

# Compatibilizing effect of polyarylate-nylon 6 block copolymers on polyarylate/nylon 6 blends: 1. Synthesis of polyarylate-nylon 6 block copolymer and its miscibility in binary blends with polyarylate or nylon 6

Tae Oan Ahn\* and Sukmin Lee

*Department of Chemical Technology, Seoul National University, Seoul 151-742, Republic of Korea*

and Han Mo Jeong

*Department of Chemistry, University of Ulsan, Ulsan 680-749, Republic of Korea*

and Sang Won Lee

*Department of Chemical Engineering, Soong Sil University, Seoul 156-743, Republic of Korea*

*(Received 19 October 1992)*

Polyarylate (PAR)-nylon 6 block copolymers of various block lengths were prepared by the anionic polymerization of  $\epsilon$ -caprolactam using the polymeric activator from hydroxy-difunctional PAR and toluene diisocyanate. Phase-separated morphology of PAR-nylon 6 block copolymer was observed by transmission electron microscopy and the thermal properties were measured by differential scanning calorimetry (d.s.c.). Partial miscibility between PAR and nylon 6 segments was more evident with shorter constituent blocks. In binary blends of PAR or nylon 6 with PAR-nylon 6 block copolymer, molecular-level mixing of homopolymers with corresponding blocks of block copolymer was supposed from the thermal properties measured by d.s.c.

**(Keywords: polyarylate-nylon 6 block copolymer; morphology; thermal properties; binary blends; miscibility)**

## INTRODUCTION

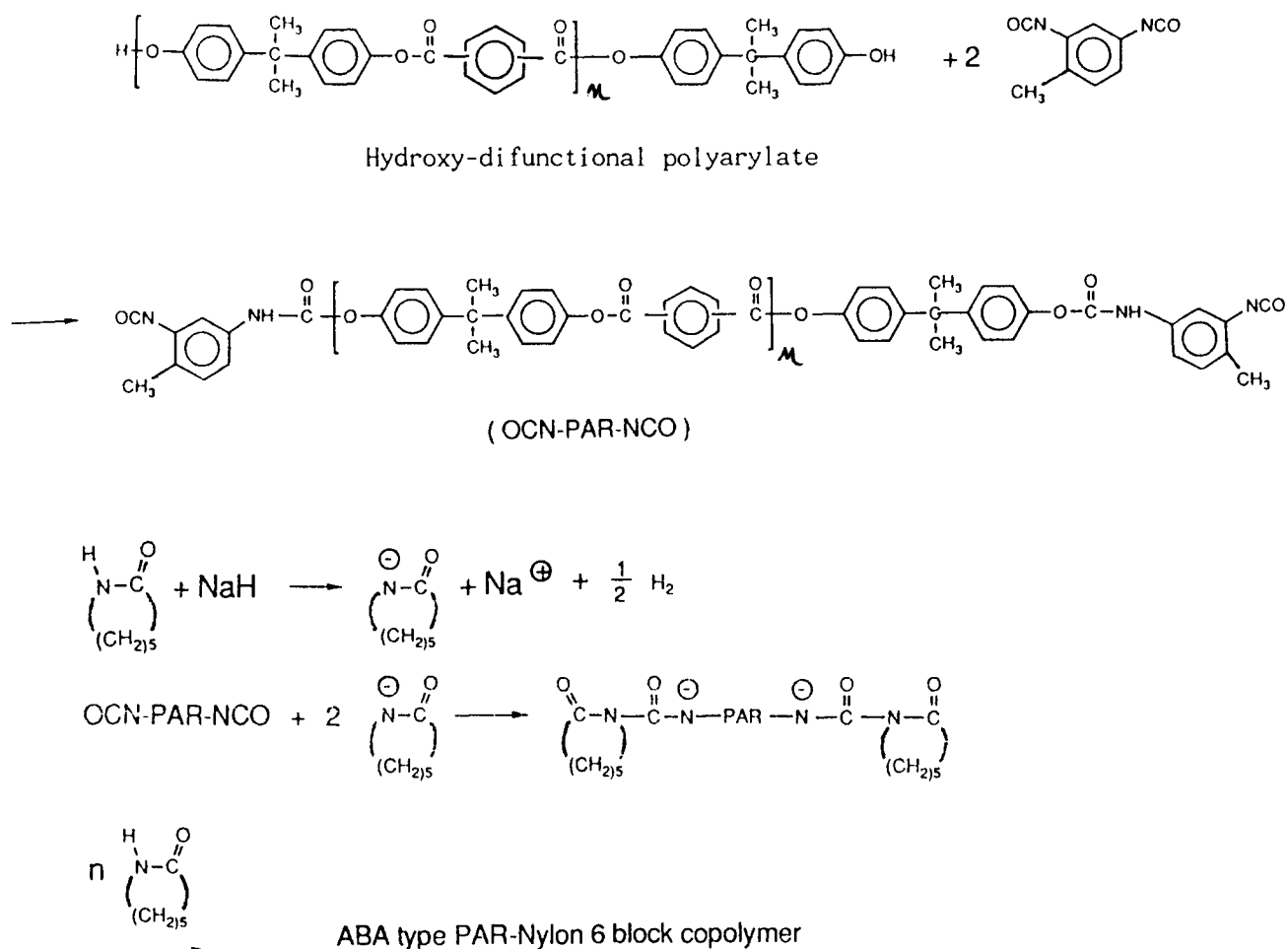
Polymer blends can form a wide variety of multicomponent systems with combinations of desirable properties. Nevertheless, in practice these favourable properties are sometimes difficult to achieve because of poor adhesion of the phases created by thermodynamic immiscibility. This difficulty can be overcome by certain polymers referred to as compatibilizers, which modify the interfacial conditions between the phases<sup>1,2</sup>. A block or graft copolymer is usually used as an interfacial agent, with segments A or B in a blend of A and B polymers. As a result, the interfacial energy between the immiscible phases is reduced, ensuring finer dispersion upon mixing and higher stability against phase segregation.

Polyarylate (PAR), composed of bisphenol A and terephthalates and isophthalates, is recognized as an important engineering plastic offering a high heat distortion temperature, excellent toughness, high resilience to deformation and excellent retention of mechanical properties after long-term ultraviolet exposure. Many studies have investigated blends of PAR with other polymers<sup>3-6</sup>. Polycarbonate, an amorphous polymer very

similar to PAR in chemical structure, has been reported to show poor adhesion and unfavourable mechanical properties in blends with nylon 6<sup>7,8</sup>. PAR/nylon 6 blends have also been reported to be partially miscible, and are not expected to have a favourable interfacial condition<sup>9</sup>. Thus a block copolymer containing PAR and nylon 6 segments is anticipated to have increased adhesion between the phases. To the knowledge of the authors, there are no published papers reporting the study of compatibilized PAR/nylon 6 blends, which is the purpose of the present work.

