

# Reactive blending of polysulfone with polyamide: a potential for solvent-free preparation of the block copolymer

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## Abstract

Reactive blending of polysulfone (PSU) and polyamide 6 (PA) was carried out at 20:80 (PSU–PA) wt. ratio using a gram-scale mixer (Mini-Max Molder). Three PSUs with different functional groups were prepared and used: maleic anhydride-grafted PSU (PSU-MAH), carboxylic acid-grafted PSU (PSU-COOH) and phthalic anhydride-terminated PSU (PSU-PhAH), having almost same molecular weight ( $M_w = \text{ca. } 20 \text{ k}$ ) and functional group content (ca.  $90 \mu\text{mole g}^{-1}$ ). The change in PSU particle size with mixing time was investigated by light scattering and transmission electron microscopy. As expected, all reactive systems yielded finer particles via faster size reduction process, compared with non-reactive system. Attainable particle diameters were: ca.  $1 \mu\text{m}$  for non-functionalized PSU, ca.  $0.6 \mu\text{m}$  for PSU-MAH,  $0.3 \mu\text{m}$  for PSU-COOH, and ca.  $40 \text{ nm}$  for PSU-PhAH. The particle size of PSU-PhAH system was comparable to that in a pre-made block copolymer synthesized by solution polymerization, suggesting a potential for the solvent-free preparation of PSU–PA block copolymer when adequate reactivity and molecular architecture are provided in reactive blending. © 1998 Published by Elsevier Science Ltd. All rights reserved.

**Keywords:** Polymer blend; Polysulfone; Polyamide

## 1. Introduction

Much attention is being paid to the reactive blending of dissimilar polymers. This approach is effective to control morphology and to design high-performance materials, such as rubber-toughened plastics and thermoplastic elastomers. Reactive blending involves in situ reaction of functionalized components to form a block or graft copolymer at the interface between the phases [1–9]. The copolymer is believed to play the role of an emulsifier, which provides a fine morphology and increases the adhesive strength between the two phases.

In this paper, we deal with polysulfone (PSU)–polyamide 6 (PA) systems. PSU is a typical amorphous polyarylether and it shows high heat resistance, nice dimensional stability and good mechanical properties. However, it has low stress crack resistance and high melt viscosity. Such drawbacks could be overcome by blending with PA, a partially crystalline polymer. Then the PSU–PA blend is expected to be an

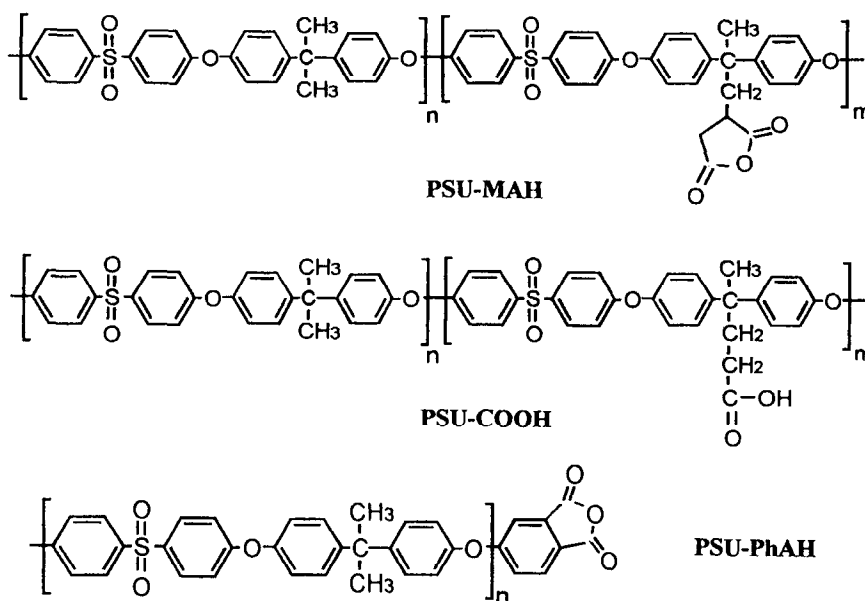
injection moldable high-temperature polymer, which could replace thermoset polymers, e.g. epoxy resin in several applications. As reactive sites on PSU chains, we employed carboxylic acid, maleic anhydride and phthalic anhydride groups. They are expected to react with amino-chain end of PA to form graft or block copolymer. Melt-blending of the functionalized PSUs with PA was carried out at 20:80 (PSU–PA) wt. ratio in a miniature mixer and the change in PSU particle size with mixing (reaction) time was investigated by light scattering and transmission electron microscopy.

