

Application of Styrene-Acrylonitrile Random Copolymer–Polyarylate Block Copolymer as Reactive Compatibilizer for Polyamide and Acrylonitrile-Butadiene-Styrene Blends

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ABSTRACT: Styrene-acrylonitrile random copolymer (SAN) and polyarylate (PAr) block copolymer were applied as a reactive compatibilizer for polyamide-6 (PA-6)/acrylonitrile-butadiene-styrene (ABS) copolymer blends. The SAN–PAr block copolymer was found to be effective for compatibilization of PA-6/ABS blends. With the addition of 3.0–5.0 wt % SAN–PAr block copolymer, the ABS-rich phase could be reduced to a smaller size than 1.0 μm in the 70/30 and 50/50 PA-6/ABS blends, although it was several microns in the uncompatibilized blends. As a result, for the blends compatibilized with 3–5 wt % block copolymer the impact energy absorption reached the super toughness region in the 70/30 and 50/50 PA-6/ABS compositions. The compatibilization mechanism of PA-6/ABS by the SAN–PAr block copolymer was investigated by tetrahydrofuran extraction of the SAN–PAr block copolymer/PA-6 blends and the model reactions between the block copolymer and low molecular weight compounds. The results of these experiments indicated that the SAN–PAr block copolymer reacted with the PA-6 during the melt mixing process via an *in situ* transreaction between the ester units in the PAr chain and the terminal amine in the PA-6. As a result, SAN–PAr/PA-6 block copolymers were generated during the melt mixing process. The SAN–PAr block copolymer was supposed to compatibilize the PA-6 and ABS blend by anchoring the PAr/PA-6 and SAN chains to the PA-6 and ABS phases, respectively. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2300–2313, 2002

Key words: polystyrene; styrene-acrylonitrile random copolymer; polyarylate; block copolymer; compatibilizer; polyamide; acrylonitrile-butadiene-styrene copolymer; transreaction; polymer blend; polymer alloy

INTRODUCTION

Polymer blending is a simple and efficient method for designing and controlling the performance of polymeric materials using easily available polymers. This procedure makes it possible to develop

a new polymeric material with synergetic performance by each polymer, to reduce the cost of engineering plastics by diluting them with lower cost polymers, or to enhance recycling of used plastics. These effects of polymer blending on the performance, economy, and ecology have accelerated R & D activities in the field of polymer blends or alloys in the academic and industrial fields.^{1–5}

However, almost all simple polymer blends fail to compatibilize with each polymer because of the low combinatorial entropy of mixing. Because of

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poor interfacial adhesion strength, among immiscible polymers the polymer blends usually lead to unsatisfactory properties with simple mechanical mixing. Hence, improvement in the interfacial adhesion strength is a key factor in developing a new polymeric material by polymer blending.

The general concept of improving the interfacial adhesion strength between immiscible polymers was summarized by Utracki.⁵ In general, the addition of a block or graft copolymer is the most representative⁶ and has been applied to several immiscible polymer systems.^{5,7-11} The constituent chain of a block or a graft copolymer has been shown to function as an anchor to the two homopolymers and reduce their interfacial tension.¹² As a result, a finer dispersion is generated during processing,¹³ leading to a dramatic increase in their interfacial adhesion strength.¹⁴ Although the addition of a block or graft copolymer appears to be effective, this method has a practical limitation for the following reason.⁶ When a block or graft copolymer is mixed with immiscible polymers, it often forms micelles by itself in either of the polymer phases instead of existing at the polymer-polymer interface.^{15,16} Formation of micelles significantly reduces the effectiveness of the block or graft copolymer as a compatibilizer.⁶ Another method is to add a polymer with functional groups, which can generate a block or graft copolymer during the blend preparation via an *in situ* interfacial reaction.¹⁷⁻²¹ This approach, which is known as “a reactive compatibilization,” has been implemented in a number of commercial products in recent years.^{5,17-23} In this method a block or graft copolymer is generated at the interface during the melt mixing process and remains there even after the cooling process. As a result, the blends could be compatibilized more effectively than the compatibilization by a pre-made block or graft copolymer.

We carried out research and development on polymer blends mainly based on polystyrene and polyarylate (PS-PAr) block copolymers.²⁴⁻³⁰ In our earlier publications we proposed a novel synthetic procedure of a PS-PAr block copolymer.²⁴⁻²⁶ We also reported its high potential for optical applications,^{24,25,27} as a moldability modifier for polycarbonate (PC),²⁹ and as a reactive compatibilizer for an immiscible blend system of high impact PS and PC.³⁰

