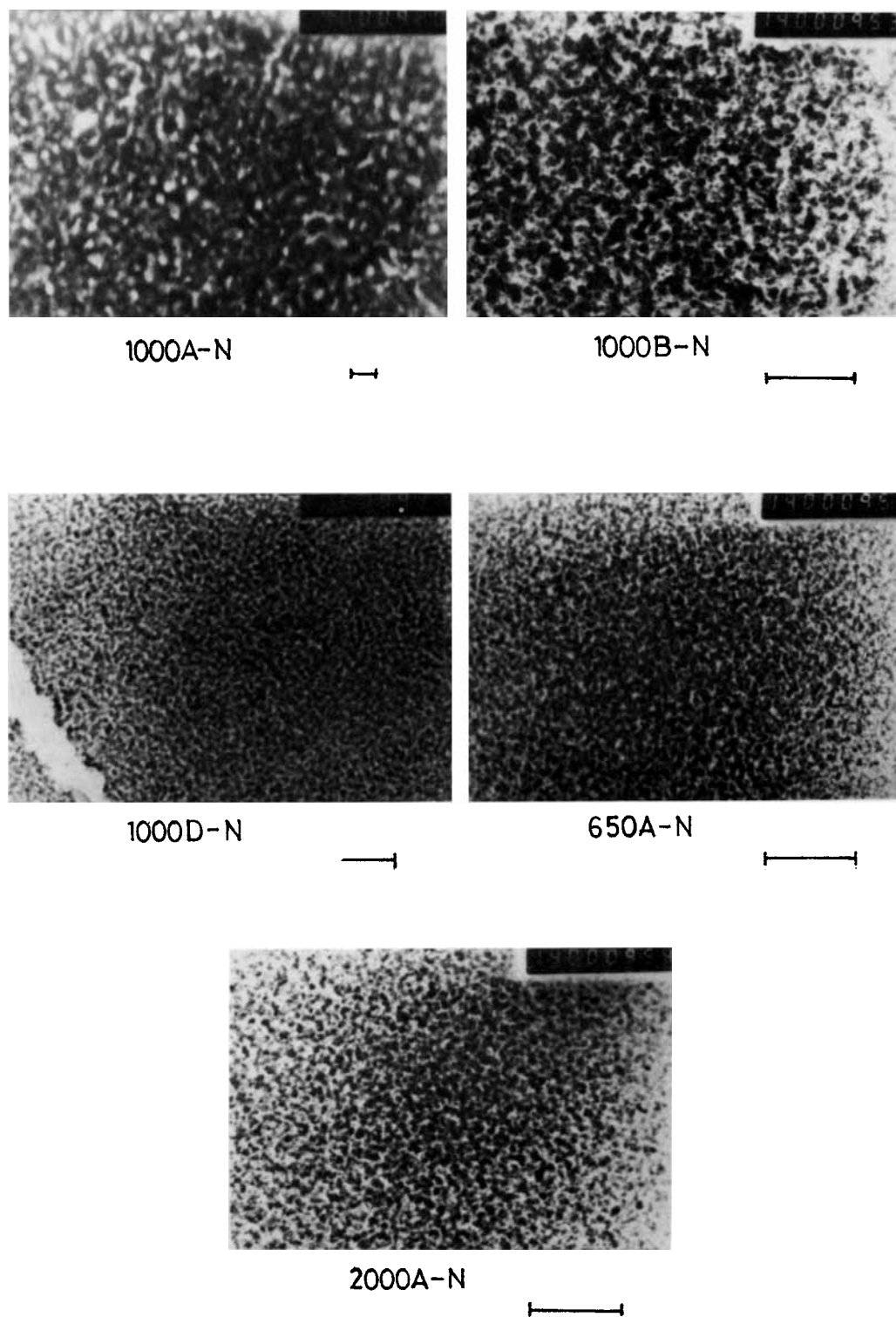


Figure 10 Transmission electron micrographs of formic acid-cast block copolymers (Bar indicates 1000 Å in size).