Block copolymers containing nylon 6 segments are commonly prepared by two routes: by coupling prepolymers with reactive end groups in condensation and addition reactions, or by building up the nylon 6 chain at end groups of the second prepolymer<sup>10,11</sup>. The latter route, which was adopted in this study (*Scheme 1*), has been employed as the preparative method for block copolymers of the AB and ABA type, where A is the nylon 6 segment formed by polymerization of  $\epsilon$ -caprolactam and B is another polymer segment. Anionic polymerization of  $\epsilon$ -caprolactam for synthesizing block copolymer containing nylon 6 segments is usually brought about by introducing polymeric activators involving *N*-acyl lactams or their precursors such as

\* To whom correspondence should be addressed



Scheme 1

isocyanates and acyl halides at the ends of chains. An activated monomeric anion is added to an *N*-acyl lactam chain end, followed by a very fast proton transfer from monomer to polymeric anion to give a new monomeric anion and *N*-acyl lactam with a chain one unit longer<sup>12-14</sup>.

In the present study, the PAR-nylon 6 block copolymers were synthesized anionically using a polymeric activator made by the reaction of diisocyanate with PAR oligomer having hydroxy functionality (Scheme 1); the characteristics of the resulting block copolymers were investigated. The miscibility in binary blends of PAR-nylon 6 block copolymers with PAR or nylon 6 is discussed; fundamental data necessary for the studies of PAR/nylon 6/PAR-nylon 6 block copolymer ternary blends have been obtained. The ultimate aim of these studies is to investigate the effects of PAR-nylon 6 block copolymers as compatibilizers on the thermal and mechanical properties of PAR/nylon 6 blends; this will be reported in a future publication.

## EXPERIMENTAL

### Materials

Bisphenol A (polymer grade, Junsei Chemical) was recrystallized from toluene, and terephthaloyl chloride and isophthaloyl chloride (Fluka) were used as received.  $\epsilon$ -Caprolactam (BASF) was recrystallized from hot *n*-hexane. The crystals were dried at 25°C under reduced pressure for 24 h. Toluene diisocyanate was freshly

distilled before use. Chloroform was washed with distilled water five times, stirred over phosphorous pentoxide for 24 h, distilled under reduced pressure and stored in molecular sieves (4 Å) until use. Triethylamine, osmium tetroxide (Merck), and NaH (Aldrich), a 50% dispersion in mineral oil, were used as received. Solvents and non-solvents such as sulfuric acid 95%, *m*-cresol and acetone were reagent grade and were used without further purification.

The PAR used was a commercial product (U-100, Unitika) with  $M_n = 21\,200$  and  $M_w = 51\,400$ . Nylon 6 (Tongyang Nylon Company of Korea) had  $M_n = 25\,000$  and  $M_w = 42\,000$ .

### Synthesis of hydroxy-difunctional PARs

Hydroxy-difunctional PARs with various molecular weights were synthesized by the solution polymerization reaction of bisphenol A with 1/1 mixture of isophthaloyl chloride and terephthaloyl chloride in the presence of triethylamine as an acid acceptor. The reaction was carried out in dry nitrogen. The molecular weight was controlled with the stoichiometric imbalance of the reactants (Table 1)<sup>15</sup>. Bisphenol A was charged into the reaction vessel and dissolved in chloroform and triethylamine. The bisphenol A solution had a concentration of about 12% (w/v) and the concentration of triethylamine was maintained at 10 mol% excess with respect to the equivalent of acyl functional group. The 1/1 mixture of isophthaloyl and terephthaloyl chloride was suspended in chloroform separately and added

**Table 1** Characteristics of hydroxy-difunctional PAR oligomers

Designation	Feed mole ratio (OH/COCl)	$M_n$ from end-group titration	$M_n$ from g.p.c. <sup>a</sup>	$M_w$ from g.p.c. <sup>a</sup>	PI <sup>b</sup>	$M_v$ <sup>c</sup>	$[\eta]$ (dl g <sup>-1</sup> )	$T_g$ (°C)
PAR 1	1.08/1	1800	2100	3200	1.52	2900	0.115	150
PAR 2	1.06/1	3300	4300	6600	1.54	6200	0.179	162
PAR 3	1.04/1	4800	5600	9600	1.58	8100	0.209	170

<sup>a</sup> Calibrated via universal calibration method using Mark-Houwink equation with  $K = 6.17 \times 10^{-3}$  and  $\alpha = 0.625$  for PAR<sup>5</sup> and  $K = 2.1 \times 10^{-2}$  and  $\alpha = 0.660$  for PS<sup>18</sup> in THF at 25°C

<sup>b</sup> Polydispersity index

<sup>c</sup> Calibrated from Mark-Houwink equation<sup>5</sup> with  $K = 1.17 \times 10^{-3}$  and  $\alpha = 0.576$

**Table 2** Characteristics of PAR-nylon 6 block copolymers

Designation	Feed mole ratio (CL/PAR)	$M_n$ of PAR block <sup>a</sup>	Nylon block		$\eta_{inh}$ of block copolymer <sup>c</sup>	Extracted amount (wt%)		PAR content (wt%) <sup>d</sup>
			$M_n$ <sup>b</sup>	$[\eta]$		By PAR selective	By nylon selective	
ARNY 1-1	63	1500	3000	0.286	0.627	<1	13	24.3
ARNY 1-2	72	1500	3700	0.337	0.758	<1	10	20.1
ARNY 1-3	81	1500	4200	0.369	0.815	<1	8	18.0
ARNY 1-4	90	1500	5000	0.422	0.830	<1	4	15.5
ARNY 2-2	81	2900	3800	0.343	0.734	<1	14	29.5
ARNY 3-1	81	3600	3200	0.300	0.685	<1	20	38.2

<sup>a</sup> Calculated from elemental analysis of block copolymer

<sup>b</sup> Calculated from degree of polymerization<sup>28</sup> =  $136.7[\eta]^{1.309}$

<sup>c</sup> Measured at the concentration of 0.6 wt%

<sup>d</sup> Measured from elemental analysis

dropwise into the chloroform solution of bisphenol A with stirring in an ice bath to dissipate the heat generated during the reaction. The reaction continued for 3 h at 15°C and the reaction mixture was poured into 10-fold volume of methanol. The filtrate was refluxed in methanol and filtered three times to extract the triethylamine hydrochloride salt complex formed during the reaction. The final precipitate was dried under vacuum at 80°C for 72 h.