In this study we attempted to apply styrene-acrylonitrile random copolymer (SAN) and PAr block copolymer²⁸ as a reactive compatibilizer for polyamide (PA)/acrylonitrile-butadiene-styrene

copolymer (ABS) blends.³¹⁻⁴⁰ PA is an important engineering polymer used in a wide variety of applications because of its high heat deformation temperature, mechanical properties, chemical resistance, and low viscosity in the molten state. However, PA has some deficient characteristics that deter its use in some areas. Low impact energy absorption and high moisture sorption are typical PA defects. On the other hand, ABS has higher impact energy absorption and lower moisture sorption than PA, although its chemical and heat deformation resistances are much inferior to PA. Thus, the focuses of our research are to improve the impact energy absorption and moisture sorption of PA by blending PA and ABS and to produce a resin with an excellent balance of properties. However, because PA and ABS are immiscible, adequate compatibilization is required to achieve the aimed properties.³¹⁻⁴⁰ In this study we paid attention to the following features of the constituent chains in the SAN-PAr block copolymer. The SAN chains are miscible with the SAN matrix in ABS while the PAr chains are polar polymers, which have the potential of interacting with PA via a transreaction^{41,42} or hydrogen bonds, although PAr by itself is immiscible in PA.^{43,44} Hence, by making use of the SAN and PAr chains as anchor units to the ABS phase and an interaction unit to the PA phase, respectively, the SAN-PAr block copolymer could be applicable as a reactive compatibilizer for a PA and ABS blend system.

The purpose of this article is to investigate the phase morphology of PA-6/ABS blends compatibilized with SAN-PAr block copolymer and show how effective the SAN-PAr block copolymer was on their impact energy absorption control. In addition, the compatibilization mechanism of the PA-6/ABS blend by the SAN-PAr block copolymer was investigated.

EXPERIMENTAL

Materials

The SAN₂₇-PAr copolymers in Table I, where the subscript to SAN represents the AN weight composition in the SAN chain, were synthesized (Fig. 1) and characterized in the same way as described previously.²⁸ The weight percentage of PAr in run 2085 is defined by eq. (1), according to the same design concept as described in ref. 29:

$$\text{PAr} = 10M_{\text{PAr}} / (M_{\text{nHOOC-SAN}_{27}\text{-COOH}} + 10M_{\text{PAr}}) \quad (1)$$

Table I Preparation and Characterization of SAN₂₇-PAr Block Copolymer

Sample	HOOC-SAN ₂₇ -COOH			Feed Characterization of SAN ₂₇ -PAr Block Copolymer			
	M_n	M_w	COOH (equiv/mol)	PS/PAr	M_n^a	M_w^a	Pure SAN ₂₇ -PAr Block Copolymer ^b (wt %)
Run 2085				85/15	32,000	85,000	89.4
Run 2050	23,000	43,000	2.1	50/50	38,000	100,000	72

^a The number-average (M_n) and weight-average (M_w) molecular weights were measured without purification.

^b Pure SAN₂₇-PAr block copolymer (wt %) was estimated from the simulation model because it could not be separated from the polymerization products due to limitations in the purification method.

where $M_{n_{\text{HOOC-SAN}_{27}\text{-COOH}}}$ and M_{PAr} are the number-average molecular weight of the HOOC-SAN₂₇-COOH in step 2 of Figure 1 and the PAr units (358 g/mol), respectively. The SAN₂₇-PAr block copolymer of run 2085 was used throughout the experiments. The SAN₂₇-PAr block copolymer of run 2050 was only used in the model experiments to examine the compatibilization mechanism. The terminals of these block copolymers were capped with *p*-*tert*-butylphenol.²⁸

The PA-6 (1013A) and ABS (UX050) were obtained from Ube Inc. JP. The matrix of this ABS consisted of SAN₂₅, and its rubber content was about 50 wt %. The low molecular weight compounds *N,N'*-diacetyl-1,6-diaminohexane, stearylamine, and *p*-dodecylphenol (Aldrich) used in the model were used without further purification.

Melt and Molding Process

The 70/30 and 50/50 PA/ABS blends were mixed with the SAN₂₇-PAr block copolymer by a V-shaped mixer. Then they were intensively melt mixed by a corotating twin-screw extruder (TEX30SS, 30-mm diameter, length/depth = 50, 120 rpm, Japan Steel Works Corp. JP) at a feed rate of 15 kg/h and a barrel temperature of 260°C. Although the addition of a catalyst such as *p*-toluenesulfonic acid is known to be effective in the transreaction between amide and ester units,^{41,42} no catalyst was added during the melt mixing process. The extruded blends were pelletized and subsequently injection molded at 260°C and 8000 kg cm⁻² using an injection machine (Ti-80G2, Toyo Machinery Metal Corp. JP) to prepare standard specimens for Izod impact strength (1/8 in. thickness) measurements. Before each processing experiment, all the polymeric materials were dried for at least 48 h at 90°C in a vacuum oven to ensure complete removal of moisture.

