

Nylon 6–polyethersulfone–nylon 6 block copolymer: synthesis and application as compatibilizer for polyethersulfone/nylon 6 blend

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Nylon 6–polyethersulfone (PES)–nylon 6 block copolymers were synthesized by anionic polymerization of ϵ -caprolactam using chlorine-terminated PES, a polymeric activator. The structure and properties of these block polymers were examined using infra-red, nuclear magnetic resonance, differential scanning calorimetry, transmission electron microscopy, and thermogravimetric analysis. The compatibilizing effects of this block copolymer on PES/nylon 6 blends were investigated by examining thermal properties, morphology and dynamic mechanical characteristics. When the block copolymer was added, the size of dispersed phase in the blend decreased dramatically, and the glass transition temperatures of the constituent polymers converge. The improvement of dynamic tensile modulus and thermal resistance due to the dispersed PES phase were enhanced by the added block copolymer. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Nowadays, polymer blends have been widely investigated because of their simplicity, and because of their efficiency for developing new high performance materials. However, most polymer blends are immiscible because of the positive enthalpy change and the small increase of entropy on mixing¹. Therefore, the stabilization and enhancement of adhesion between the separated phases is very important for obtaining satisfactory properties. Block or graft copolymers can be used as compatibilizers to modify the morphology and mechanical performance of polymer blends^{2,3}. It is known that the compatibilizers reduce the size of dispersed phase, enhance the adhesion between the phases, and stabilize the dispersed phase^{4,5}. The compatibilizing mechanism of the block copolymer varies according to the degree of miscibility between the two homopolymers or the component blocks of block copolymer.

If a random copolymer which has a middle value of polarities or solubility parameters of two homopolymers is added, the unfavourable interaction between two homopolymers is alleviated. This solubilization effect can also be observed by the addition of non-microphase separated block copolymer⁶. In this case, the copolymer

with the smaller molecular weight is favourable because of the high entropy increase on mixing.

When a microphase-separated block copolymer of high block length is added as a compatibilizer for homopolymer blend with poor miscibility, the block copolymer migrates to the interface to reduce the interfacial tension between the phases of homopolymers. The constituent blocks in the added block copolymer are expected to diffuse into the homopolymer phases of identical chemical structure⁷.

Polyethersulfone (PES) has been recognized as an important plastic offering a high heat distortion temperature, excellent impact strength and high resistance to hydrolysis. However, it is notch-sensitive and easily cracked under stress, as are other amorphous polymers⁸. Hence, there are good reasons to blend PES with crystalline polymers⁹. Nylon 6 is a well known engineering plastic offering high toughness and high resistance to chemicals and oils. However, nylon 6 has a low glass transition temperature (T_g) and a low heat distortion temperature and it is necessary to blend nylon 6 with other polymers which have high thermal resistance. In these respects, the shortcomings of each polymer can be remedied when PES and nylon 6 are blended. Because these two polymers have poor miscibility, a compatibilizer will be necessary. The block copolymer containing PES and nylon 6 block can be used to improve the

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miscibility and the adhesion between the phases. References on the synthesis of polysulfone–nylon 6 block copolymer and properties of binary blends of this block copolymer with homopolymers are available^{9–12}. However, within the present knowledge of the authors, no published paper has been reported on the study of compatibilized PES/nylon 6 blend.

In the present study, nylon 6–PES–nylon 6 block copolymers were synthesized and the characteristics of the block copolymers were investigated. The later part of this paper deals with the compatibilizing effects of these block copolymers on the morphology, and the thermal and mechanical properties of PES/nylon 6 blends.

EXPERIMENTAL

Material

4,4'-Sulfonyldiphenol (bisphenol S, Aldrich), bis(*p*-chlorophenyl)sulfone (DCDPS, Aldrich), potassium carbonate (K₂CO₃, Aldrich), and sodium hydride (55–60% dispersion in oil, Fluka) were used without further purification. ϵ -Caprolactam (CL, BASF) was recrystallized from acetone. The crystals were dried at 70°C under reduced pressure for a week. Osmium tetroxide (OsO₄, Aldrich) was used without further purification and solubilized in H₂O/formalin (50/50 v/v) to 1 wt% concentration before use. Methanol was used after distillation. Solvents such as sulfolane (Aldrich), phenol (Showa), tetrachloroethane (TCE, Yakuri Pure Chemicals), and formic acid (Junsei) were reagent grade and used without further purification. PES (Aldrich, low molecular weight, $\bar{M}_v = 20\,000$) was reprecipitated using phenol/TCE (50/50 v/v) as a solvent, methanol as a non-solvent. The precipitate was dried at 70°C under reduced pressure for 3 days. Nylon 6 (Tongyang Nylon Company, 1031 grade, $\bar{M}_v = 30\,000$) was also reprecipitated before use using formic acid as a solvent, H₂O as a non-solvent. The precipitate was dried by the same way as in PES.

Synthesis of nylon 6–PES–nylon 6 block copolymer

Synthesis of PES oligomer. Chlorine-terminated PESs

with various molecular weights were synthesized by the solution polymerization reaction of bisphenol S with DCDPS. The molecular weights were controlled with the stoichiometric imbalances of reactants (*Table 1*), using excess DCDPS. Bisphenol S and DCDPS were charged into the reaction vessel and dissolved in sulfolane. After addition of toluene, the reaction vessel was heated to 120°C for 4 h in order to azeotropically distill toluene and water in the reaction medium. Then the reaction vessel was heated to 225°C for 5 h to complete the polymerization reaction. After the reaction was completed, the reaction mixture was poured into 10-fold methanol. The filtrate was washed in methanol/water (50/50) for 2 days and in methanol for 1 day. The final precipitate was dried under reduced pressure at 100°C for 72 h.