#### Synthesis of polyarylate-nylon 6 block copolymers

The preparation of isocyanate-terminated PAR as polymeric activator was carried out under dry nitrogen in a flash-dried glass reactor equipped with heating and stirring apparatus. A 1.00 equivalent of hydroxy-difunctional PAR was reacted with 2.05 equivalents of toluene diisocyanate in chloroform at 50°C for 5 h. The slight excess of isocyanate was used to compensate for the small amount of moisture possibly contained in the reactants and also to prevent chain extension during reaction<sup>16</sup>. Chloroform was then removed from the reaction system under a vacuum of about 667 Pa. After putting  $\epsilon$ -caprolactam into the reactor, the temperature was raised to 160°C and  $\epsilon$ -caprolactam melted rapidly. With continuous stirring, the polymeric activator dissolved completely in the molten  $\epsilon$ -caprolactam medium. Sodium hydride as catalyst was added with continuous stirring. After 1 h, stirring became impossible due to the increased viscosity, but the reaction was continued without stirring for 12 h at 105°C. The crude product was cut into pieces and extracted with

chloroform as the selective solvent for PAR, followed by 0.5 wt% formic acid aqueous solution and 5 wt% LiCl solution of methanol as the selective solvent for nylon 6 oligomer. The ratio of NaH/NCO was fixed at 2 and the molecular weight of the nylon 6 block was controlled by varying the amount of  $\epsilon$ -caprolactam in the feed (Table 2).

#### Blending

Binary blends of PAR-nylon 6 block copolymers with PAR or nylon 6 were prepared by a dissolution-precipitation method. The required amount was dissolved in *m*-cresol to obtain 2% (w/v) solution. This solution was poured into a 10-fold volume of acetone, causing rapid coprecipitation. The precipitate was filtered off and washed with acetone, then dried in vacuum for 72 h at 80°C.

#### Characterization of hydroxy-difunctional PAR, block copolymers and blends

The  $M_n$  of hydroxy-difunctional PARs was determined by titration of the hydroxy end group using a Metron potentiometer (E536) and a Mettler micropipette (Dosimat 645). The PAR oligomers were dissolved in freshly distilled tetrahydrofuran and titrated with 0.2 N solution of tetrabutyl ammonium hydroxide in methanol<sup>15</sup>.

Intrinsic or inherent viscosity was measured with an Ubbelohde viscometer at  $25 \pm 0.2^\circ\text{C}$  in 1,2-dichloroethane for PAR oligomer and in *m*-cresol for block copolymers and nylon 6.

Infra-red spectra were obtained with a Bruker IFS-88 Fourier transform infra-red (FTi.r.) spectrometer at a resolution of  $2\text{ cm}^{-1}$  at room temperature. A minimum of 200 scans were signal averaged. The frequency scale was calibrated internally with a reference helium-neon laser to an accuracy of  $0.2\text{ cm}^{-1}$ . The pellet was made with KBr and its thickness was about 0.1 mm.

Nuclear magnetic resonance (n.m.r.) spectra were recorded at room temperature with a Bruker AC80 (80 MHz) FTn.m.r. spectrometer in trifluoroacetic acid with tetramethyl silane as a reference.

Elemental analyses were run on a Yanaco MT-2CHN recorder. Gel permeation chromatography (g.p.c.) was accomplished with a Waters LG-240 g.p.c. apparatus at room temperature, using tetrahydrofuran as eluent and polystyrene as a standard for calibration.

Differential scanning calorimetry (d.s.c.) measurements were achieved with a Perkin-Elmer DSC-4 instrument at heating and cooling rates of  $20^\circ\text{C min}^{-1}$  with a sensitivity of  $10\text{ mcal s}^{-1}$ . Temperature calibration was performed with an indium standard. All runs were carried out using samples of about 13 mg in nitrogen atmosphere. Before scanning, samples were quenched to  $-20^\circ\text{C}$  after maintaining for 5 min at  $240^\circ\text{C}$ . The glass transition temperature of the nylon 6 phase ( $T_{g,\text{nylon}}$ ) and the PAR phase ( $T_{g,\text{PAR}}$ ), the melting temperature of nylon 6 ( $T_m$ ) and the heat of fusion ( $\Delta H_f$ ) at  $T_m$  were measured on subsequent heating to  $240^\circ\text{C}$ . Crystallization temperature ( $T_c$ ) and heat of crystallization ( $\Delta H_c$ ) were measured during the next cooling cycle from  $240^\circ\text{C}$ .

Transmission electron micrographs of the block copolymer were taken on a Jeol 100CX II at an acceleration voltage of 80 kV. Samples were stained by immersion for 48 h in a 1%  $\text{OsO}_4$  solution of formalin/ $\text{H}_2\text{O}$  (1/1 by volume)<sup>17</sup>, followed by washing, drying and cutting with an ultramicrotome.

Scanning electron micrographs of blends were taken on a Jeol SEM (JSM-35CF) at an acceleration voltage of 15 kV. Samples were prepared by etching the PAR phase with chloroform, in cases where PAR was the minor component, and etching the nylon 6 phase with 5% LiCl-methanol, in cases where the nylon 6 was the minor component, by refluxing for 72 h.

#### Hydrolysis of PAR-nylon 6 block copolymers

The molecular weight of the nylon block in the block copolymer was determined after selective hydrolysis of

the PAR block with concentrated sulfuric acid. That is, the block copolymer was dissolved in 95% concentrated sulfuric acid at a concentration of  $15\text{ g l}^{-1}$ . The solution was stirred for 1 h at room temperature, then poured into a 10-fold volume of acetone. The obtained nylon block was washed with acetone and hot methanol and dried at  $60^\circ\text{C}$  before molecular weight measurement.

## RESULTS AND DISCUSSION

### Synthesis of hydroxy-difunctional PAR oligomers

The structural analysis of hydroxy-difunctional PARs was accomplished with FTi.r. and  $^1\text{H}$  n.m.r. Figure 1 presents a typical i.r. spectrum of the PAR oligomer. The characteristic adsorption band located at  $2915\text{ cm}^{-1}$  was assigned to stretching of the aliphatic methyl group, that at  $1739\text{ cm}^{-1}$  to carbonyl stretching of the ester group, and those at  $1504$  and  $723\text{ cm}^{-1}$  to stretching of the aromatic group. Adsorption at  $3450\text{ cm}^{-1}$ , assigned to OH stretching of the terminal hydroxy group, was observed as a trace because of its low concentration. In addition, the absorption shoulder located at around  $1720\text{ cm}^{-1}$  was assigned to the carbonyl stretching band partly shifted to lower wavenumber induced by a hydrogen bond between the carbonyl and hydroxy groups.

A typical  $^1\text{H}$  n.m.r. spectrum for hydroxy-difunctional PAR is presented in Figure 2, together with proton assignments. The proton of phenolic OH was not detected due to its low concentration and the resolution ability of the apparatus.