Observations of Phase Morphology and Measurements of Impact Energy Absorption

The blend morphologies were examined by scanning electron microscopy (SEM). For SEM observation the Izod specimens were fractured in liquid nitrogen, followed by tetrahydrofuran (THF) etching in an ultrasonic bath for 15 min to extract the ABS phases. The etched specimens were washed several times with distilled water, dried, and then coated with gold (30-nm thickness). The SEM observation was carried out using a Hitachi JP SEM microscope (S-2100A) at an accelerating voltage of 20 kV. In the SEM micrographs the darker portions were assigned to the ABS-rich phases that were eliminated by the etchant and the brighter portions were assigned to the PA-6-rich phases. The samples transverse to the flow direction were obtained from the center.

The impact energy absorption of the blends was obtained by the notched Izod impact method at room temperature according to ASTM D 256 using a pendulum-type tester. The as-molded dry specimens were used for each data point, and at least 10 specimens were tested. The experimental error bars of these results showed the range of data, excluding the maximum and minimum values.

Characterization of Samples

The 15/85 blends of the SAN₂₇-PAr block copolymer (run 2085)/PA-6 were melt mixed with a Bra-bender batch mixer at 260°C and 70 rpm in a 25-cm³ mixing head with a standard rotor. The blend was crushed in a coffee mill to obtain the powdered sample. Then the samples were fractionated by Soxhlet extraction with THF for 240 h. The molecular weight of the SAN₂₇-PAr block copolymer and the PA-6 was measured by size exclusion chromatography (SEC, GPC-244, Waters Co.). For the SAN₂₇-PAr block copolymer

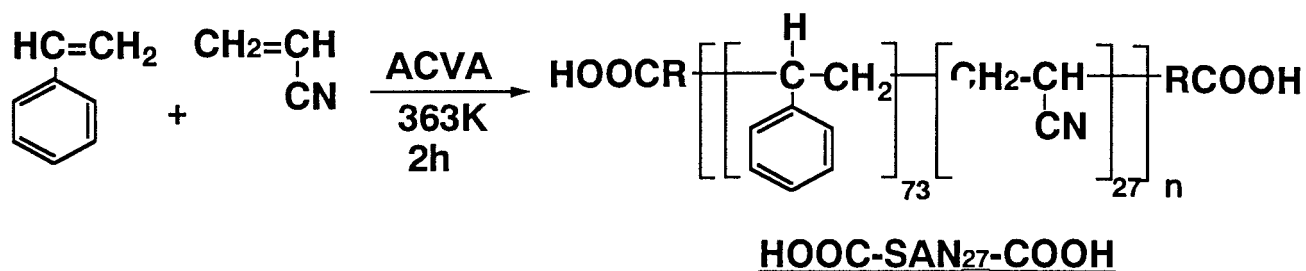
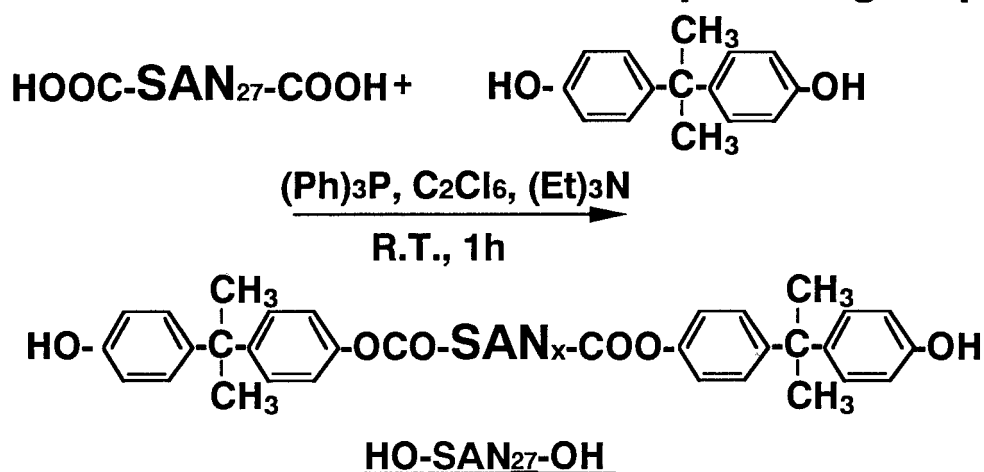
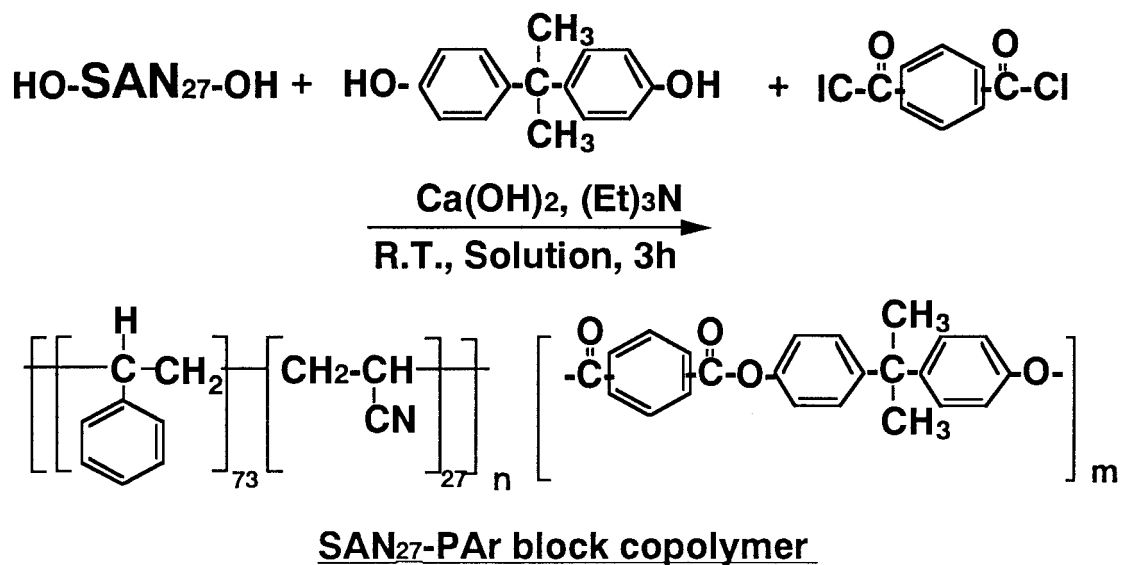
(Step 1) Preparation of HOOC-SAN₂₇-COOH**(Step 2) Conversion of carboxyl groups of HOOC-SAN₂₇-COOH into phenol groups****(Step 3) Synthesis of SAN₂₇-PAR block copolymer**