## 2. Experimental

### 2.1. Synthesis of the polyarylethers

Three different types of functionalized PSUs were prepared following synthetic procedures given in the literature [10–12]. As a control sample, PSU without functional group (nf-PSU) was also synthesized.

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### 2.1.1. *nf-PSU*

287.08 g (1 mol) dichlorodiphenylsulfone, 223.83 g bisphenol-A (0.9805 mol) and 140.97 g  $K_2CO_3$  were dissolved in 1600 ml dry *N*-methyl-2-pyrrolidone (NMP, dried with  $CaH_2$  and distilled). The mixture was heated to 190°C for 6 h in a nitrogen atmosphere. During this time, the azeotropic mixture of NMP and water was continuously removed. The solution was cooled to room temperature, diluted with NMP (1600 ml) and filtered. Then, the polymer was isolated by precipitation in water. The polymer was extracted 3 times with hot water and dried for 12 h at 130°C. The amount of chlorine-end groups was 98% (detected by elemental analysis). The properties of this product are summarized in Table 1.

### 2.1.2. *PSU-MAH*

50 g of *nf-PSU* was dissolved in chlorobenzene, the solution was heated to reflux. 11.3 g of maleic anhydride and 3.5 g dicumylperoxide were added over a period of 4 h. After refluxing for another hour, the solution was cooled to room temperature and the polymer was isolated by precipitation in ethylalcohol. The polymer was filtered and redissolved in NMP and again precipitated in a mixture of NMP– $H_2O$  (1:4). After filtration the polymer was extracted with hot water and dried. Finally, the product was dried at

130°C in the vacuum for 12 h. The amount of anhydride groups was determined by potentiometric titration. The properties of the product are given in Table 1.

### 2.1.3. *PSU-COOH*

28.71 g (0.1 mol) dichlorodiphenylsulfone, 20.08 g bisphenol-A (0.088 mol), 2.80 g diphenolic acid (DPA) (9.78 mmol) and 14.1 g  $K_2CO_3$  (0.102 mol) were dissolved in 160 ml dry NMP. The mixture was heated to 190°C for 6 h in a nitrogen atmosphere. During this time, the azeotropic mixture of NMP and water was continuously removed. The solution was cooled to room temperature, diluted with NMP (160 ml) and filtered. Then, an excess of acetic acid was added to the solution and after further stirring (30 min), the polymer was isolated by precipitation in water. The polymer was extracted 3 times with hot water and dried for 12 h at 130°C. The amount of incorporated DPA units was estimated by  $^1H$  n.m.r. spectroscopy (in  $CDCl_3$ – $CF_3COOD$  1:1). The ratio of monomer units derived from DPA and bisphenol-A was calculated using the signal intensities in the  $^1H$  n.m.r. spectra, taking into account the signal intensities of the  $CH_2$ -groups of DPA ( $\delta = 2.2$  ppm and 2.5 ppm) with respect to the signal intensity of the  $CH_3$ -groups of the units derived from bisphenol-A ( $\delta = 1.6$  ppm). The properties of this product are summarized in Table 1.

### 2.1.4. *PSU-PhAH*

287.08 g (1 mol) dichlorodiphenylsulfone, 228.28 g bisphenol-A (1 mol) and 140.97 g  $K_2CO_3$  were dissolved in 1600 ml dry NMP. The mixture was heated to 190°C for 4 h in a nitrogen atmosphere. During this time, the azeotropic mixture of NMP and water was continuously removed. Then, 26.58 g (0.16 mol) of 4-fluorophthalic anhydride and 9.3 g (0.16 mol) KF were added and the solution was further stirred for 1 h. The solution was cooled to room temperature, diluted with NMP (1600 ml) and filtered.

Table 1  
Characteristics of polysulfones synthesized

	$M_n^a$	$M_w^a$	Functionality <sup>b</sup>
<i>nf-PSU</i>	5700	28 800	—
<i>PSU-MAH</i>	8000	21 300	93
<i>PSU-COOH</i>	5300	23 700	84
<i>PSU-PhAH</i>	5310	20 600	85

<sup>a</sup>By g.p.c.