Table 1 presents the molecular weight and other characteristics of a series of hydroxy-difunctional PAR oligomers. The  $M_n$  values obtained from g.p.c. are a little higher but show the same trend as those obtained from end-group titration. The molecular weight dependence of the Mark-Houwink constants for universal calibration might be one reason for this discrepancy<sup>18</sup>. The exact measurement of  $M_n$  of PAR oligomers is very important because hydroxy-difunctional PAR oligomers are used in the subsequent reaction with toluene diisocyanate, where the stoichiometric ratio of hydroxy functionality over isocyanate functionality is critical; unreacted toluene diisocyanate resulting from excess of isocyanate group would ultimately create nylon 6 homopolymer in the next step.

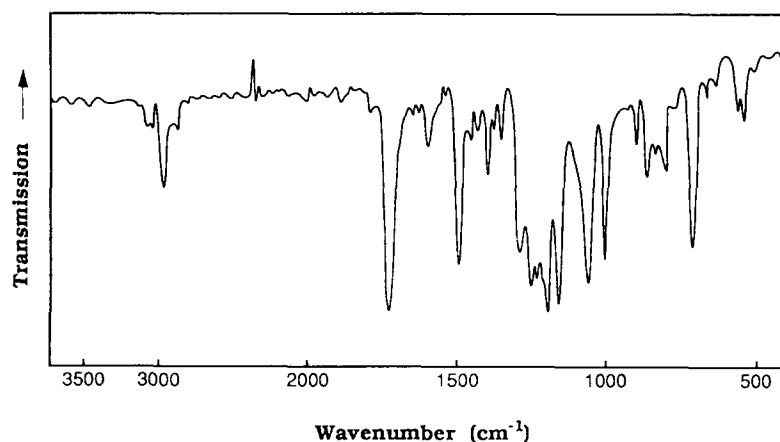


Figure 1 I.r. spectrum of hydroxy-difunctional polyarylate (PAR 1)

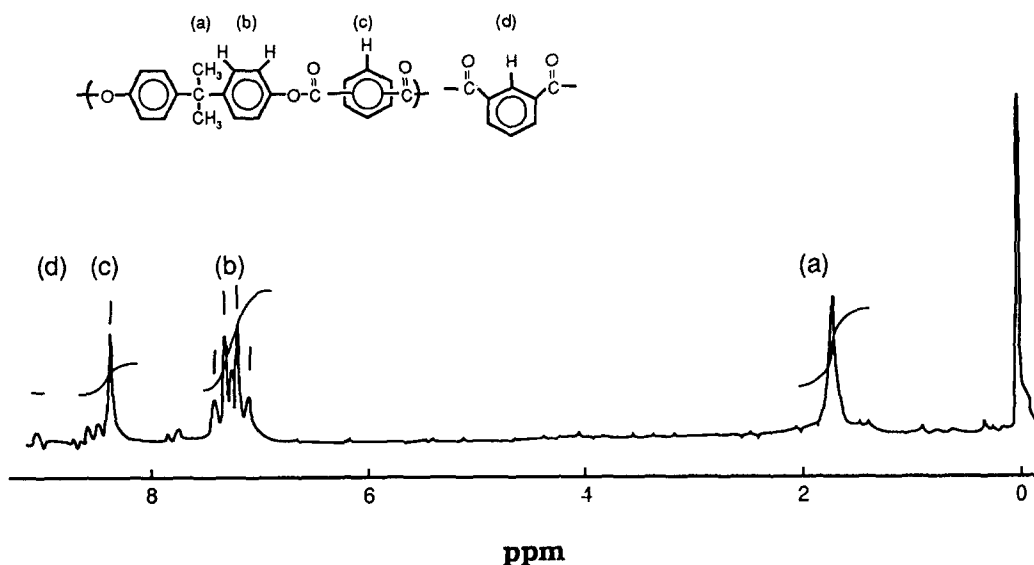


Figure 2 N.m.r. spectrum of hydroxy-difunctional polyarylate (PAR 1)

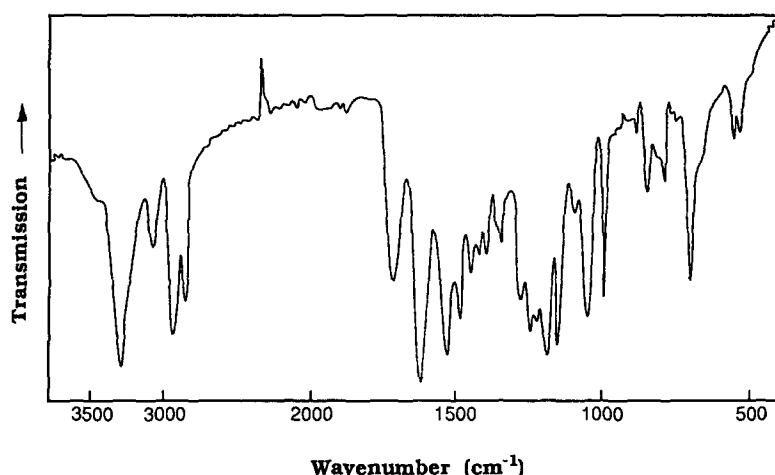


Figure 3 I.r. spectrum of PAR-nylon 6 block copolymer (ARNY 3-1)

#### Synthesis of PAR-nylon 6 block copolymers

Reactions for the synthesis of PAR-nylon 6 block copolymers were accomplished in a homogeneous system where isocyanate-terminated PARs were dissolved in molten  $\epsilon$ -caprolactam to give a high concentration (~40%) at a high temperature of about 160°C. The typical i.r. spectrum of PAR-nylon 6 block copolymer purified after extraction with selective solvents, as described in the Experimental section, is presented in Figure 3. Absorption at about 1640  $\text{cm}^{-1}$ , assigned to the amide I band, and 3300 and around 1540  $\text{cm}^{-1}$ , assigned to the amide II band, are due to the nylon 6 block. Absorption at 1739  $\text{cm}^{-1}$  is assigned to carbonyl stretching of the PAR block.

Figure 4 presents a typical n.m.r. spectrum with proton assignments. This spectrum shows both proton peaks due to the corresponding homopolymers, suggesting effective formation of block copolymer.

The characteristics of PAR-nylon 6 block copolymers are shown in Table 2. The first number of the code (ARNY) representing the block copolymer indicates the class of dihydroxy-functional PAR used for synthesis of the block copolymer, which is designated in Table 1. The molecular

weight of PAR block in the block copolymer was calculated by the ratio of PAR composition to nylon 6 composition in the block copolymer, multiplied by the sum of the molecular weights of two nylon blocks in a copolymer molecule. The molecular weight of PAR block existing in the block copolymer is almost preserved after copolymer reaction, and this is more evident at lower molecular weight. Successive extraction with selective solvents for the purification of block copolymers gave a high yield (> 80%) of block copolymer. It may be noticed that the yield of block copolymer is lower when the polymeric activator used for reaction has a higher molecular weight. The result is attributed to the poorer solubility of PAR oligomer with higher molecular weight in molten  $\epsilon$ -caprolactam and to the chain cleavage reaction, which might occur to some degree as a result of an activated monomer anion attacking an ester linkage of a polymeric chain<sup>12</sup>.