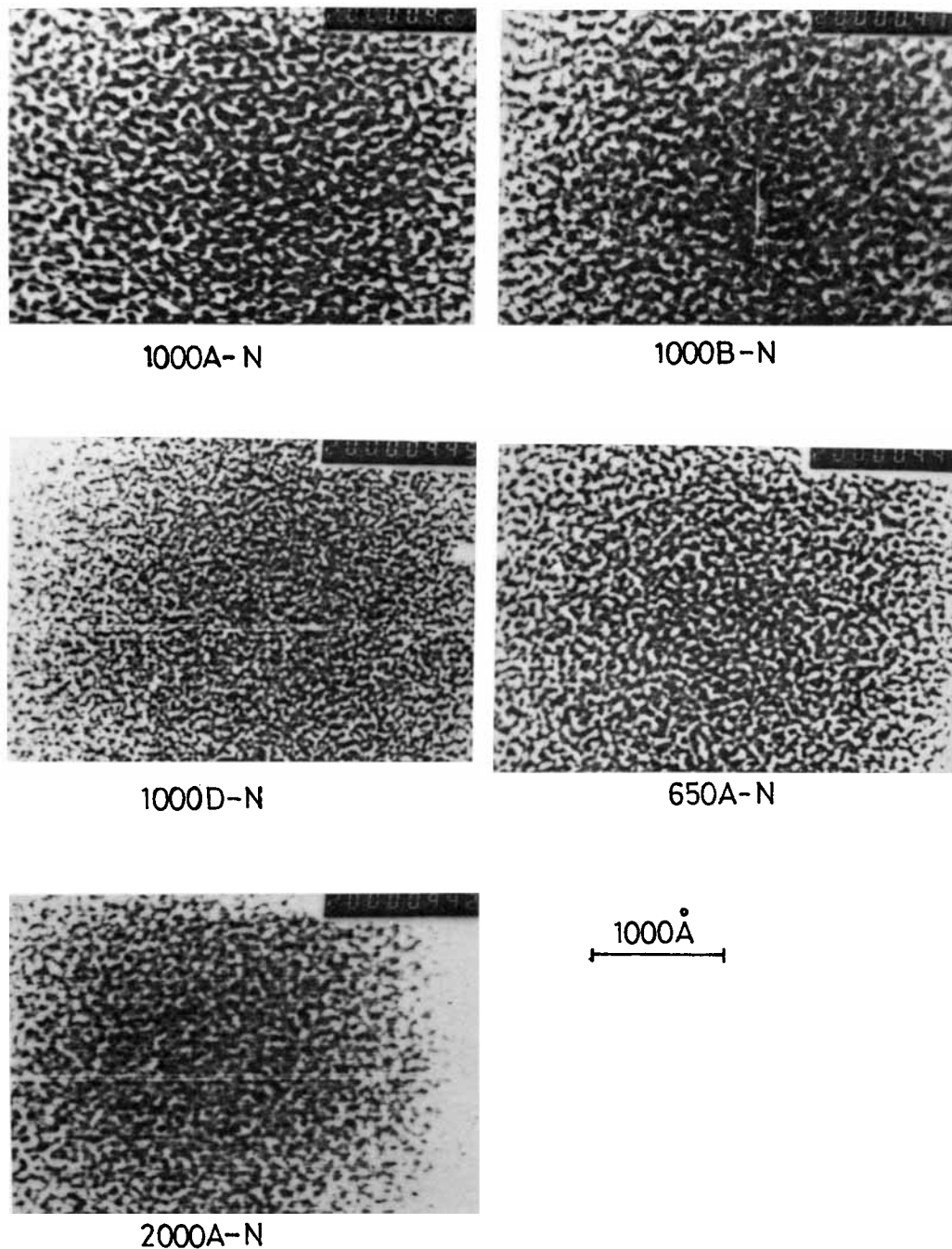


Figure 11 Transmission electron micrographs of *m*-cresol-cast block copolymers.

one should expect the mixture to exhibit only a single glass transition or melting temperature between that of the homopolymer and that of the corresponding unmixed microphase. The determination of whether or not the block copolymer and Nylon 6 blends are heterogeneous or homogeneous is accomplished by examining the results of the DSC experiments. Figure 12 shows the DSC thermograms of the block

copolymer 650A-N and Nylon 6 blends. Only single T_g and T_m were observed, their temperatures being intermediate between those of the block copolymer and Nylon 6 over the entire range of composition, indicating an extensive mixing of the blend. The DSC thermograms of nonisothermal crystallization are also illustrated in Figure 13. Again, single peaks are observed in the case of T_g and T_m . This is also