<sup>b</sup>Content of functional group ( $\mu\text{mol g}^{-1}$ )

Then, the polymer was isolated by precipitation in water. The polymer was extracted three times with hot water and dried for 12 h at 150°C. The amount of anhydride endgroups was determined by FTi.r. The properties of this product are summarized in Table 1.

#### 2.1.5. PSU-*b*-PA

A premade block copolymer of PA and PSU was also prepared as follows. Twenty-five grams of an amorphous polyamide (consisting of isophthalic acid, hexamethylene diamine and 4,4'-diamino-3,3'-dimethyldicyclohexylmethane,  $M_n = 9400$ ) were dissolved in 250 ml NMP and stirred at room temperature under nitrogen atmosphere. To this solution, a solution of 25 g PSU-PhAH ( $M_n = 5500$ , 2.8 wt% PhAh endgroups) in 250 ml NMP was added over a period of 30 min. After further stirring for 1 h, the solution was heated to 195°C for further 6 h. Then, the solution was cooled to room temperature and the polymer was precipitated in water and dried at 100°C in the vacuum for 12 h. In order to remove unreacted homopolymers, the product was extracted two times with dimethylformamide and two times with formic acid. The yield of the final product was 80%. The final product was soluble in 1,1,1,3,3,3-hexafluoro-2-isopropanol. The copolymer composition was 52 wt% PSU and 48 wt% PA (elemental analysis).

#### 2.2. Melt mixing

PA used in this study was a commercial polyamide 6 (Ultramid B, BASF;  $M_n = 13\,000$ ,  $M_w = 25\,000$ ).

Melt mixing was carried out in a miniature mixer of one gram-scale, Mini-Max Molder (CS-183 MM, Custom Scientific Instruments Inc.) at 240°C and 260°C setting rotor speed at 100 rpm. Weight ratio of PSU-PA was fixed at 20:80. During the mixing, a small amount of mixed melt (40 mg) was picked up by pincette at appropriate intervals and was quickly quenched in water to freeze the two-phase structure in the melt. Thus, we prepared a series of mixed-and-quenched specimens with various residence times in the mixer. The specimens were subjected to light scattering and transmission electron microscopy (TEM) analyses as follows.

#### 2.3. Morphology analysis

The quenched specimen was placed between two cover glasses and melt-pressed to a thin film (ca. 15  $\mu\text{m}$ ) at 260°C on a hot stage set on a light scattering apparatus. Immediately after the melt-pressing, the time-resolved measurement of scattering profile (angular dependence of scattered light intensity) with a time slice of 1/30 s started. The scattering apparatus consisted of a highly sensitive CCD camera with  $576 \times 382$  pixels, a He-Ne laser of 632.8 nm wavelength and Vv (parallel polarization) optical alignment [13]. Since the two-phase structure in the melt is

at a non-equilibrium state, it coarsens with time after the re-melt. A scattering profile just after the re-melt provides information on the two-phase structure in the mixed-and-quenched blend. By the time variation of scattering profile, one could discuss the structure coarsening during isothermal annealing, which may be affected by the in situ formed block or graft copolymer.

For TEM observation, the quenched specimen was cryo-microtomed at  $-65^\circ\text{C}$  by ultramicrotome (Reichert Ultracut-Nissei). The ultrathin section of ca. 60 nm thickness was mounted on 200 mesh copper grid and exposed to the vapor of ruthenium tetroxide ( $\text{RuO}_4$ ) above a 0.5 wt% aqueous solution of  $\text{RuO}_4$  for 10 min.  $\text{RuO}_4$  preferentially stains the PSU phase to provide nice contrast under TEM. The two-phase morphology was observed by transmission electron microscopy, JEM-100CX (JEOL), at an accelerating voltage of 100 KeV. TEM picture was digitized using scanner (EPSON GT-8500). The area of individual particle  $a_i$  was directly determined using a software (PIAS-VII-Personal Image Analysis System). The diameter of dispersed particles  $D_i$  was calculated by  $D_i = 2(a_i/\pi)^{1/2}$ , assuming the shape of particle being circular. Then, we obtained an average:

$$D_{\text{TEM}} = \frac{\sum^N D_i^3}{\sum^N D_i^2} \quad (1)$$

where  $N$  was 200–500 in a TEM picture. The average by Eq. (1) may be appropriate for the comparison with that by light scattering, because the particle size by light scattering is based on the surface area per unit volume  $S_{\text{sp}}$  (see Eqs. (2)–(4)), which corresponds to the ratio of volume-average diameter (numerator in Eq. (1)) and surface-average diameter (denominator in Eq. (1)). Note that, to make a more strict comparison, a correction for random cutting through the particles for TEM observation is required, e.g. by Saltzykov's method [14]; however, such correction is not so serious for the two-phase systems having rather spherical particles [15].