Synthesis of nylon 6–PES–nylon 6 block copolymers. The preparation of block copolymer was carried out under dry nitrogen atmosphere in dried glass reactor equipped with heating and stirring apparatus. After weighed chlorine-terminated PES oligomer and ϵ -caprolactam were charged into the reactor, the temperature was raised to 175°C. When PES oligomer was dissolved completely in molten ϵ -caprolactam medium, the catalyst, sodium hydride was added with continuous stirring. After the stirring became impossible due to the increased viscosity, the temperature was lowered to 105°C and retained at this temperature for 3 h. The product was collected and extracted with methanol, *N,N'*-dimethyl formamide, 0.5 wt% aqueous solution of formic acid in order to remove unreacted ϵ -caprolactam, PES oligomer, and nylon 6 oligomer. The final product was washed with methanol and dried under reduced pressure at 100°C for 72 h. The recipe for the synthesis of nylon 6–PES–nylon 6 block copolymer is shown in *Table 2*.

Blending

Ternary blends of nylon 6–PES–nylon 6 block copolymers, PES, and nylon 6 were prepared by the dissolution–precipitation method. The required amount of polymers were dissolved in phenol/TCE (50/50 v/v) to obtain a 20 wt/v% solution, and this was poured into

Table 1 Recipe for the synthesis of chlorine-terminated polyethersulfone oligomer

Designation	Feed						Monomer feed mole ratio ^a	Yield (%)
	Bisphenol S (g)	DCDPS (g)	K ₂ CO ₃ (g)	Sulfolane (ml)	Toluene (ml)			
PES 2	10.49	14.51	6.95	100	50	0.824	85.9	
PES 5	11.06	13.93	7.28	100	50	0.917	91.6	
PES 7	11.28	13.72	7.48	100	50	0.937	84.8	

^a Monomer feed mole ratio: bisphenol S(mol)/DCDPS(mol)

Table 2 Recipe for the synthesis of nylon 6–PES–nylon 6 block copolymers

Designation	Name	PES oligomer		ϵ -Caprolactam		NaH		Yield (%)
		g	mol ($\times 10^3$)	g	mol	g	mol ($\times 10^2$)	
SN-2-85	PES 2	6.0	2.22	34.0	0.30	0.50	2.08	80
SN-5-75	PES 5	10.0	1.97	30.0	0.27	0.24	1.00	63
SN-7-95	PES 7	2.0	0.28	38.0	0.34	0.04	0.17	93
SN-7-75	PES 7	10.0	1.40	30.0	0.24	0.27	1.12	43

10-fold methanol, causing rapid coprecipitation. The precipitate was filtered off and washed with methanol, and dried in reduced pressure for 72 h at 100°C.

Characterization

Characterization of chlorine terminated PES oligomer and nylon 6–PES–nylon 6 block copolymer. Infra-red (i.r.) spectra were obtained using a Perkin Elmer Fourier transform i.r. (FTi.r.) spectrometer 725X. Nuclear magnetic resonance (n.m.r.) spectra were obtained using a Joel JNM-MH-100 with tetramethylsilane as a reference. The n.m.r. solvent of PES oligomer was DMSO- d_6 and that of the block copolymer was trifluoroacetic acid. Elemental analysis was run on a Yanaco MT-2 CHN analyzer to determine the composition of the block copolymer. The chlorine content of PES oligomer was determined with Rigaku 3270S X-ray fluorescence analysis (X.r.f.).

Morphology analysis. The morphology of block copolymer was observed by transmission electron microscopy (TEM, Joel 100 CX II). The samples were stained by a 1 wt% H_2O /formalin (50/50 v/v) solution of OsO_4 for 72 h followed by washing, drying, and cutting with microtome. Scanning electron microscopy (SEM) of blends were carried out by a Joel SEM (JSM-35F). Samples were prepared by fracturing the blended materials in liquid nitrogen or by etching nylon 6 with formic acid, the selective solvent of nylon 6.

Thermal analysis. Differential scanning calorimetry (d.s.c.) was carried out by using a Perkin Elmer d.s.c. 4. The samples were quenched to liquid nitrogen temperature after being maintained at 280°C for 5 min. The T_g , the cold crystallization temperature (T_{cc}), and the melting temperature (T_m) were measured on heating from 0°C to 260°C at a heating rate of 20°C min^{-1} . The melt crystallization temperature (T_{mc}) was measured on cooling at a cooling rate of 10°C min^{-1} . The T_g of PES was measured on heating from 200 to 260°C at a rate of 20°C min^{-1} after annealing at 280°C for 5 min and quenching to 200°C at the rate of 320°C min^{-1} . Thermogravimetric analysis (t.g.a.) was carried out by Shimadzu thermogravimeter (TH-30) at a heating rate of 20°C min^{-1} .

Dynamic mechanical thermal analysis. The dried samples were compression moulded with a pressure of 200 $kg_f cm^{-2}$, at a temperature of 205°C for nylon 6 and block copolymer, and 280°C for PES. The samples were examined by dynamic mechanical thermal analyzer (d.m.t.a., PL Thermal Science, MK11DM/DATA.DMTA) from -50°C to 250°C at a heating rate of 3°C min^{-1} with a frequency of 1 Hz.

RESULTS AND DISCUSSION

Synthesis of chlorine terminated PES oligomer

PES can be synthesized by polyetherification or polysulfonation reaction^{13–19}. In our study, PES oligomers were synthesized by polyetherification reaction with weak base which causes little side reaction. Three kinds of PES oligomers with molecular weights of 2000,

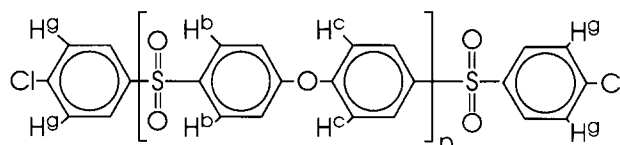
Table 3 Characterization of chlorine-terminated PES oligomers

Designation	Number average molecular weight				T_g (°C)
	N.m.r.	I.r.	X.r.f.	Calculated ^a	
PES 2	2700	2000	2300	2400	189
PES 5	5100	3700	3900	5300	205
PES 7	7100	7300	6600	7200	219

^a Calculated by degree of polymerization = $(1 + r)/(1 - r)$, r = monomer feed ratio

5000, and 7000 were synthesized by controlling the stoichiometric imbalances of the reactants. Terminal chlorine was guaranteed by the excess amount of DCDPS over bisphenol S. I.r., n.m.r. and X.r.f. analyses were performed to investigate chemical structures and determine molecular weights of synthesized PES oligomers. The results and T_g s of PES oligomers are given in Table 3.