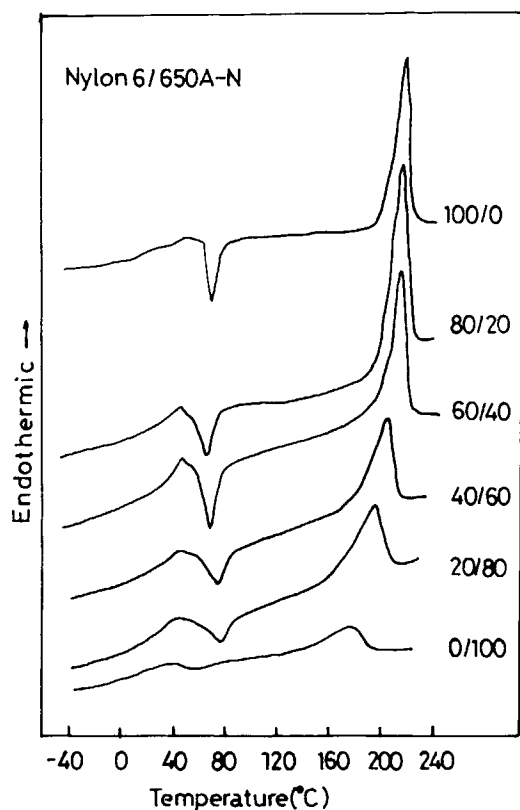


Figure 12 DSC thermograms of Nylon 6 and block copolymer 650A-N blends.

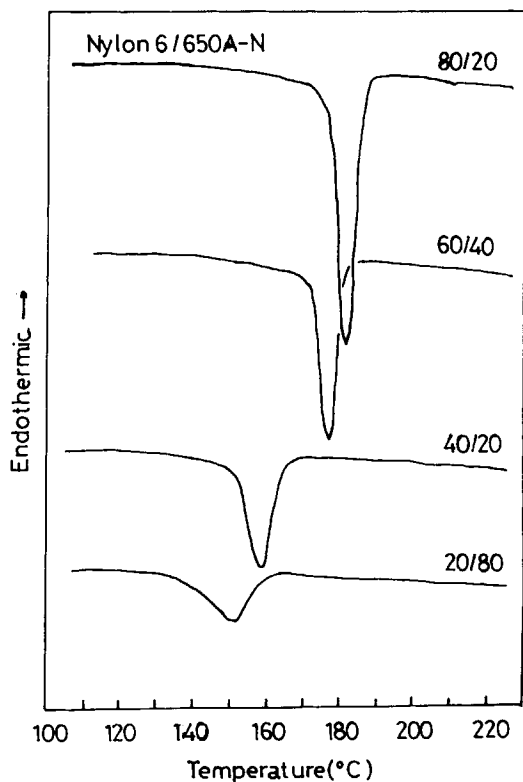


Figure 13 Nonisothermal crystallization thermograms of Nylon 6 and 650A-N blends.

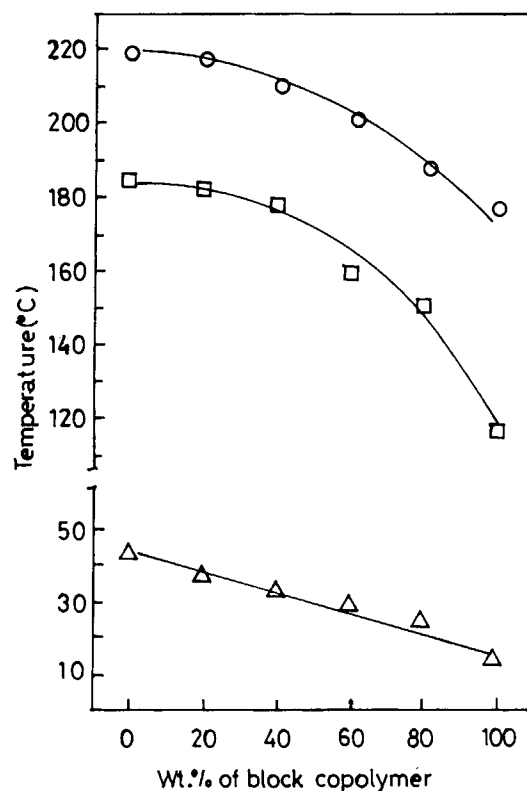


Figure 14 Plots of glass transition (Δ), nonisothermal crystallization (\square), and melting (\circ) temperatures in Nylon 6/650A-N blends vs. wt % of 650A-N.