#### 2.4. Melt viscosity

The complex dynamic viscosity  $\eta^*$  was measured at 260°C by Rheometrics Dynamic Spectrometer (Model RDS-7700) at parallel-plate mode (plate radius 12.5 mm, gap 1.0 mm) and 10% strain amplitude.

### 3. Results and discussion

All blend specimens in this study exhibited a light scattering profile of monotonously decreasing function, i.e. the intensity of scattered light  $I$  decreased monotonously with increasing scattering angle  $\theta$ . From such scattering profile, one can obtain a series of morphology parameters by the Debye-Bueche plot; i.e. by the plot of  $I(q)^{-1/2}$  versus  $q^2$

where  $q$  is the magnitude of scattering vector, given by  $q = (4\pi/\lambda')\sin(\theta/2)$ ;  $\lambda'$  being the wavelength of light in specimen [16,17]. Typical examples of the light scattering profiles in terms of the Debye–Bueche plot are shown in Fig. 1<sup>1</sup>. One can obtain the correlation length  $\xi$  from the slope and the intercept of the  $I(q)^{-1/2}$  axis by

$$I(q)^{-1/2} = (8\pi \langle \eta^2 \rangle \xi^3)^{-1/2} (1 + \xi^2 q^2) \quad (2)$$

where  $\langle \eta^2 \rangle$  is the mean-square fluctuation of the refractive index. Once the value of  $\xi$  is given, other morphology parameters, such as the specific interfacial area  $S_{sp}$  and the mean diameter of the dispersed particles  $D_{scatt}$  can be calculated:

$$S_{sp} = 4\phi(1 - \phi)/\xi \quad (3)$$

$$D_{scatt} = 6\phi/S_{sp} \quad (4)$$

where  $\phi$  is the volume fraction of the dispersed PSU phase.

Fig. 2 shows the mean particle size by light scattering as a function of mixing (reaction) time. One can see a very rapid decrease in the particle size. The size decreases in three decades, from mm scale (pellet size of starting materials) to  $\mu\text{m}$  level, in a short time (2 min). One also sees the effect of functional component on the size reduction process. This point will be discussed in detail later.

In Fig. 2, size reduction levels off at around 8 min mixing (except PSU-PhAH system). TEM pictures after 8 min mixing are shown in Fig. 3. The morphological parameters by light scattering and TEM are summarized in Table 2. One can see a nice agreement between two analyses by light scattering and TEM.

In Figs 2 and 3, the PSU-MAH system yields smaller particles than the non-reactive system (nf-PSU-PA). This is an expected result since the reactive system may generate the PSU-PA graft copolymer which would play a role of emulsifier to reduce the interfacial tension and prevent particle coalescence.

The particle size in PSU-MAH system is larger than that in the PSU-COOH system. This result seems to be unexpected, if one think about the reactivity: MAH group is known to react with amino-chain end group much faster than COOH group [18] so that the higher production of PSU-PA graft copolymer is expected in the PSU-MAH system to yield the smaller particles. The finer dispersion in PSU-COOH system may be caused by the lower viscosity of PSU-COOH, compared with PSU-MAH. The complex melt viscosity  $\eta^*$  at a frequency range of 10–100  $\text{rad s}^{-1}$  at 260°C was 2000 Poise for PSU-MAH and it was 470 for PSU-COOH. Then, the smaller particles are expected for the PSU-COOH system; e.g. on the basis of the