Figure 1 The reaction scheme.

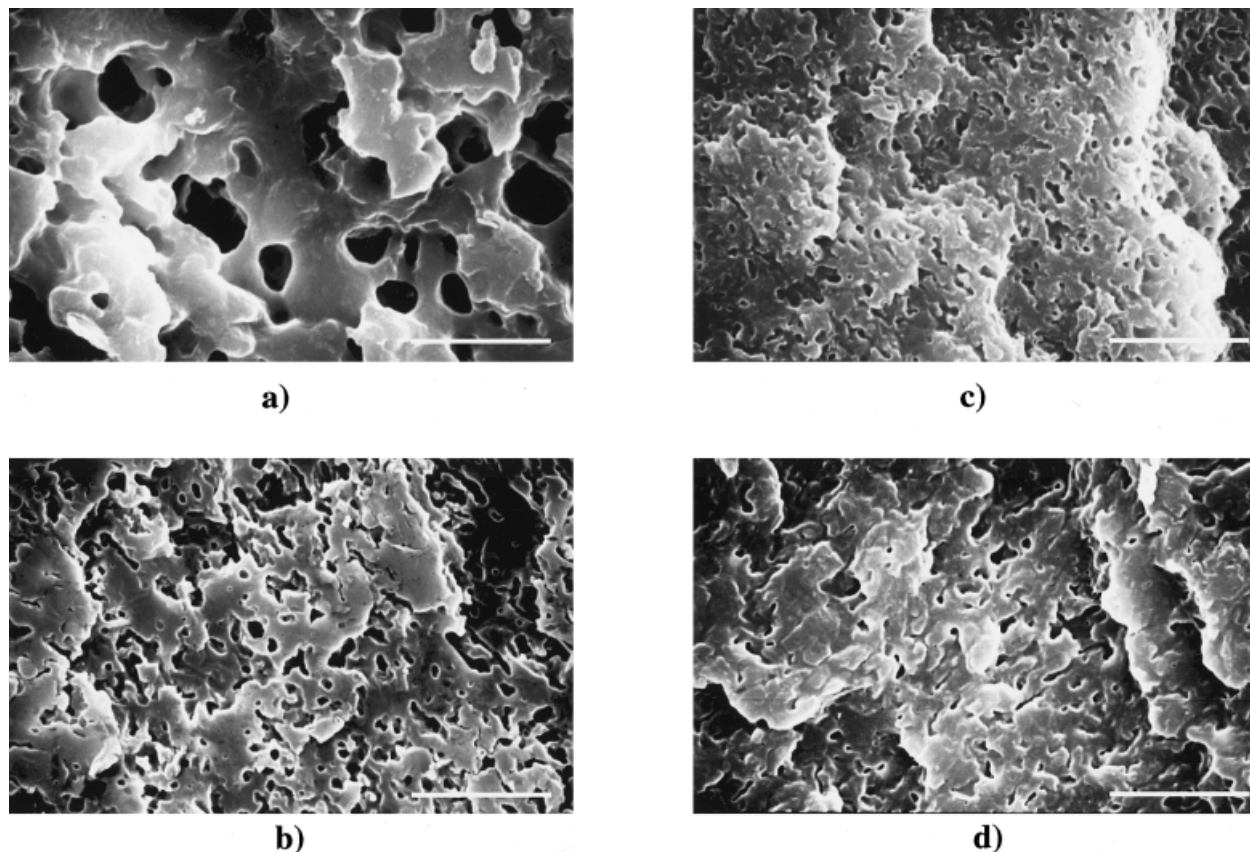


Figure 2 The phase morphology of the PA-6/ABS (70/30) blends (a) without a compatibilizer and (b–d) with 1, 3, and 5 wt % SAN₂₇-PAr block copolymer. Scale bar = 10 μm .