an indication of a miscible blend, resulting in the suppression of crystal formation of Nylon 6, causing retardation in the rate of nucleation and growth. These results are plotted against weight % of the block copolymer in the blend as shown in Figure 14. With increasing weight % of the block copolymer, T_g , T_m , and nonisothermal crystallization temperature, T_c are decreased, resulting in the formation of the homogeneous phase in the blend. Similar trends were observed for the other block copolymers. All the results of the various block copolymer blends are concentrated in Figures 15 and 16, in which T_m , T_c , and T_g are plotted against PTMG mol % in the blend. Substantial T_g , T_c , and T_m depressions are clearly noted, depending strongly on the PTMG mol % in the blend. These results show that the block copolymer and Nylon 6 mixture is compatible over the entire composition range mainly due to the specific interaction between the urethane and the amide groups in the blend through hydrogen bonding.

Nylon 6/Block Copolymer/Polyurethane Ternary Blend

Ternary blend experiments were carried out with the aim of practical application. When a block co-

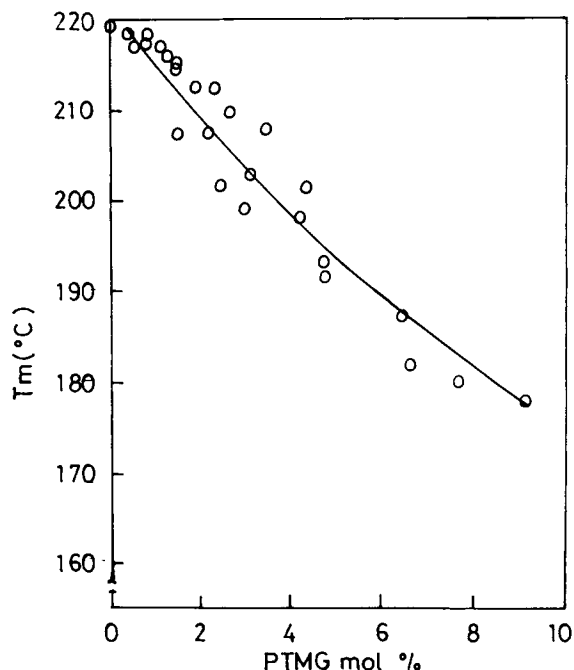


Figure 15 Plot of melting temperature vs. PTMG mol % in the blend.

polymer is added to its corresponding homopolymers, it has been recognized that the block copolymer additive acts as a compatibilizer lowering the interfacial tension, and therefore may facilitate phase dispersion, just as the detergent promotes the mixing of oil and water in the colloidal field, which is referred to as the “emulsifying effect.”¹⁸ Another fact that was known is that the block copolymer is soluble in either of the two corresponding homopolymers, lowering the block copolymer/homopolymer enthalpy of mixing, which is also known as “homogenizing effect” or “solubilizing effect.”^{19,20} These two effects lead to better adhesion between phases, resulting in improved ultimate mechanical properties. Fayt et al.²¹ observed in the case of 80/20 low density polyethylene (LDPE)/polystyrene (PS) blends having 0–10% of added block copolymer, that the mean size of the dispersed PS phase was reduced 10- to 20-fold even when 5% of block copolymer is added to the blend. Similar results were obtained for PS/Nylon 6,²² for PS/polyisoprene (PI),²³ for PS/PMMA,²⁴ etc. Direct morphological observation that block copolymer promotes interfacial interaction between phases was made by Fayt et al.²¹ who reported the results of the fractographic analysis of some LDPE/PS blends. In the fracture surfaces of ternary blend, the block copolymer not only stabilized the interlocked PS and PE phases but also increased significantly the fineness of the continuous two phase morphology, indicating an

emulsifying effect of the block copolymer. Cohen and Ramos¹⁹ suggested that in the case of 1,4-polybutadiene/cis-1,4-PI blend, the block copolymer was found to be soluble in either of the corresponding homopolymers from the results of dynamic mechanical analysis and TEM observation, which appeared to have a homogenizing or solubilizing effect on the block copolymer. In the present work these two effects in Nylon 6/PU/PEU-nylon 6 block copolymer ternary blend system were examined. The surface of ternary blends fractured in liquid nitrogen was observed. Under the present experimental condition, as can be seen in Figure 17, the Nylon 6/PU (6/4 by weight) binary blend shows a relatively fine dispersion, but some adhesive fracture surface, and also shows the forming of phase separation. On the other hand, by the addition of block copolymer 1000C-N to the binary blend, the phase morphology is strictly modified, and shows that there is no evidence of separated domains. The above observation suggests that in the ternary blend containing the block copolymer, PU is finely dispersed and/or dissolved in the Nylon 6 phase. The dispersed PU phase was extracted with tetrahydrofuran, and the results