The calibration curve for the determination of chlorine content in PES oligomer by i.r. was prepared from the area ratio around the 760 cm^{-1} , C–Cl band, and the 1150 cm^{-1} , SO_2 band measured using the mixtures of DCDPS and bisphenol S^{20,21}. The molecular weight of the PES oligomer can be calculated from the chlorine content measured by i.r. or X.r.f., assuming the presence of chlorine at both terminal positions. These are shown in Table 3. In the n.m.r. spectrum, terminal aromatic hydrogen peak (g, 7.7 ppm) can be separated from the internal aromatic hydrogen peak (b and c, 8.0 ppm and 7.3 ppm). So, from the area value of these peaks, the molecular weights can be calculated^{22,23}.



Synthesis of nylon 6–PES–nylon 6 block copolymers

When anionic ring opening polymerization of ϵ -caprolactam is performed with an activator, the activator itself is included in the nylon 6 chain. Since DCDPS has been known as an activator for the anionic polymerization of ϵ -caprolactam, it may be possible to use chlorine-terminated PES oligomer as an activator to synthesize PES incorporated nylon 6, i.e. nylon 6–PES–nylon 6 block copolymer^{9–12}. A mechanism for block copolymer synthesis is suggested in Figure 1^{24,25}.

The recipe for the synthesis of nylon 6–PES–nylon 6 block copolymers is shown in Table 2. It can be seen from the table that the yield of block copolymer decreases as the molecular weight of PES oligomer or the feed ratio of PES oligomer/ ϵ -caprolactam increases. As the molecular weight of PES and the ratio of PES oligomer/ ϵ -caprolactam increase, the solubility of PES oligomer in the ϵ -caprolactam molten phase decreases. As a consequence, the reaction mixture becomes more inhomogeneous and the mobility of the end group of the activator decreases. And the mobile time for the ϵ -caprolactam monomer to approach to the reactive terminal of the growing chain is shortened. These seem to be the cause of the decreased yield.

A typical i.r. spectrum of block copolymer is presented in *Figure 2*. Amide bands at 1640 cm^{-1} and 1540 cm^{-1} , the N–H stretching band at 3300 cm^{-1} , the aliphatic C–H band at 2900 cm^{-1} , and the SO_2 bands of PES block at 1100 cm^{-1} and 1150 cm^{-1} are observable^{26–28}. The content of nylon 6 in the block copolymer was determined by i.r. using the calibration curve obtained from the mixtures of PES and nylon 6 homopolymers. The SO_2 band of PES at 1150 cm^{-1} and the aliphatic C–H band of nylon 6 were used for calibration.

Figure 3 shows a typical n.m.r. spectrum of nylon 6–PES–nylon 6 block copolymer with proton assignments.

It can be seen from *Table 4* that the content of nylon 6 block in the block copolymer is generally equal to or higher than the ϵ -caprolactam content in the feed. It is reasonable to presume that the reason for this result is that not all the activator was participated in the reaction with ϵ -caprolactam, or that block copolymer with low nylon 6 block content could be removed during successive extractions²⁹.

The molecular weight of the nylon 6 block shown in *Table 4* was calculated using the molecular weight of the PES oligomer determined by n.m.r. (*Table 3*) and the content of nylon 6 in block copolymer determined by elemental analysis (*Table 4*) under the assumptions that

the synthesized block copolymer is nylon 6–PES–nylon 6 triblock copolymer and the molecular weight of the PES oligomer activator is preserved without chain scission during polymerization.

Phase behaviour of block copolymers

Block copolymers show a variety of phase behaviours which are dependent on the chemical structure, the molecular weight, and the number of constituent blocks. According to the theory of Meier³⁰, Fedors³¹ and Krause³², it is known that the minimum molecular weight of constituent blocks in block copolymer necessary for phase separation is 2.5–5.0 times higher than that of the homopolymer in the homopolymer blend because chain mobility is restricted due to the covalent bonding connecting blocks. The degree of phase separation will increase when the molecular weight of the constituent block and the interaction parameter value between constituent blocks increase³³.

From the studies done by Krause, who considered enthalpy and entropy change on phase segregation from the mixed state, the critical interaction parameter $(\chi_{ab})_{cr}$ between constituent blocks of block copolymer can be calculated (equation (1)). If the interaction parameter value between blocks of block copolymer (χ_{ab}) is greater than the critical interaction parameter value (if f is