we used THF and monodisperse PS for the mobile phase and the calibration, respectively. For the PA-6 we used 1,1,1,3,3,3-hexafluoro-2-propanol and standard PA-6 (molecular weight calibrated by light scattering) for the mobile phase and the calibration, respectively. The chemical shifts in the SAN₂₇-PAr block copolymer were analyzed in a ¹³C-NMR spectrum^{41–43} in CDCl₃ using a Varian Unity Inova 400. Fourier transform IR spectroscopy (FTIR) analysis was carried out using Perkin–Elmer System 2000.

RESULTS AND DISCUSSION

Phase Morphology of PA-6/ABS Blends Compatibilized with SAN₂₇-PAr Block Copolymer

Figures 2 and 3 show the phase morphologies of the 70/30 and 50/50 PA-6/ABS blends, respectively. At both compositions the size of the ABS-rich phases was reduced dramatically by the addition of a small amount of SAN₂₇-PAr block co-

polymer. Furthermore, the eliminated areas of the ABS-rich phases became smaller as the amount of added SAN₂₇-PAr block copolymer increased at both compositions. These results indicated that the interfacial adhesion between the ABS and PA-6 phases became stronger with the increase in the amount of added block copolymer. There was a little difference between the 70/30 and 50/50 blends in how the amount of the added block copolymer affected the shape and size of the ABS-rich phases.

In the 70/30 blend without block copolymer, the ABS-rich phase was dispersed in the PA-6-rich matrix with the size of around 4 μm . At this composition the addition of the 1 wt % block copolymer seemed to change the morphology from a simple dispersion of the ABS spheres in PA-6 matrix to a different shape where both the ABS- and PA-rich phases tended to form a finer cocontinuous structure. The size of the ABS-rich phase was <1 μm . Neither the size nor the shape of the ABS-rich phase changed much, even if the