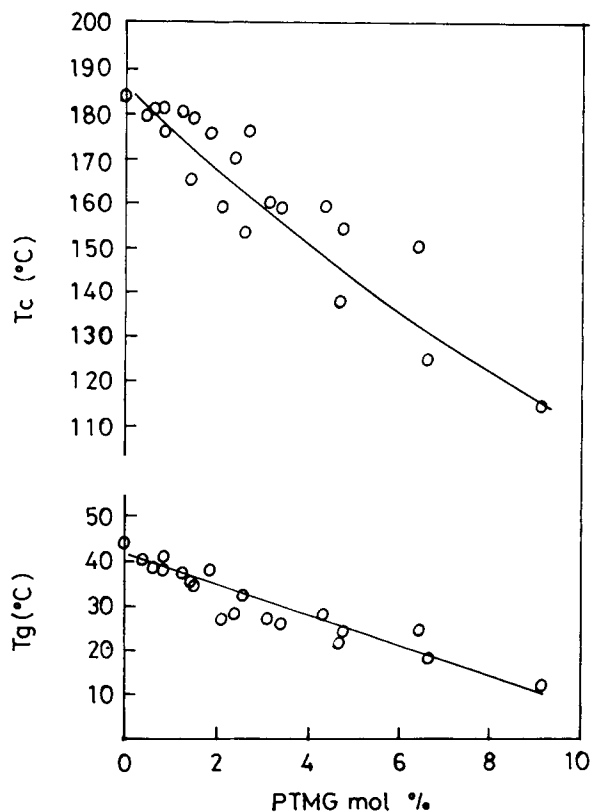


Figure 16 Plots of nonisothermal crystallization temperature and glass transition temperature vs. PTMG mol % in the blends.