The  $M_n$  of nylon 6 in the block copolymer was evaluated by measuring the intrinsic viscosity of an isolated nylon 6 block after hydrolysis of the PAR block in concentrated sulfuric acid, as described in the Experimental section. This reaction condition for selective

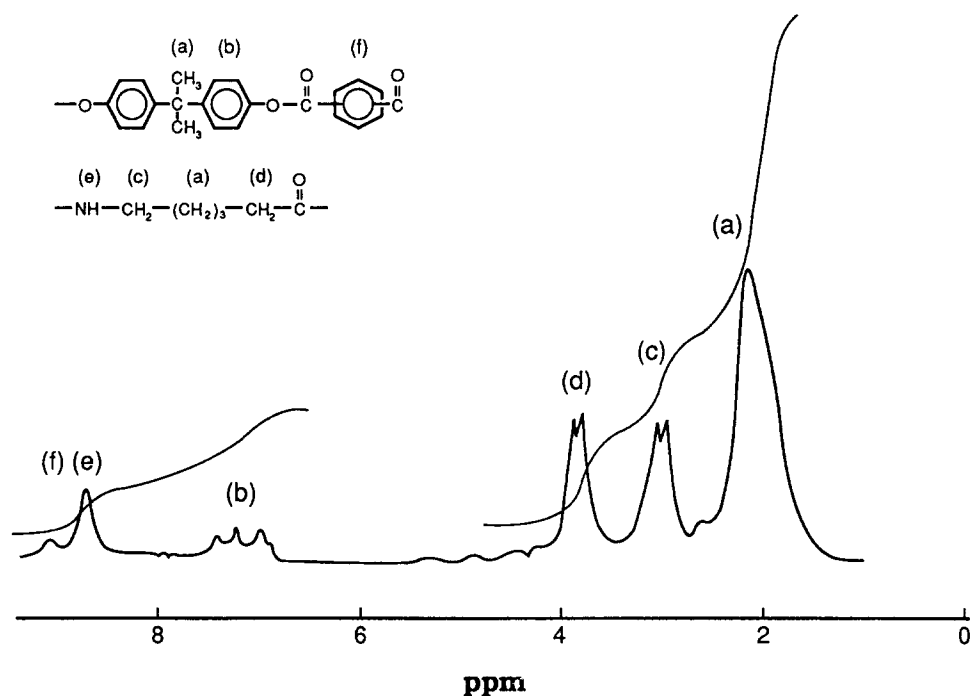


Figure 4 N.m.r. spectrum of PAR-nylon 6 block copolymer (ARNY 1-4)

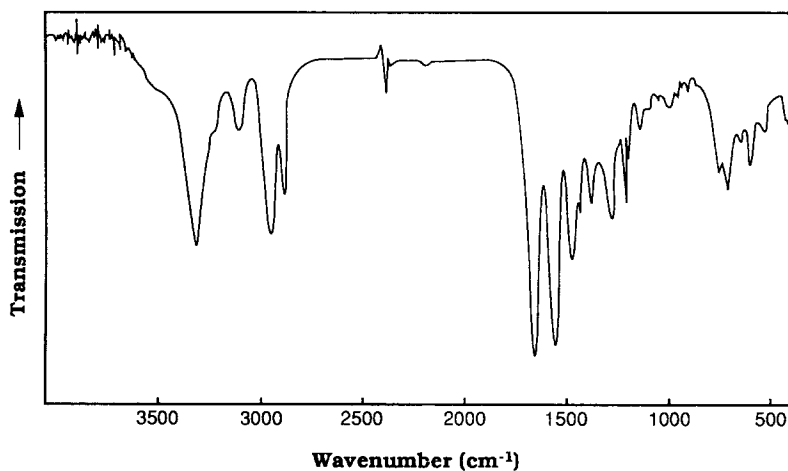


Figure 5 I.r. spectrum of PAR-nylon 6 block copolymer (ARNY 3-1) after selective hydrolysis of PAR block

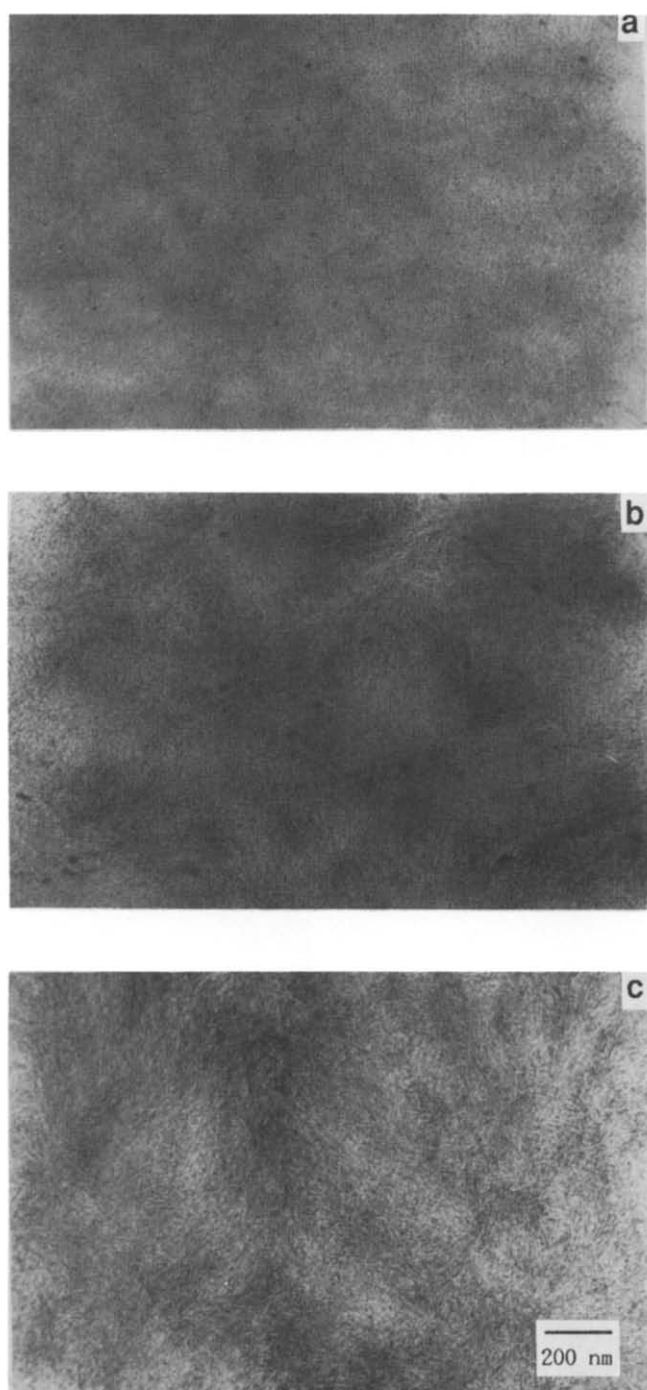
hydrolysis is commonly used for the measurement of solution viscosity of nylon 6, so little damage to the nylon 6 block during selective hydrolysis of PAR segments is expected<sup>19</sup>. The i.r. spectrum of the isolated nylon 6 block is presented in Figure 5, which is absolutely consistent with the i.r. spectrum of nylon 6 homopolymer; it shows that the PAR block is completely hydrolysed under this condition.