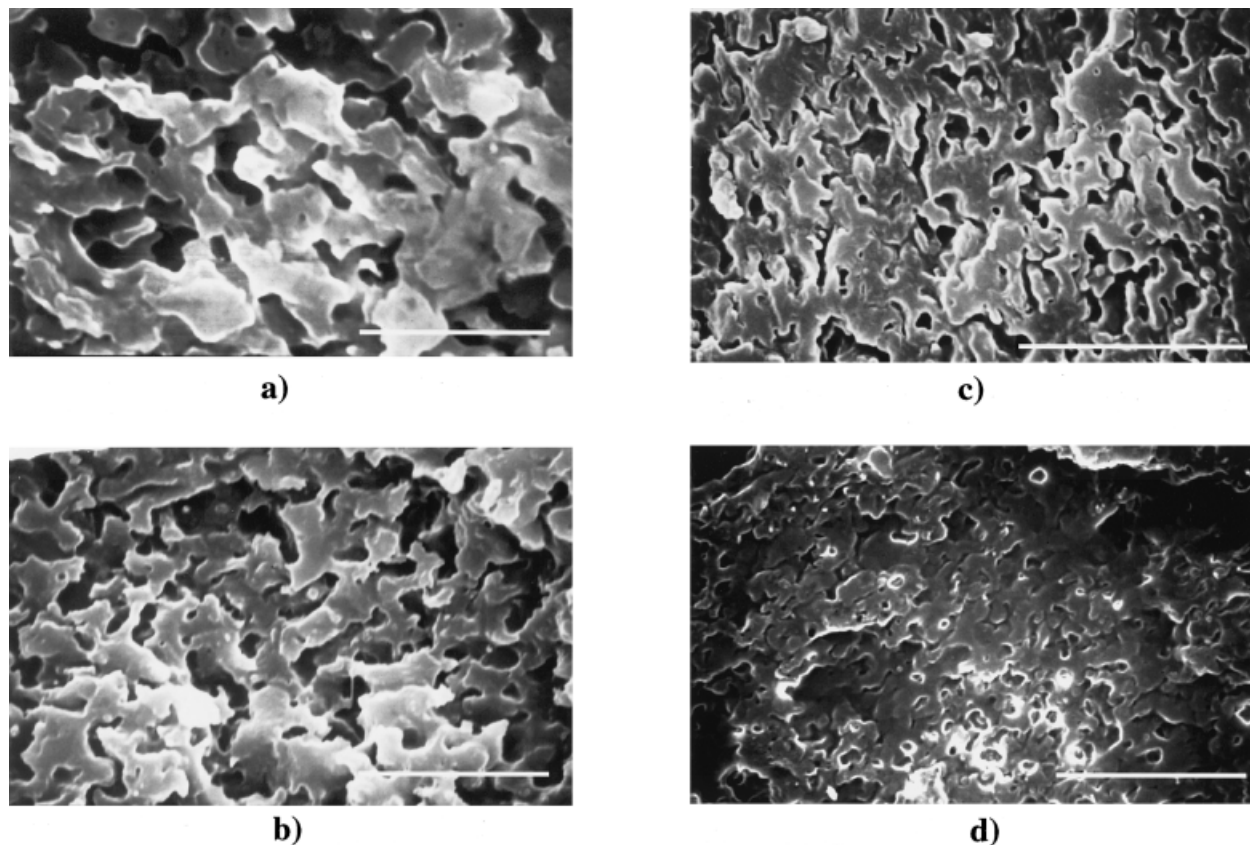


Figure 3 The phase morphology of the PA-6/ABS (50/50) blends (a) without a compatibilizer and (b–d) with 1, 3, and 5 wt % SAN₂₇-PAR block copolymer. Scale bar = 10 μm .

amount of added block copolymer was increased from 1 to 5 wt %. On the other hand, at the PA-6/ABS composition of 50/50, the PA-6- and ABS-rich phases formed a cocontinuous phase^{32,33} in blends with and without SAN₂₇-PAR block copolymer (Fig. 3). In addition, the size of the ABS-rich phase changed according to the amount of added SAN₂₇-PAR block copolymer. In the uncompatibilized blend the large ABS-rich phases, which were larger than several microns, were apparent. The size of the ABS-rich phase was reduced with an increase of the amount of added block copolymer. When the added amount of the block copolymer reached 3 wt %, the ABS-rich phase was reduced to around 1 μm . With the addition of 5 wt % of the block copolymer, the size of the ABS-rich phase was reduced to almost 500 nm.

From these results the SAN₂₇-PAR block copolymer was found to be an effective compatibilizer for PA-6 and ABS blends. With the addition of 3.0–5.0 wt % SAN₂₇-PAR block copolymer, the

size of the ABS-rich phase could be reduced to smaller than 1.0 μm for 70/30 and 50/50 PA-6/ABS blends.

Impact Energy Absorption of PA-6/ABS Blends Compatibilized with SAN₂₇-PAR Block Copolymer

Figure 4 shows the impact energy absorption properties of PA-6/ABS blends as a function of the blend composition and the amount of SAN₂₇-PAR block copolymer added. The Izod impact strengths were lower for the uncompatibilized blends than those of the original PA-6 at the ABS composition of 30 wt %. Even when the ABS was increased to 50 wt %, the blend exhibited the same level of Izod impact strength as the original PA-6.

With an adequate amount of SAN₂₇-PAR block copolymer, the Izod impact strength of the PA-6/ABS was dramatically improved. At the 30 wt % ABS composition, the Izod impact strength was increased >580 J/m by the addition of only 1 wt % SAN₂₇-PAR block copolymer. No further improve-