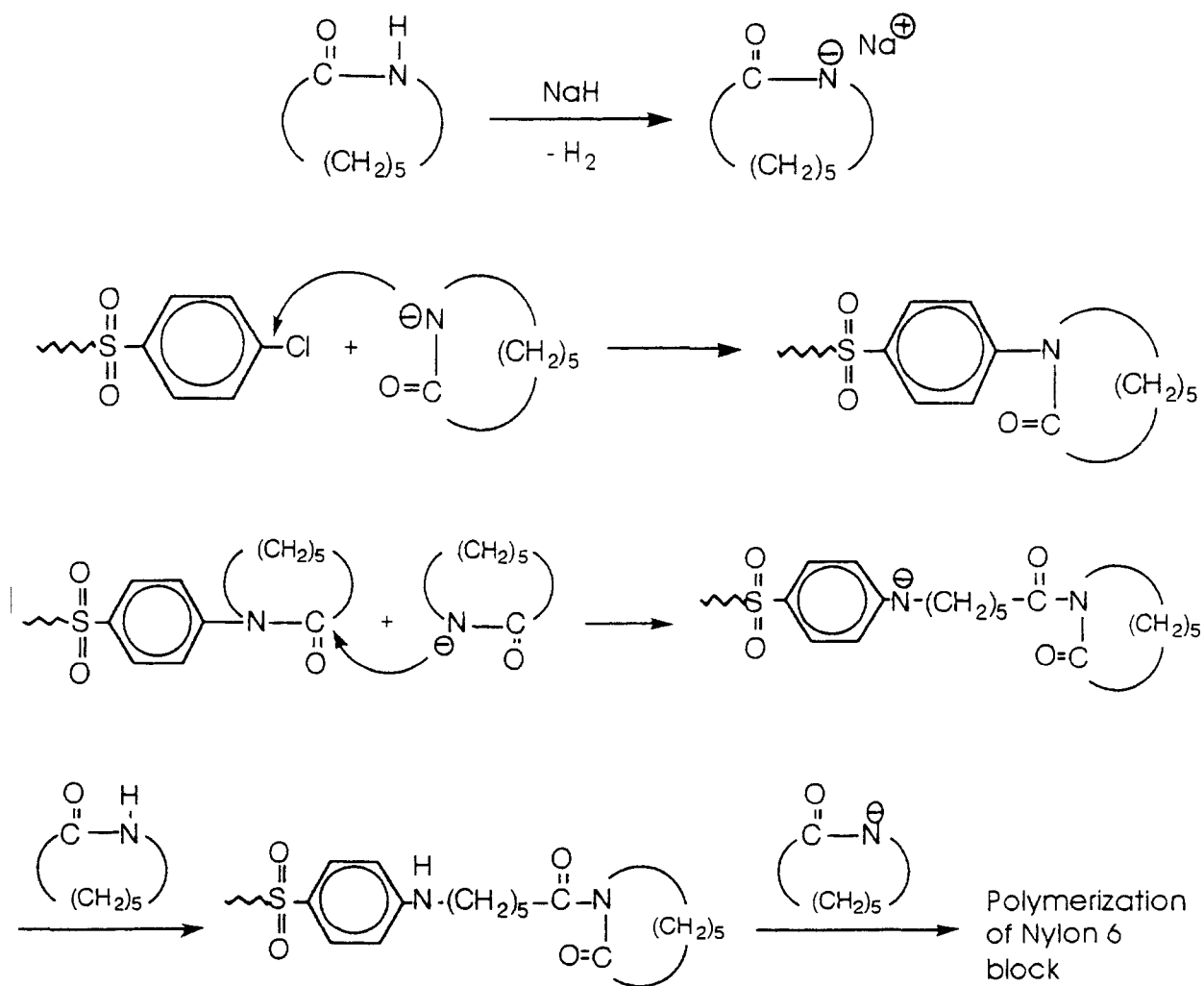
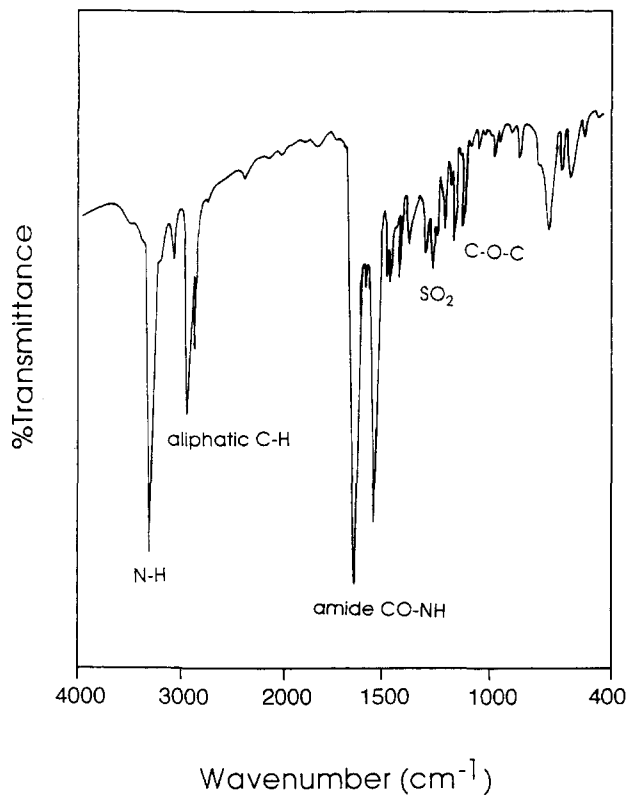


Figure 1 Mechanistic scheme of block copolymer synthesis


Figure 2 I.r. spectrum of block copolymer (SN-5-75)

positive (equation (2)), it can be predicted that the block copolymer will separate into microphase^{1,32}.

The critical interaction parameter $(\chi_{ab})_{cr}$, and f are given by

$$\begin{aligned}
 (\chi_{ab})_{cr} = & \frac{Z \times V_r}{(Z - 2) \times V_{a,c} \times V_{b,c}} \times \frac{N_c}{V} \\
 & \times \left[-V_{a,c} \ln V_{a,c} - V_{b,c} \ln V_{b,c} \right. \\
 & \left. + 2(m - 1) \frac{\Delta S_{dis}}{R} - \ln(m - 1) \right] \quad (1)
 \end{aligned}$$

Table 4 Characterization of nylon 6-PES-nylon 6 block copolymers

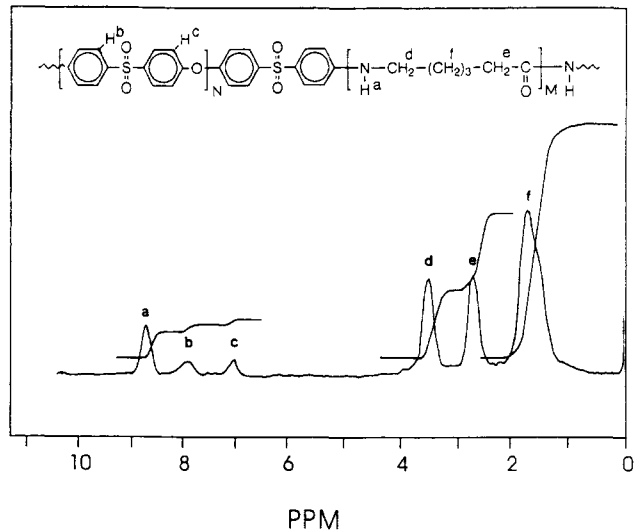
Designation	CL wt% in feed	Nylon 6 wt% in block copolymer				Nylon 6 block	
		I.r.	N.m.r.	Elemental analysis ^a	$[\eta]^b$	\bar{M}_n	$T_g(^{\circ}\text{C})$
SN-2-85	85	88.5	84.9	87.9	—	9800	60
SN-5-75	75	84.9	81.3	83.0	0.846	12500	58
SN-7-75	75	79.6	84.8	73.3	0.717	9700	54
SN-7-95	95	95.7	—	95.7	2.293	79000	52