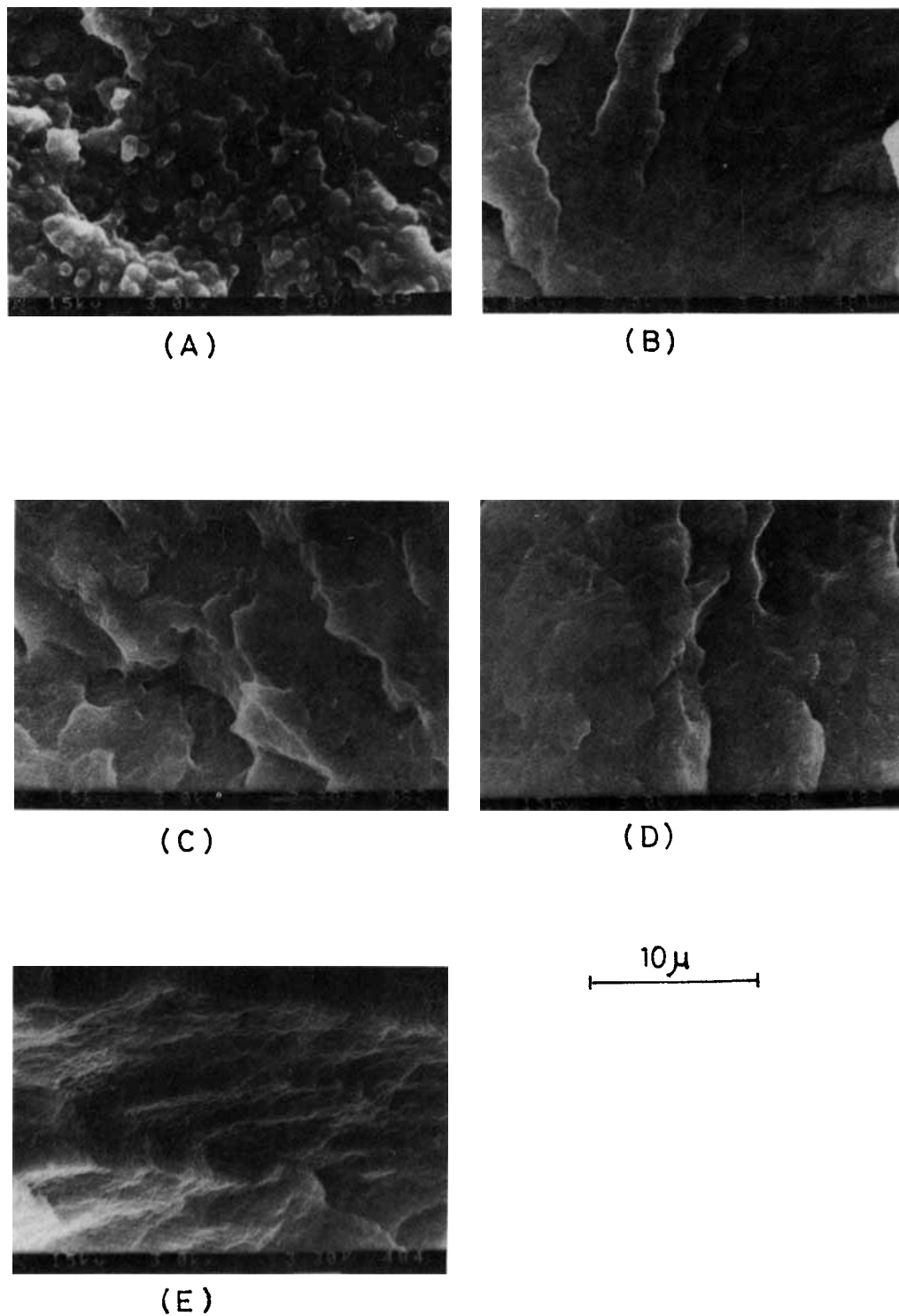


Figure 17 Scanning electron micrographs of Nylon 6/PU/1000C-N ternary blend fractured in liquid nitrogen; (A), Nylon 6/PU (6/4) control; (B), 100C-N 2%; (C), 1000C-N 5%; (D), 1000C-N 8%; (E), 1000C-N 15%.