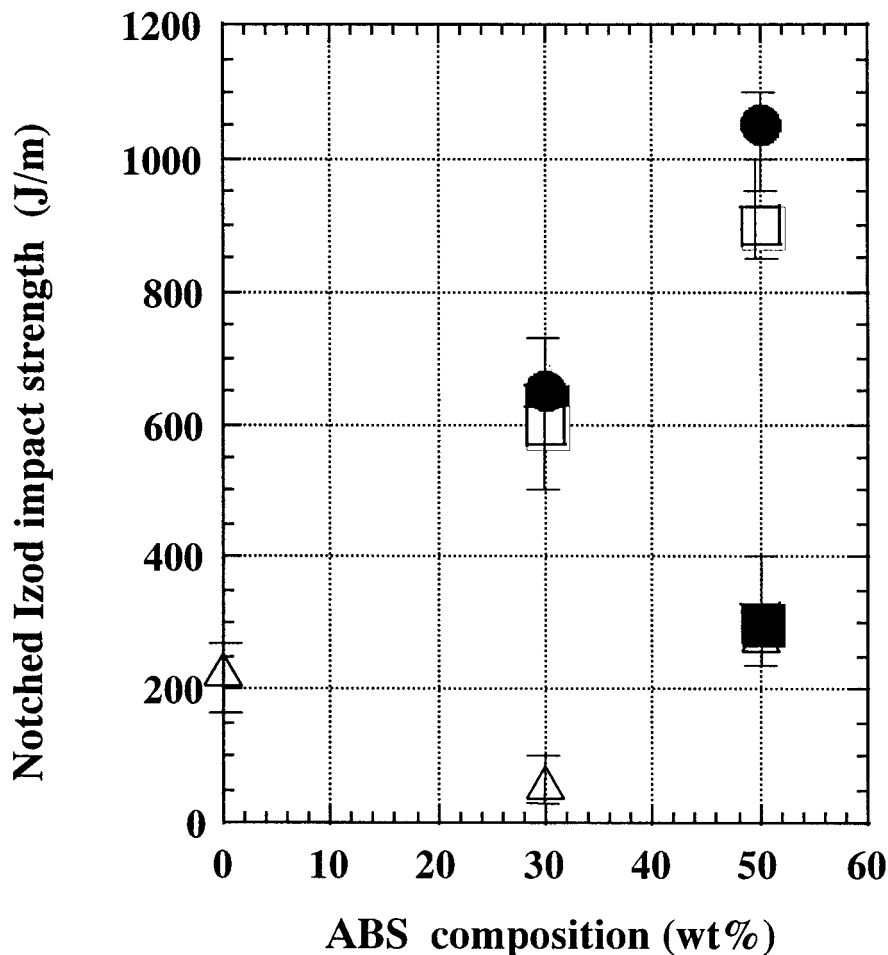


Figure 4 The impact energy absorption of PA-6/ABS blends (Δ) without SAN₂₇-PAR block copolymer (\blacksquare , \square , \bullet) with 1, 3, and 5 wt % of the SAN₂₇-PAR block copolymer, respectively.

ment in the Izod impact strength was observed with an increase of the block copolymer up to 5 wt %. This may be due to the fact that the size of the ABS-rich phase reached $<1.0 \mu\text{m}$ with the addition of only 1 wt % block copolymer and the size never changed with an increase in the block copolymer from 1 to 5 wt %. At 50 wt % ABS, on the other hand, the impact energy absorption increased with the amount of the added block copolymer. The blend compatibilized with 1 wt % block copolymer showed almost the same Izod impact strength as the uncompatibilized blend. However, when compatibilized with 3 or 5 wt % block copolymer, the PA-6/ABS blends exhibited $>900 \text{ J/m}$ Izod impact strength. The sizes of the ABS-rich phases were reduced to a small enough size ($<1 \mu\text{m}$) in these blends.

These results showed that the impact energy absorption of the PA-6/ABS blend was sensitive to the size of the ABS-rich phase. When the size of

the ABS-rich phase was smaller than $1.0 \mu\text{m}$, the impact energy absorption could reach the super toughness region ($>580 \text{ J/m}$)⁴⁵ at both 70/30 and 50/50 PA-6/ABS compositions. The necessary condition for super toughness in our experimental analysis was to add 3.0–5.0 wt % SAN₂₇-PAR block copolymer in the PA-6/ABS (70/30 and 50/50) blends.

Compatibilization Mechanism of PA-6/ABS Blends by SAN₂₇-PAR Block Copolymer

When a block or graft copolymer compatibilizes an immiscible polymer blend, its constituent chains function as an anchor to each phase because of their miscibility to each phase.¹² In our experimental system, however, the PAR chains in the SAN₂₇-PAR block copolymer are immiscible with PA-6,^{43,44} although the SAN₂₇ chains are

miscible in the SAN₂₅ matrix of ABS. To make the PAR chains function as an anchor to the PA-6 phase, some interaction should occur between the PAR chains and the PA-6 during the melt mixing process. The possible schemes that mainly occur between the PAR chain and the PA-6 are listed in Figure 5. They are transreactions between

1. the ester and the amide units,
2. the ester and the terminal amine of PA-6,
3. the amide and the terminal phenol of the block copolymer generated by reaction 2, and
4. the hydrogen bonds in the C=O in the PAR chain and the N—H in the PA-6.

Which of these interactions actually occurred was established by the following three steps. In the first step, to confirm the fact that the PAR chains really interacted with the PA-6, the THF extraction results were compared before and after melt mixing of the SAN₂₇-PAR block copolymer and the PA-6. In the second step the reaction in parts 1–3 in Figure 5 was confirmed by the model experiments between the low molecular weight compounds and the SAN₂₇-PAR block copolymer or the PA-6. This is because in the actual polymer–polymer systems the change in the molecular weight and the chemical shift is difficult to evaluate by conventional SEC or ¹³C-NMR measurement because of overlapping peaks. In the third step the hydrogen bonds in part 4 of Figure 5 were confirmed by FTIR.