^a Determined by C,H,N analysis

^b Measured at 25°C in *m*-cresol

Table 5 Parameters for the calculation of critical interaction parameter

Designation	Volume of a block (cm ³ mol ⁻¹)	Volume of b block (cm ³ mol ⁻¹)	$V_{a,c}$	$V_{b,c}$	$N_c/V (\times 10^5)$ (mol cm ⁻³)	$(\chi_{ab})_{cr}$	f
SN-2-85	1989.4	7975.8	0.1109	0.8891	5.574	0.2537	-0.1477
SN-5-75	3773.0	10177.1	0.1564	0.8436	4.145	0.1443	-0.0383
SN-7-75	5247.9	7893.0	0.2995	0.7505	4.754	0.1009	0.0051
SN-7-95	5247.9	64297.0	0.0392	0.9608	0.747	0.0846	0.0214


Figure 3 N.m.r. spectrum of block copolymer (SN-7-75)

$$f = \chi_{ab} - (\chi_{ab})_{cr} \quad (2)$$

where Z represents a lattice coordination number, N_c is the number of molecules of block copolymer, V is total volume of system, V_r is the volume of unit lattice, $V_{a,c}$ is the volume fraction of A block, $V_{b,c}$ is the volume fraction of B block, m is the number of blocks in a block copolymer, $\Delta S_{dis}/R$ is the disorientational gain per segment of a molecule. Values of $Z = 8$ and $\Delta S_{dis}/R = 1$ were assumed by Krause.

The various numerical values used for the calculation of critical interaction parameters are shown in *Table 5*, where a and b represent PES and nylon 6 respectively. The interaction parameter value calculated from the solubility parameter was 0.1060.

Morphology investigation by TEM was carried out to ascertain the phase behaviour of block copolymers. Because Krause's idea is that for the amorphous polymers³², we prepared thin films by pressing at 280°C followed by the subsequent quenching to room

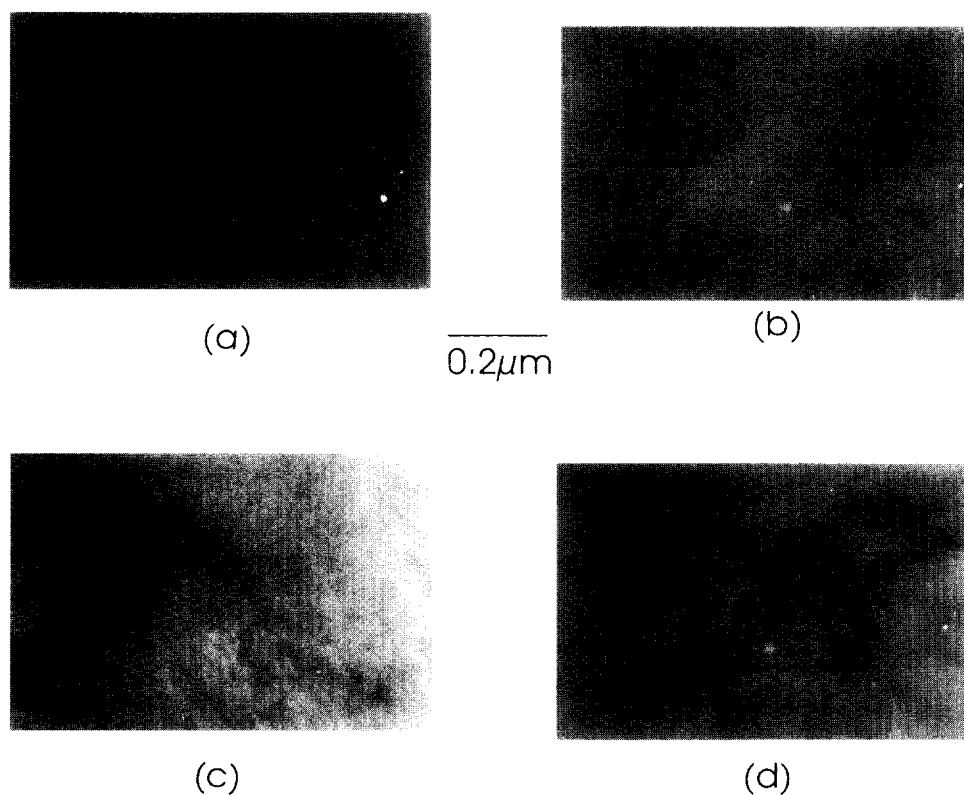


Figure 4 TEMs of block copolymers: (a) SN-2-85; (b) SN-5-75; (c) SN-7-95; (d) SN-7-75

temperature to minimize the effect of crystallinity. The samples were stained with OsO_4 /formalin, which stained the carbamide unit in the nylon 6 block³⁴. Figure 4 shows the morphology of block copolymers with selectively stained nylon 6 domains.

Microphase-separated morphology can hardly be observed with SN-2-85 and SN-5-75. However SN-7-75 shows white PES domains which are segregated finely up to about 150–200 Å. These results are very consistent

with the predictions in Table 4. The reason why SN-7-75 shows microphase-separated morphology seems to be that the molecular weights of both blocks exceed 5000, and that its composition is not inclined extremely towards one component. The microphase-separated morphology is not observed with SN-7-95 by TEM, which is not consistent with the prediction in Table 4. This seems to be due to the extremely small PES content in block copolymer.

Thermal properties of block copolymers

The thermal properties of block copolymers are shown in Table 6.