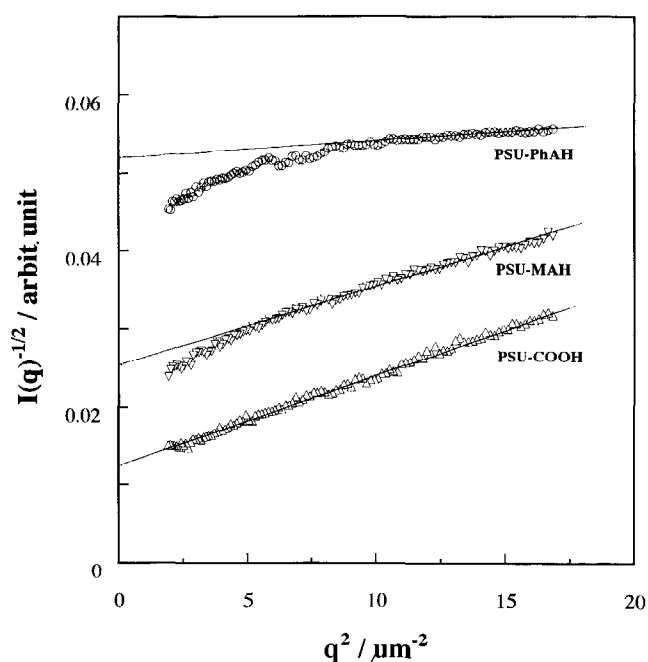


Fig. 1. Typical examples of the Debye–Bueche plots: (20:80) PSU\*–PA blends, melt-mixed at 260°C for 8 min. (\*) Reactive PSUs with -PhAH, -MAH and -COOH groups.

empirical equation by Wu [19]:

$$D = \frac{4\sigma}{\gamma\eta_m} \left( \frac{\eta_d}{\eta_m} \right)^{\pm 0.84} \quad (5)$$

where  $\eta_d$  is the viscosity of dispersed phase,  $\eta_m$  is the matrix viscosity ( $\eta_{PA}^* = 2200$  Poise),  $\sigma$  is the interfacial tension, and  $\gamma$  is the shear rate. That is, the viscosity effect seems to predominate over the reactivity effect.

The finest dispersion is obtained in the PSU-PhAH system. In this system, size reduction still continues even after 8 min mixing to yield  $D_{scatt} \sim 50$  nm after 13 min mixing. The size is close to the lower limit of resolution by light scattering so that one should discuss the detail on the basis of TEM observation. Fig. 4(a) shows TEM picture of PSU-PhAH system after 13 min mixing. One sees that PSU particle size is very small,  $D_{TEM} \sim 40$  nm, and the size distribution is quite narrow. It reminds us the domain structure of block copolymer. TEM picture of the premade PSU-PA block copolymer is shown in Fig. 4(b).

The  $M_n$  of premade block copolymer is 7000 and its PSU content is 48 wt%, while the in situ formed block copolymer in the PSU-PhAH system is expected to be PSU( $M_n = 5300$ )–PA( $M_n = 13000$ ) (see Table 1). That is, there are big differences both in molecular weight and copolymer composition. Furthermore, the functionality (number of reactive sites per chain) of PSU-PhAH is 0.45 (less than one) so that 55% of PSU chains would remain unreacted with PA at least. Then, one could not have a direct comparison between the morphologies in Fig. 4(a) and (b). However, one may undertake a rough estimation for the particle size in the reactive system as follows.

<sup>1</sup> From the linear part of the Debye–Bueche plot at large  $q$  values, the  $\xi$  can be obtained. For PSU-PhAH and PSU-MAH systems, there is a deviation from linearity at small  $q$  range. From the deviation, one could obtain other morphology parameters, such as the interparticle correlation length and the volume of heterogeneity [17].

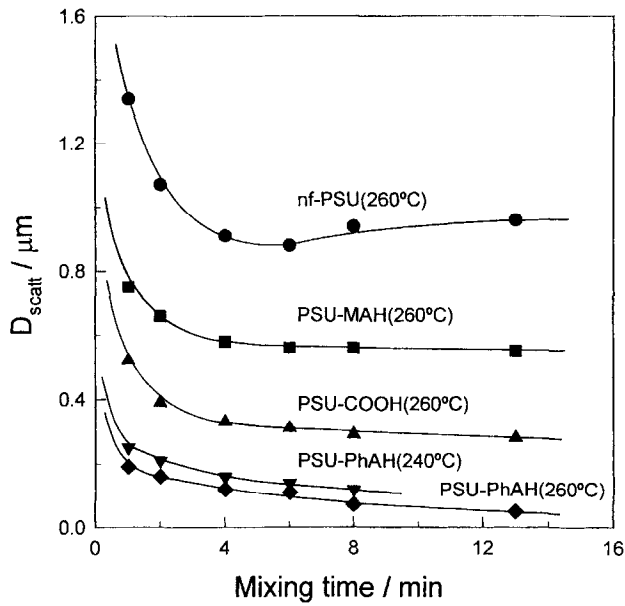


Fig. 2. Time variation of PSU particle diameter  $D_{scatt}$  during melt mixing.