#### Phase behaviour of block copolymers

Figure 6 represents the morphology of block copolymers with selectively stained nylon 6 domains. Overall morphology shows microphase separation on a scale of 200–300 Å. The finely separated phase morphology might be ascribed to the entropy gain due to the covalent bonds linking the PAR and nylon 6 blocks, although the difference in solubility parameter of the constituent blocks<sup>20</sup> ( $\delta_{\text{nylon}} = 22.5 \text{ (J cm}^{-3}\text{)}^{1/2}$  and  $\delta_{\text{PAR}} = 19.2 \text{ (J cm}^{-3}\text{)}^{1/2}$ ) is relatively large for maintaining

homogeneous phase behaviour of the block copolymer. The difference in morphology caused by the different molecular weights of the constituent blocks appears to be too minor for quantitative detection by transmission electron microscopy, but PAR-nylon 6 block copolymers with blocks of lower molecular weight show qualitatively finer phase-separated morphology.

The miscibility between constituent blocks in block copolymer is related to the miscibility between homopolymers of the corresponding chemical structure. In block copolymers with glassy-rubbery blocks such as poly(styrene-*b*-butadiene), poly(styrene-*b*-isoprene) and poly(styrene-*b*-dimethyl siloxane), where the corresponding homopolymers have been reported to be immiscible<sup>21</sup>, the  $T_g$  of the polystyrene block does not show dependence on the composition or molecular weight of the rubbery block<sup>22</sup>. In contrast, when homopolymers have partial miscibility in binary blends, the  $T_g$ s of the corresponding blocks in the block copolymer are also dependent on the composition and molecular weight of the blocks. In block



**Figure 6** TEM photographs of PAR-nylon 6 block copolymers stained by OsO<sub>4</sub>: (a) ARNY 1-2; (b) ARNY 1-4; (c) ARNY 3-1

copolymers whose constituent blocks have total or partial miscibility, such as poly(butadiene-*b*-isoprene)<sup>23</sup> composed of low molecular weight non-polar blocks, and poly(urethane-*b*-butylene terephthalate)<sup>24</sup> and poly(arylate-*b*-styrene)<sup>25</sup> composed of polar block, the  $T_g$ s of the blocks vary due to miscibility between blocks. Blends of PAR and nylon 6 have been reported to show partial miscibility<sup>9</sup>, so the corresponding blocks in PAR-nylon 6 block copolymer are expected to show enhanced miscibility stemming from entropy gain induced by the covalent bond existing between blocks.

Table 3 shows the thermal properties of block copolymers and nylon 6 homopolymer measured by d.s.c. All the  $T_g$ s of the nylon 6 phase in block copolymers are higher than that of nylon 6 homopolymer. As the molecular weight of the nylon 6 block increases in the series of block copolymers with molecular weight of the PAR block fixed at 1500 (Table 3, ARNY 1-1 to ARNY 1-4), the degree of  $T_g$  shift of the nylon 6 phase in the block copolymers becomes smaller, although absolute values are still higher than that of nylon 6 homopolymer. The larger  $T_g$  increase at shorter block lengths is thought to be due to two factors: (1) the enhanced mutual dissolution of constituent blocks due to entropy gain at shorter block length; (2) the constrained chain mobility of the nylon 6 segment by the rigid PAR block jointed chemically to the nylon 6 segment is anticipated to be more evident when the nylon 6 block is shorter.

In block copolymers composed of nylon 6 blocks of similar lengths and PAR blocks of different lengths (ARNY 1-1 and 3-1 or ARNY 1-2 and ARNY 2-2 in Table 3), the  $T_g$  of the nylon 6 domain is higher in block copolymers having a shorter PAR block, which may be ascribed to the increased miscibility between the two blocks due to entropy gain. The  $T_g$  of the PAR phase was detectable with d.s.c. only when there was a relatively high content of long PAR blocks, in spite of the phase-separated morphology (Figure 6). A small heat capacity change at  $T_g$  of the PAR domain and a diffused phase boundary due to partial miscibility between the two blocks may be the cause of the difficulty in  $T_g$  detection by d.s.c.

Melting and crystallization behaviours were also influenced by the molecular weights of blocks, i.e. decreased  $T_m$ , decreased crystallinity (reduced values of  $\Delta H_f$  and  $\Delta H_c$ ), and decreased crystallization rate (from increased supercooling,  $T_m - T_c$ ) for crystallization were observed for the block copolymers with shorter blocks (Table 3). These results can also be explained by the

**Table 3** Thermal properties of PAR-nylon 6 block copolymers

Designation	$T_{g,nylon}$ (°C)	$T_{g,PAR}$ (°C)	$T_m$ (°C)	$T_c$ (°C)	$T_m - T_c$ (°C)	$\Delta H_f$ (J g <sup>-1</sup> ) <sup>a</sup>	$\Delta H_c$ (J g <sup>-1</sup> ) <sup>a</sup>
ARNY 1-1	61	—	200	125	75	17	25
ARNY 1-2	59	—	205	132	73	19	28
ARNY 1-3	56	—	210	145	65	23	33
ARNY 1-4	52	—	214	152	62	30	40
ARNY 2-2	56	155	212	150	62	25	35
ARNY 3-1	54	160	209	142	67	21	31
Nylon 6	48	—	223	177	46	48	60

<sup>a</sup> Heat per unit weight of nylon 6 segment

enhanced partial miscibility and constrained chain mobility of the nylon 6 block, as in the  $T_g$  behaviour previously described.