The T_g of the PES block in the block copolymer was not detected by d.s.c. even though microphase-separation was observed using TEM for one sample. The small content of PES block in the block copolymer, the small heat capacity change at the T_g of PES, and the overlap of the T_g of the PES block and the T_m of the nylon 6 block seem to be the causes.

In Table 6, the T_g of the nylon 6 block is generally higher than that of the nylon 6 homopolymer. This is attributable to the constraint against the flexibility of the nylon 6 block which may be originated from the covalent bond between nylon 6 and the rigid PES block, and the

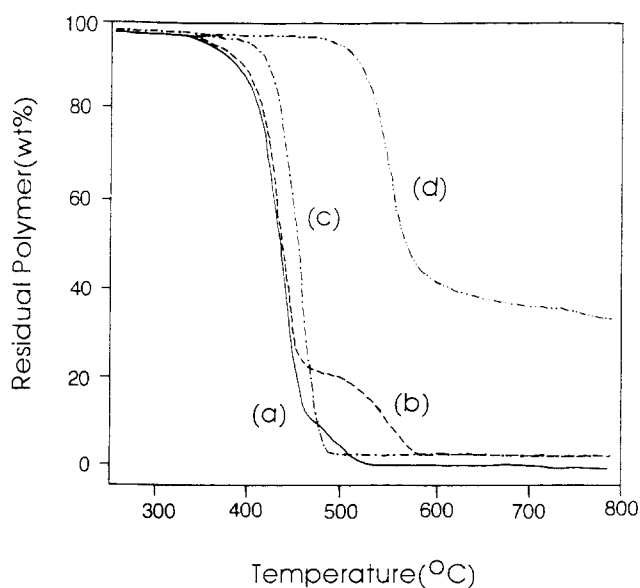


Figure 5 Thermogravimetric curves: (a) nylon 6; (b) PES/nylon 6 (30/70) blends; (c) block copolymer (SN-7-75); (d) PES 7

Table 6 Thermal properties (°C) of block copolymers

Designation	T_g	T_{cc}	T_m	T_{mc}	$T_{cc} - T_g$	$T_m - T_{mc}$
SN-2-85	60	99	217	171	39	46
SN-5-75	57	93	223	185	36	38
SN-7-75	55	86	225	191	31	34
SN-7-95	54	80	225	188	26	37
Nylon 6	52	76	228	189	24	39

solubilization of PES into the nylon 6 phase due to the partial miscibility between nylon 6 and the PES block. This explanation can be supported by the fact that the T_g of the nylon 6 phase increases to the order of SN-7-95, SN-7-75, SN-5-75, and SN-2-85. This shows that as the possibility for the dissolution of PES into nylon 6 phase is heightened due to the lower molecular weight of the PES block, the degree of restriction on the mobility and the consequent T_g rise of the nylon 6 block increase. The decrease of T_m and the increase of the degree of overheating ($T_{cc} - T_g$) to the order of SN-7-95, SN-7-75, SN-5-75, and SN-2-85 can also be explained by the same reason. In miscible polymer blends, the change in chemical potential due to miscible diluent result in a decreased melting temperature. However, when the value of χ_{ab} is positive, as in our case, thermodynamic considerations predict a minor change in melting temperature. So the above change in T_m can be explained by kinetic considerations. If the polymer crystals are developed from nonequilibrium conditions, a kinetic contribution to the melting point can take place³⁵. When two blocks are miscible, the crystallization of the nylon 6 block will be hindered greatly by the PES block, and the degree of imperfection of the nylon 6 crystals will

increase. This seems to be the main cause of T_m depression. The reason for the decrease of supercooling ($T_m - T_{mc}$), necessary for the crystallization of nylon 6 blocks in SN-7-75 and SN-7-95 compared with that of nylon 6 homopolymer, might be the nucleation effect of microphase-separated rigid PES block on the crystallization of nylon 6.

The results of thermogravimetric analysis are given in Figure 5. Compared with the stepwise thermal decomposition behaviour of the nylon 6/PES blend, block copolymer shows single decomposition behaviour^{22,27}. This behaviour seems to be due to the microphase-separated morphology of the block copolymer, which differs from the macrophase-separated morphology of the homopolymer blend. The increment of thermal stability of SN-7-75 is about 20°C compared with that of nylon 6.

Morphology of blends

The morphology of the fractured surfaces of the PES/nylon 6 blend compatibilized by block copolymer was observed by SEM as shown in Figure 6. In Figure 7, the dispersed nylon 6 phase was extracted by a selective solvent, formic acid to enhance contrast.