Let's employ the 2/3 power relationship between domain spacing  $d$  and molecular weight ( $d \sim M_n^{2/3}$ ) for lamellar domain morphology [20]. Then, the domain diameter of (neat) in situ formed block copolymer is estimated to be 18 nm [(Fig. 4(b))  $\times (18\,300/7000)^{2/3} = 36$  nm]. Then, if equal amount of homo-PSU is added and solubilized in the domain, the domain swells up to  $2^{1/3}$  times to yield a domain diameter of 43 nm. This value is very close to the result in Fig. 4(a). If this is the case for the PSU-PhAH system, the result in Fig. 4(a) implies that almost all of the functionalized PSU chains have reacted with PA (and remaining non-functionalized chains are solubilized in PSU domains).

In Fig. 5 are shown TEM pictures of the PSU-PhAH system at very early stages of mixing. In Fig. 5(a), elongated big PSU particles and/or PSU sheets are seen at this early

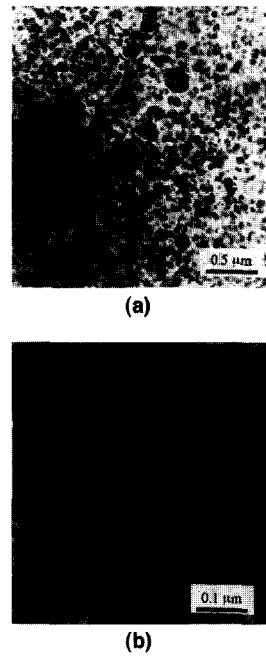


Fig. 4. TEM pictures of: (a) (20:80) PSU-PhAH-PA blend mixed at 260°C for 13 min; and (b) premade PSU-PA block copolymer (PSU content = 48 wt%,  $M_n = 7000$ ).

stage of mixing (1 min mixing). It should be noted that very small PSU domains with diameter of ten rim order are present even at this stage. Similar situation is seen at 2 min mixing in Fig. 5(b). The results imply that a lot of PSU-PA block copolymers are formed in situ at the early stages and they are escaping from the interfacial region as micelles. At present we are not sure whether the copolymers escape by themselves, due to thermodynamic instability at

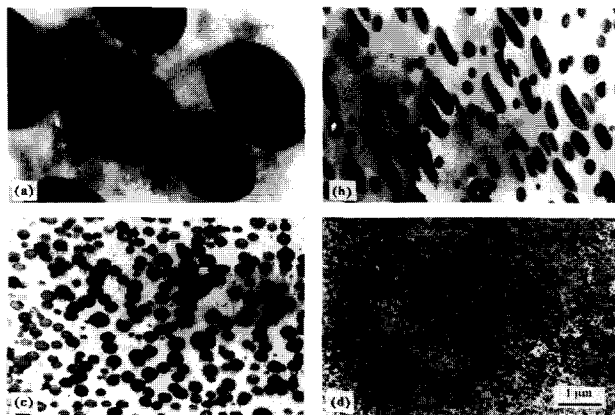


Fig. 3. TEM pictures of (20:80) PSU-PA blends melt-mixed at 260°C for 8 min: (a) nf-PSU-PA; (b) PSU-MAH-PA; (c) PSU-COOH-PA; and (d) PSU-PhAH-PA.

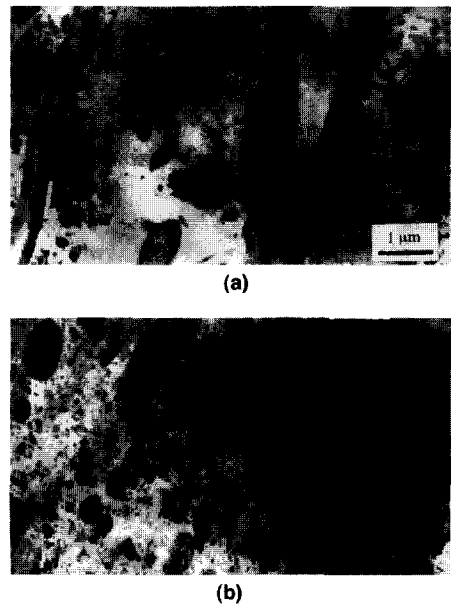


Fig. 5. TEM pictures of PSU-PhAH-PA blend at early stages of melt-mixing at 240°C: (a) 1 min mixing and (b) 2 min mixing.