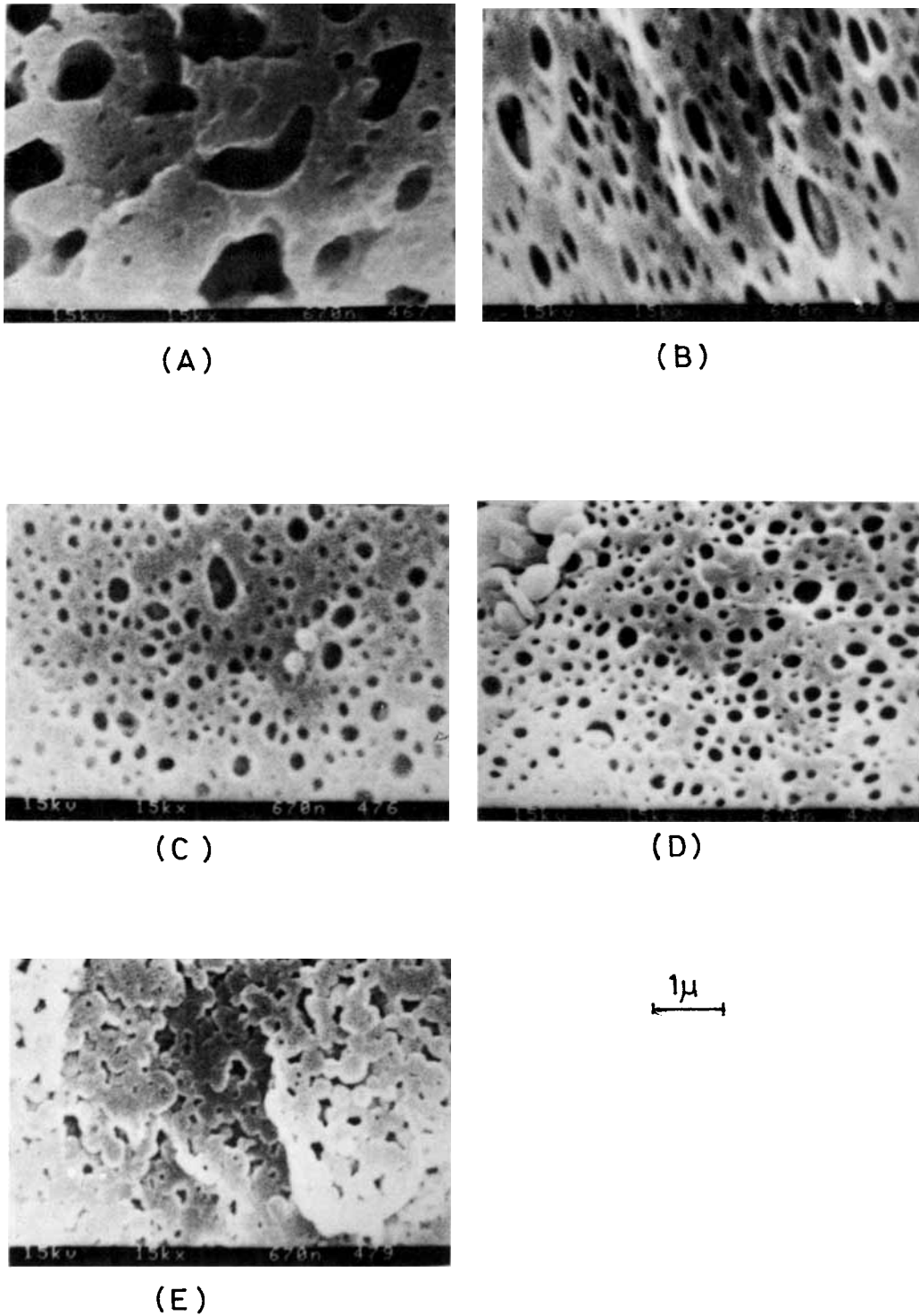


Figure 18 Scanning electron micrographs of nylon 6/PU/1000C-N ternary blend fractured in liquid nitrogen and extracted with THF; (A), Nylon 6/PU(6/4) control; (B), 1000C-N 2%; (C), 1000C-N 5%; (D) 1000C-N 8%; (E), 1000C-N 15%.

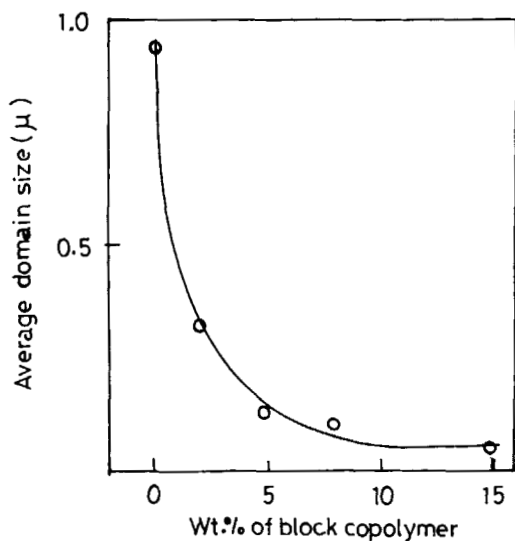


Figure 19 Effect of block copolymer as a compatibilizer in Nylon 6/PU (6/4) blend.

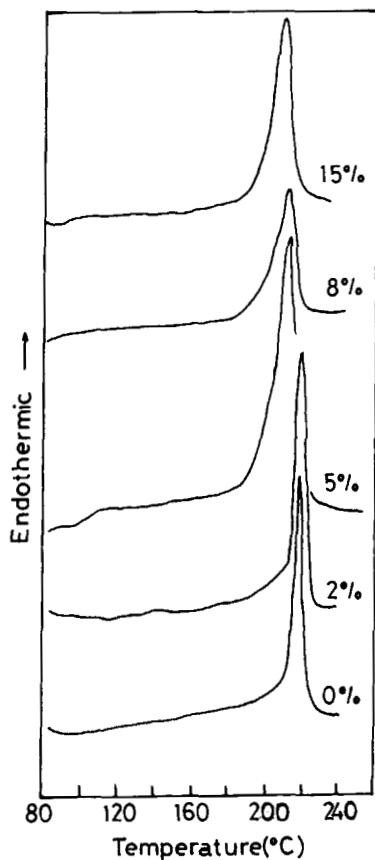


Figure 20 Changes of DSC thermograms for Nylon 6/PU/1000C-N ternary blend with the addition of 1000C-N (wt %).

are shown in Figure 18. The unmodified Nylon 6/PU binary blend exhibits a rather large domain size, its diameter being about $1 \mu\text{m}$. However, it is noted that the addition of the block copolymer to the binary blend produced a drastic reduction of the average domain size of the phase. The size reduction plotted against the added block copolymer is shown in Figure 19. A considerable effect of the block copolymer on the reduction of domain size is clearly observed. The mean size of the dispersed PU phase is reduced about 7-fold to reach approximately $0.15 \mu\text{m}$ or less when 5% of the block copolymer is added to the binary blend. Furthermore, when 15% of block copolymer is added to the binary blend, the size of the dispersed PU phase is less than $0.1 \mu\text{m}$ and it is hard to observe the domains. These results indicate that the block copolymer may act as an "interfacial agent" promoting adhesion between the Nylon 6 matrix and PU-dispersed phase. Similar trends were also observed by adding other block copolymers.