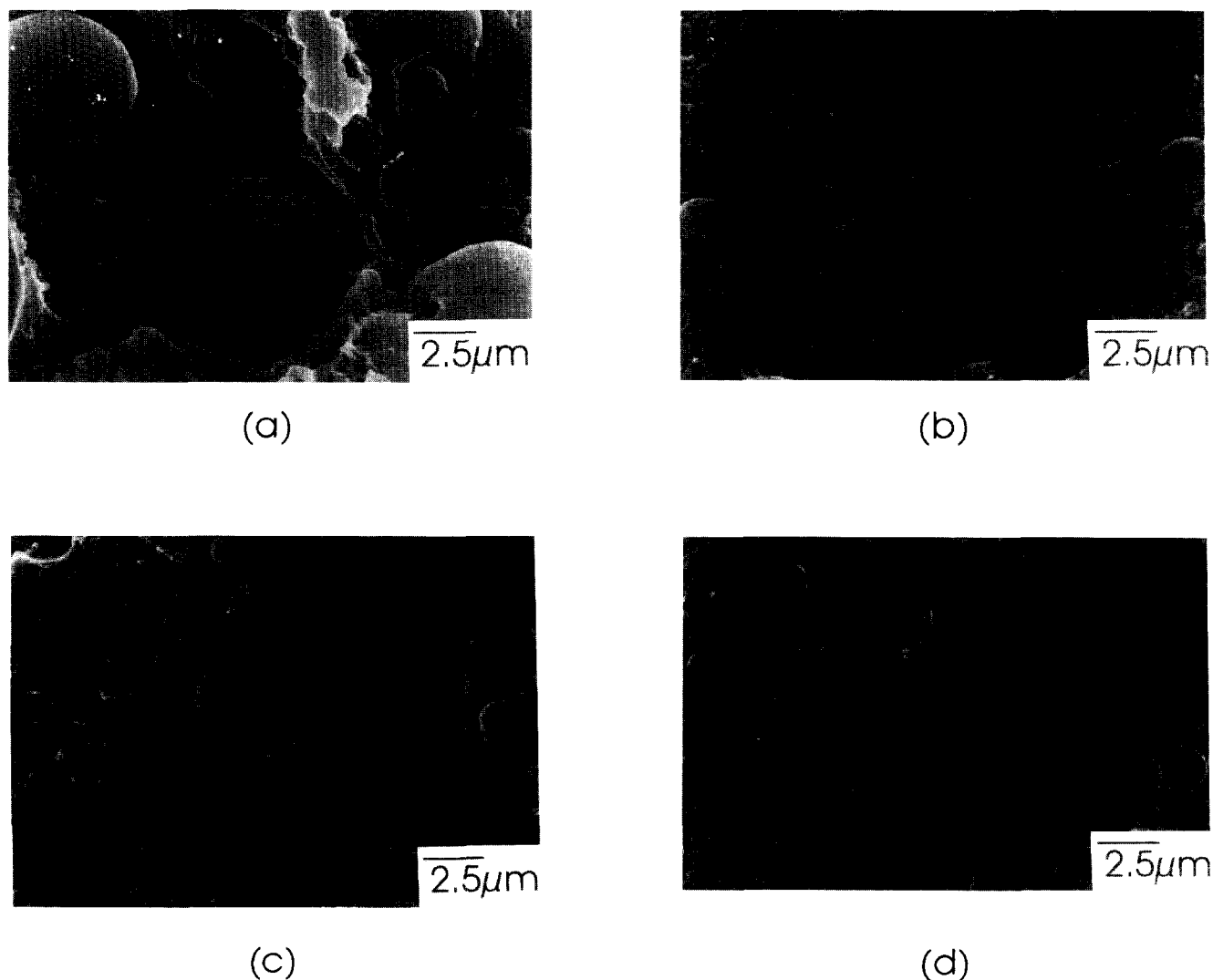


Figure 6 SEMs of fractured surfaces of PES/nylon 6 (70/30) blends containing: (a) 0; (b) 2; (c) 5; (d) 10 phr block copolymer (SN-5-75)

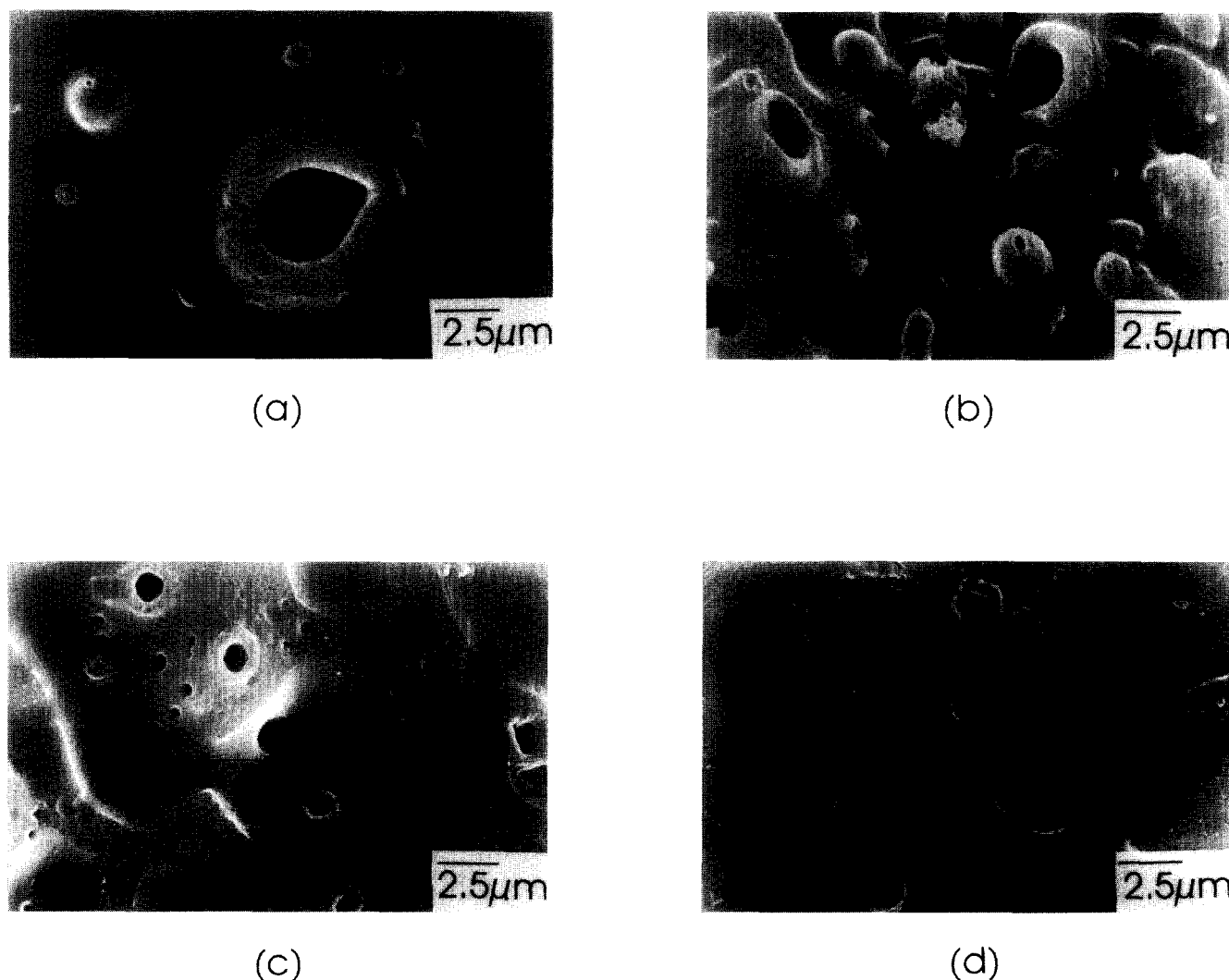


Figure 7 SEMs of etched surfaces of PES/nylon 6 (70/30) blends containing: (a) 0; (b) 2; (c) 5; (d) 10 phr block copolymer (SN-5-75)

As the amount of added block copolymer increases it can be perceived that the size of dispersed phase decreases dramatically.