Table 2  
Morphological parameters of blends mixed at 260°C for 8 min

	$\xi$ ( $\mu\text{m}$ )	$S_{\text{sp}}$ ( $/\mu\text{m}^{-1}$ )	$D_{\text{scatt}}$ ( $\mu\text{m}$ )	$D_{\text{TEM}}$ ( $\mu\text{m}$ )
nf-PSU-PA	0.55	1.10	1.02	
PSU-MAH-PA	0.30	2.0	0.55	0.51
PSU-COOH-PA	0.15	4.02	0.28	0.27
PSU-PhAH-PA	0.038	15.9	0.070	0.097

$\xi$ , correlation length;  $S_{\text{sp}}$ , specific interfacial area;  $D_{\text{scatt}}$  and  $D_{\text{TEM}}$ , mean diameters of PSU particles by light scattering and TEM, respectively

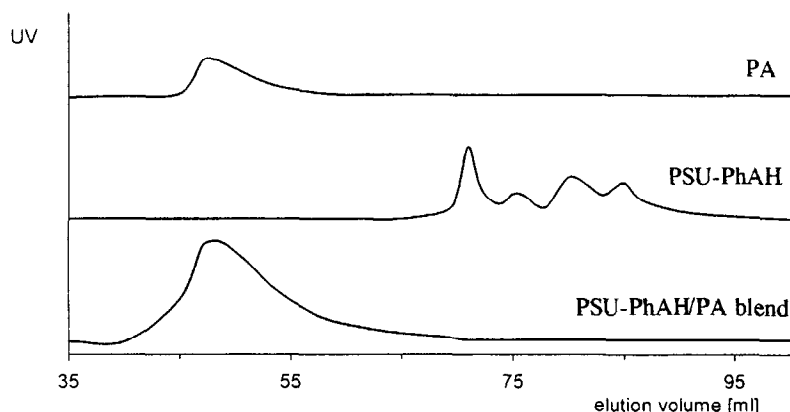


Fig. 6. G.p.c. chromatograms of neat PA, PSU-PhAH, and a 20:80 PSU-PhAH-PA blend mixed at 260°C for 12 min.

the interface, or they are mechanically pulled out under shear fields during melt-mixing. In contrast such micelles are never seen in other reactive systems (see Fig. 2(b) and (c)), suggesting the pull-out or escape does not occur in PSU-MAH and PSU-COOH systems, which may yield graft copolymer. Do the results suggest that the pull-out or escape takes place for block copolymer but not for graft copolymer?

According to the theory of polymer-polymer interface by Leibler [21], symmetric block copolymer prefers to locate at the interface, whereas asymmetric copolymer tends to go to the bulk as micelles. The in situ formed copolymers in this study should have almost same symmetry (see Table 1). Then, one cannot expect a big difference in stability of the copolymer chain at the interface between the block and graft copolymers. A plausible interpretation may be given by the difference in molecular architecture, i.e. the block copolymer is a linear polymer, while the graft copolymer is a branched polymer with Y-shape. That is, two PSU-branches residing in PSU phase may have higher resistance to be pulled out when PA-branch in the matrix is subjected to external shear force during melt mixing.

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#### Appendix A

To justify the formation of block copolymer by reactive processing, one should confirm the coupling reaction between the amino-chain end of PA and the PhAH-chain end of PSU by i.r. or n.m.r. in terms of a decrease in  $\text{NH}_2$  content or an increase in amide content with reaction time. However, such spectroscopic analyses were impossible, since the concentration of such reactants and products were too low to be detected qualitatively. It is well known that gel permeation chromatography (g.p.c.) is powerful and convenient to characterize the block copolymer prepared by anionic polymerization. For PSU-PA system, however, it is hard to find a common solvent for the component polymers. Hexafluoroisopropylalcohol (HFIP) was the only one common solvent we found. Using HFIP, g.p.c. analysis was undertaken, using Shodex HFIP803-805 columns at polymer concentration of 0.15 wt% at 25°C. The results are shown in Fig. 6. One sees a series of peaks for PSU-PhAH in high elution volume. The peaks may be an artefact caused by the insufficient solvent power of HFIP, which could lead to an undesirable adsorption of PSU-PhAH chains on g.p.c. gels. Anyhow, after the reactive processing, such strange peaks disappear and the peak position shifts to high molecular weight side, compared with the peak of PA. These are the supplemental evidences of the formation of block copolymer by reactive processing.

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