Figure 20 shows the DSC thermograms of the ternary blends. While increasing the content of the block copolymer in the ternary blend, the melting temperature was slightly depressed. In Figure 21, the loss tangent curves for the ternary blends are presented. The binary blend exhibits two distinct

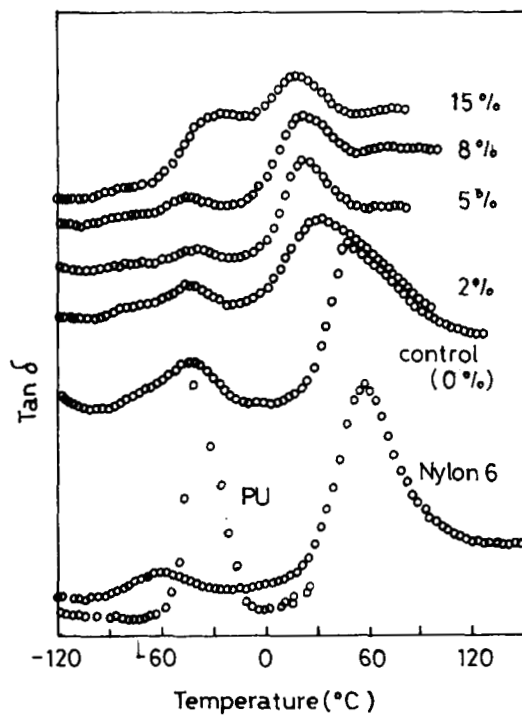


Figure 21 Changes of tan δ curves for nylon 6/PU/1000C-N ternary blend with the addition of 1000C-N (wt %).

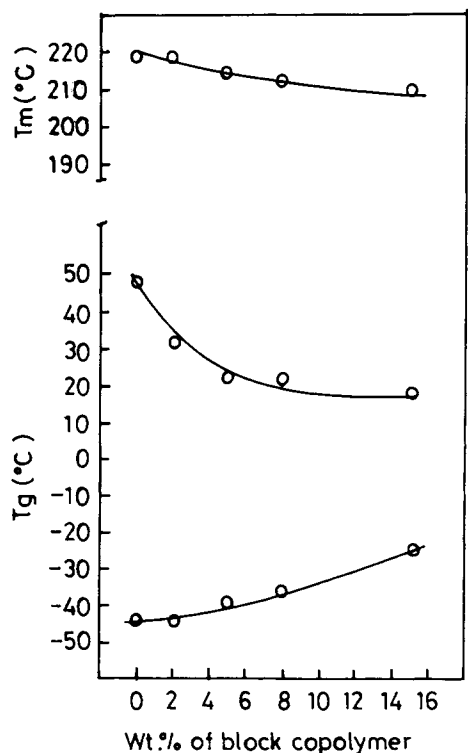


Figure 22 Plots of melting and glass transition temperatures vs. added wt % of block copolymer 1000C-N.

maxima in $\tan \delta$. One is at the same location as the PU at -44°C , and the other is located at 49°C , being slightly shifted as compared to Nylon 6, resulting in some adhesive fracture surface as was observed in Figure 17. Figure 22 shows the changes of the T_m and T_g of the ternary blend samples by the addition of the block copolymer. It results from the fact that PU and Nylon 6 are not truly miscible under the present processing condition. However, by the addition of the block copolymer to the binary blend, it is clear that the loss tangent maxima of the PU shift up, while those of Nylon 6 shift down. The temperature shift in $\tan \delta$ of Nylon 6 is larger than that of PU when the block copolymer is added up to 8 wt %, indicating that the block copolymer is solubilized preferentially into the Nylon 6 phase. From the above results, it is suggested that in the ternary blend, the block copolymer is soluble in either of the two corresponding homopolymers, resulting in the promotion of hydrogen bond formation between the amide groups in Nylon 6 and urethane groups in PU, which appears to provide the homogenizing effect.

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