This decreased size of dispersed nylon 6 phase supports the compatibilizing effect of the block copolymer.

Thermal properties of blended materials

The T_g variation according to the increment of the amount of added block copolymer is shown in Figure 8.

It can be observed that the T_g s of each polymer approach one another. The block copolymer solubilized in bulk phase and the enhanced mutual dissolution of homopolymers by the compatibilizing of added block copolymer seem to be the causes of this change in thermal property.

The melting and crystallizing behaviours of nylon 6 in blends are shown in Table 7. It can be seen that as the amount of added block copolymer increases, the degree of supercooling ($T_m - T_{mc}$) and overheating ($T_{cc} - T_g$) for crystallization increase. This shows that the crystallization of nylon 6 is retarded in the compatibilized blend by PES segments which are partially dissolved into the nylon 6 domain.

The dynamic mechanical properties of blends

The changes in dynamic tensile modulus on heating PES/nylon 6/block copolymer blends are shown in Figure 9. The modulus of the uncompatibilized blend is even lower than those of the homopolymers. This seems to be due to the lack of interfacial adhesion between segregated phases as observed by SEM.

In Figure 9 we can also observe that the rigidity is maintained to a higher temperature when the block copolymer is added as compatibilizer. This shows that the property of the minor component, dispersed PES phase, appears more effectively in compatibilized blends, by good interfacial adhesion.

Table 7 Melting and crystallization temperatures ($^{\circ}\text{C}$) of nylon 6 in PES/nylon 6/block copolymer (SN-5-75) blends

Composition	T_m	$T_m - T_{mc}$	$T_{cc} - T_g$
70/30/0	221	44	28
70/30/2	221	46	28
70/30/5	219	46	30
70/30/10	221	48	30
70/30/20	222	49	31
70/30/50	215	49	38

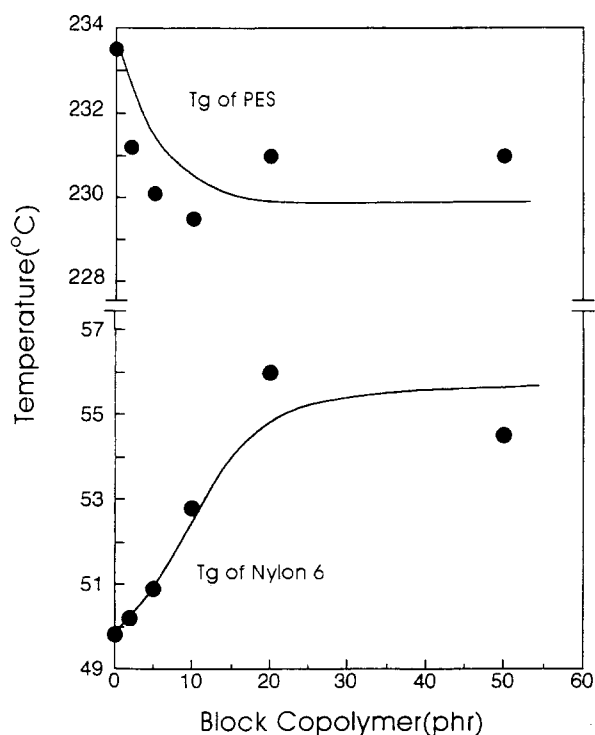


Figure 8 T_g change of PES/nylon 6 (70/30) blends by the added block copolymer (SN-5-75)

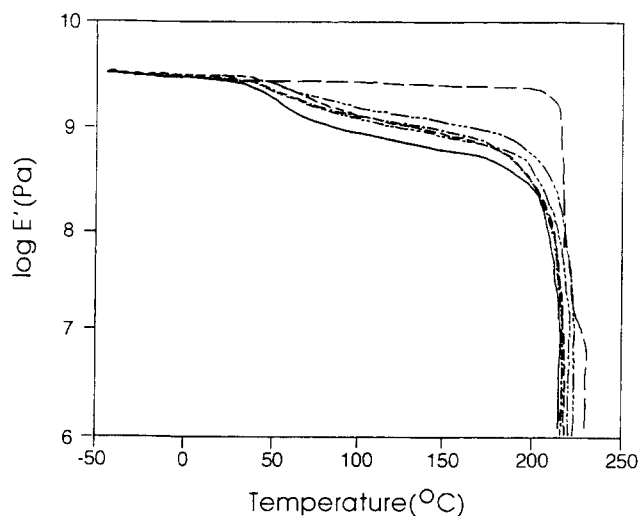


Figure 9 Storage modulus ($\log E'$) vs temperature of: (---) PES; (---) nylon 6; and PES/nylon 6 (30/70) blends containing (—) 0; (---) 2; (---) 5; (---) 10 phr of block copolymer (SN-5-75)

CONCLUSION

Nylon 6–PES–nylon 6 block copolymers were effectively synthesized by the anionic polymerization of ϵ -caprolactam using the polymeric activator, chlorine-terminated PES. The phase-separated morphology of the block copolymer could be observed by TEM when the molecular weights of constituent blocks were more

than 5000 and its composition was not inclined to one component. Thermal properties suggested that the dissolution of PES block into nylon 6 phase occurred and this was more evident when the molecular weight of PES block was small. When the nylon 6–PES–nylon 6 block copolymer was added to the PES/nylon 6 blends, the compatibilizing effect of this block copolymer was observed from thermal properties, dynamic mechanical thermal properties, and morphology.

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