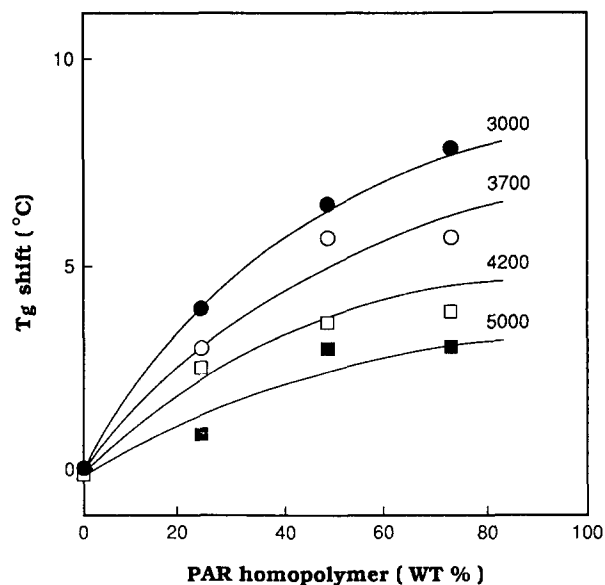
#### Binary blends of PAR-nylon 6 block copolymers with PAR or nylon 6

The ultimate aim of this study is to investigate the compatibilizing effect of PAR-nylon 6 block copolymer in PAR/nylon 6 blends. In these blends, a greater compatibilizing effect is anticipated when each block penetrates easily into the corresponding homopolymer phase to form interlinks between the homopolymer phases. Thus, we studied the miscibility in binary blends of PAR-nylon 6 block copolymers with PAR and nylon 6 homopolymers. There have been extensive experimental and theoretical studies on blends of homopolymers with phase-separated block copolymers having a block with chemical structure identical to the homopolymer, and it is now well known that molecular-level mixing is not always achieved between homopolymer and block with the same chemical structure due to restrictions such as molecular weight<sup>26,27</sup>.

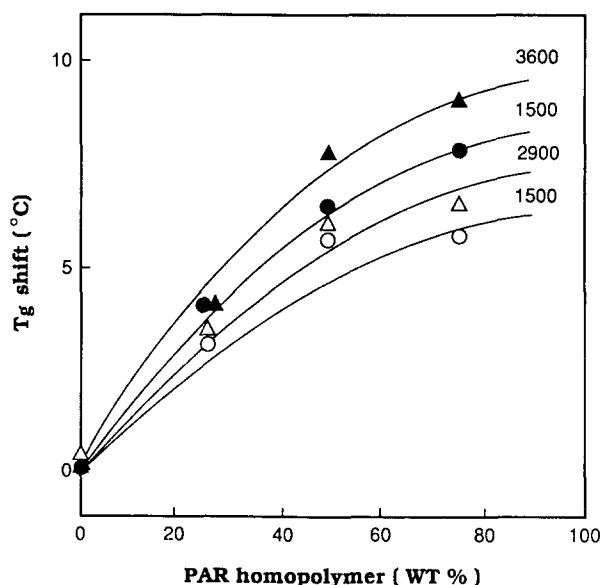
Table 4 represents the thermal properties of PAR-nylon 6 block copolymer blends with PAR homopolymer, measured by d.s.c. The single  $T_g$  behaviour in the amorphous PAR phase shows the intimate molecular-level mixing of PAR homopolymer and PAR blocks of copolymers. In Table 4, it is observed that  $T_{g,nylon}$  increases with PAR content in the binary blend. This trend is more evident when the length of the nylon block is shorter at fixed  $M_n$  of the PAR block (Figure 7) and when the length of the PAR block is larger with similar  $M_n$  of the nylon block (Figure 8). This increase in  $T_{g,nylon}$  shows that PAR segments that have higher  $T_g$  dissolve into the nylon 6 domain due to partial miscibility, and that this dissolution of homopolymer into the domain of the block with different chemical structure is enhanced when the block

**Table 4** Thermal properties (°C) of PAR homopolymer/PAR-nylon 6 block copolymer blends

	PAR/block copolymer				
	0/100	25/75	50/50	75/25	100/0
<b>ARNY 1-1</b>					
$T_{g,nylon}/T_{g,PAR}$	61/-	65/-	68/-	69/-	-/200
$T_m$	200	196	195	194	
$T_c$	125	115	108	107	
<b>ARNY 1-2</b>					
$T_{g,nylon}/T_{g,PAR}$	59/-	62/-	68/-	68/-	-/200
$T_m$	205	203	202	201	
$T_c$	132	123	118	116	
<b>ARNY 1-3</b>					
$T_{g,nylon}/T_{g,PAR}$	56/-	59/-	60/-	60/-	-/200
$T_m$	210	208	208	207	
$T_c$	145	136	132	131	
<b>ARNY 1-4</b>					
$T_{g,nylon}/T_{g,PAR}$	52/-	53/-	56/-	56/-	-/200
$T_m$	214	213	213	212	
$T_c$	152	144	142	141	
<b>ARNY 2-2</b>					
$T_{g,nylon}/T_{g,PAR}$	56/155	60/159	62/166	63/175	-/200
$T_m$	212	209	208	207	
$T_c$	150	139	135	134	
<b>ARNY 3-1</b>					
$T_{g,nylon}/T_{g,PAR}$	54/160	58/165	62/174	63/181	-/200
$T_m$	209	205	204	203	
$T_c$	142	129	121	119	



**Figure 7**  $T_g$  shift of nylon phase in PAR homopolymer/PAR-nylon 6 block copolymer blend with various  $M_n$  values of nylon block (designated on the curves) at fixed  $M_n$  of PAR block (1500): ●, ARNY 1-1; ○, ARNY 1-2; □, ARNY 1-3; ■, ARNY 1-4



**Figure 8**  $T_g$  shift of nylon phase in PAR homopolymer/PAR-nylon 6 block copolymer blend with various  $M_n$  values of PAR block (designated on the curves) at similar  $M_n$  of nylon block (solid symbols, 3000-3200; open symbols, 3700-3800): ●, ARNY 1-1; ▲, ARNY 3-1; ○, ARNY 1-2; △, ARNY 2-2

copolymer has the longer block of the same structure and the shorter block of different structure. The same trend in miscibility can also be confirmed from melting and crystallization behaviour of nylon 6 in Table 4, that is, decrease of  $T_m$  and decreased crystallization rate (increased supercooling,  $T_m - T_c$ , for crystallization) at high content of PAR homopolymer in binary blends is more prominent when the block copolymer has a shorter nylon block and longer PAR block.

Table 5 shows the thermal properties of nylon 6 homopolymer/PAR-nylon 6 block copolymer blends.  $T_{g,nylon}$  varies smoothly with composition in the binary blend. Although two  $T_g$ s are too contiguous to refer to miscibility, this result, together with the values of  $T_m$  and



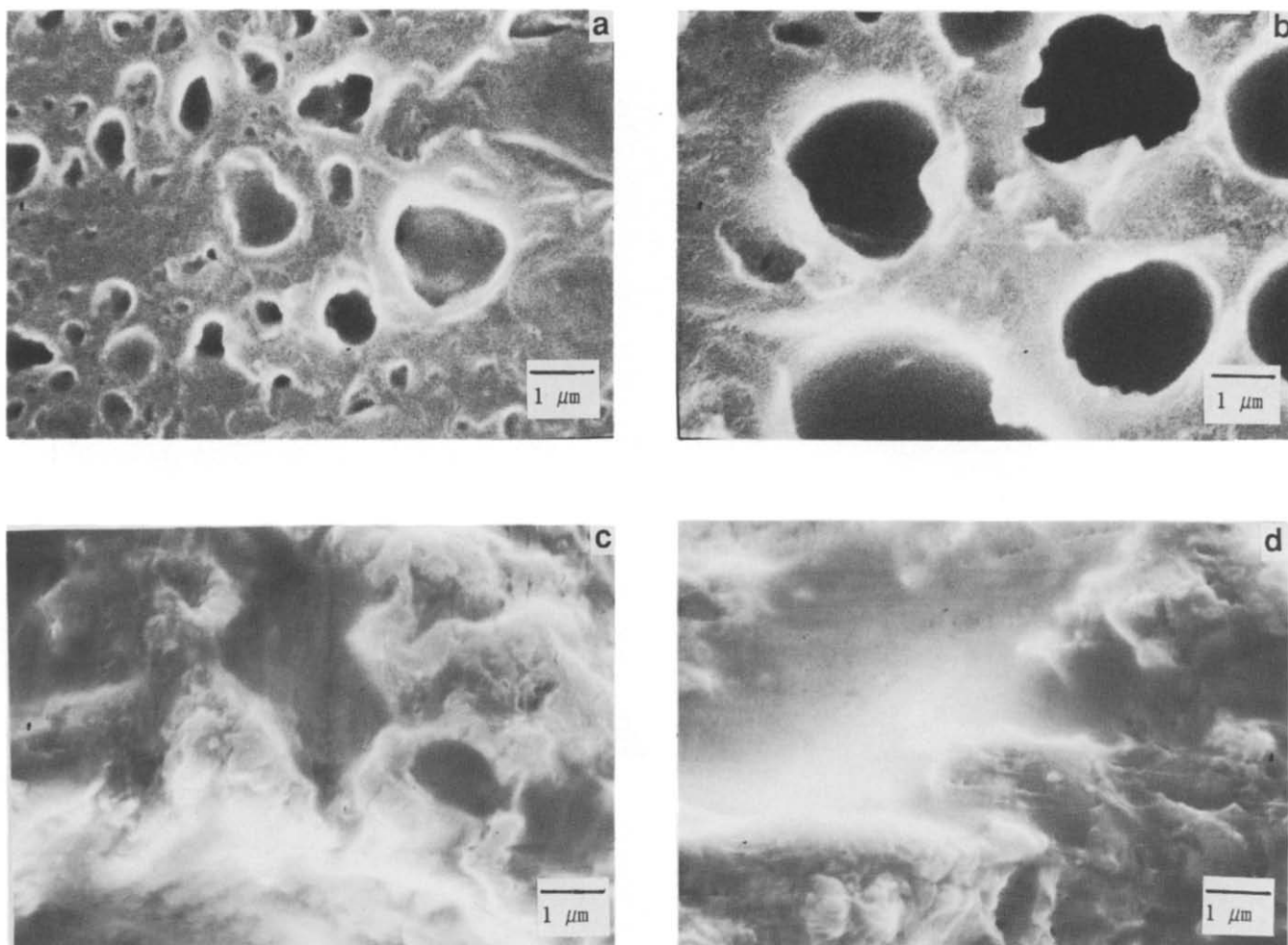


Figure 9 SEM photographs of etched surfaces: (a) PAR/nylon 6 (70/30); (b) PAR/nylon 6 (30/70); (c) ARNY 1-2/PAR (70/30); (d) ARNY 1-2/nylon 6 (70/30)

Table 5 Thermal properties (°C) of nylon 6 homopolymer/PAR-nylon 6 block copolymer blends

	Nylon 6/block copolymer				
	0/100	25/75	50/50	75/25	100/0
<b>ARNY 1-1</b>					
$T_{g,nylon}/T_{g,PAR}$	61/-	59/-	56/-	52/-	48/-
$T_m$	200	204	207	211	223
$T_c$	125	154	162	166	177
<b>ARNY 1-2</b>					
$T_{g,nylon}/T_{g,PAR}$	59/-	57/-	53/-	51/-	48/-
$T_m$	205	207	212	214	223
$T_c$	132	157	164	167	177
<b>ARNY 1-3</b>					
$T_{g,nylon}/T_{g,PAR}$	56/-	54/-	52/-	50/-	48/-
$T_m$	210	214	216	216	223
$T_c$	145	167	169	172	177
<b>ARNY 1-4</b>					
$T_{g,nylon}/T_{g,PAR}$	52/-	50/-	49/-	49/-	48/-
$T_m$	214	218	220	221	223
$T_c$	152	172	173	175	177
<b>ARNY 2-2</b>					
$T_{g,nylon}/T_{g,PAR}$	56/155	53/-	51/-	49/-	48/-
$T_m$	212	216	218	220	223
$T_c$	150	169	171	173	177
<b>ARNY 3-1</b>					
$T_{g,nylon}/T_{g,PAR}$	54/160	52/-	50/-	49/-	48/-
$T_m$	209	210	214	215	223
$T_c$	142	161	165	170	177

$T_c$  which change monotonically in binary blends, suggests molecular-level mixing of nylon 6 and nylon 6 block in the block copolymer.

Figures 9a and b represent the morphology of etched surfaces of unmodified PAR/nylon 6 binary blends. The holes, which range from 1 to 3 μm, suggest the incompatibility of unmodified PAR/nylon 6 blends<sup>9</sup>. However, the etched surfaces of PAR-nylon 6 block copolymer blended with PAR (Figure 9c) or nylon 6 (Figure 9d) do not show any distinct phase segregation on the microscopic scale, as expected for the intimate mixing of homopolymers with blocks of identical structure.

### CONCLUSIONS

PAR-nylon 6 block copolymers were effectively synthesized by the anionic polymerization of ε-caprolactam using the polymeric activator obtained by the reaction of hydroxydifunctional PAR and toluene diisocyanate.

The partial miscibility between PAR and nylon 6 segments was enhanced in the block copolymer, and was more evident with shorter lengths of the constituent blocks.

In binary blends of PAR-nylon 6 block copolymer with PAR or nylon 6 homopolymer, homopolymer seems to be mixed at the molecular level with the

corresponding blocks in the block copolymer. In binary PAR-nylon 6 block copolymer/PAR blends, the partial miscibility of the nylon 6 block with the PAR segment was more evident when the PAR-nylon 6 block copolymer had shorter nylon 6 block or longer PAR block.

#### ACKNOWLEDGEMENT

This research was supported by the Ministry of Education, Republic of Korea, Research Fund (1990) for Advanced Materials.

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