Confirmation of Interaction between PAR Chains in SAN₂₇-PAR Block Copolymer and PA-6 by THF Extraction

Figure 6 shows the THF extraction results of the 15/85 blends of SAN₂₇-PAR block copolymer (run 2085)/PA-6 and HOOC-SAN₂₇-COOH/PA-6 as a function of the melt mixing time. When the SAN₂₇-PAR block copolymer was melt mixed with the PA-6 at 260°C for 3 min, more than 90% of the fed SAN₂₇-PAR block copolymer changed from THF soluble to insoluble. Furthermore, when melt mixing them for 10 min, the amount of the extracted SAN₂₇-PAR block copolymer was outside the identification limit. For the HOOC-SAN₂₇-COOH/PA-6 blends, almost all of the fed HOOC-SAN₂₇-COOH could be extracted by THF, even after melt mixing for 10 min. These results indicated the PAR chains actually interacted with the PA-6 during the melt processing. By 3 min of melt mixing more than 90 wt % of the SAN₂₇-PAR

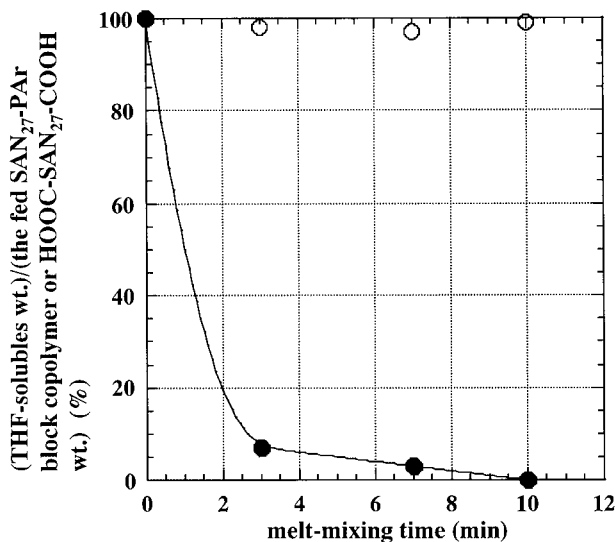


Figure 6 The THF solubles ratio in the 15/85 blends of (●) SAN₂₇-PAR block copolymer/PA-6 and (○) HOOC-SAN₂₇-COOH/PA-6 as a function of the melt mixing time.

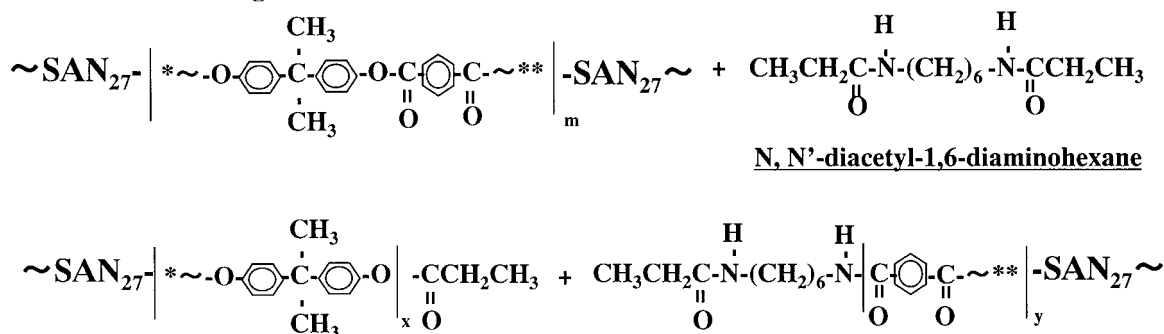
block copolymers interacted with the PA-6. After 10 min of melt mixing almost all of the block copolymers interacted with the PA-6.

Transreaction of Ester–Amide, Ester–Amine, and Amide–Phenol Units by Model Compounds

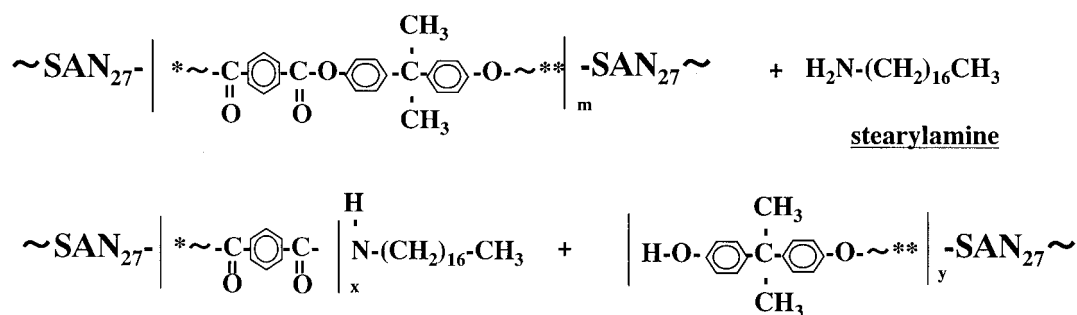
N,N'-Diacyl-1,6-diaminohexane, stearylamine, and *p*-dodecylphenol were selected as the model compounds that contained similar amide units, an amine, and a phenol, respectively, as the PA-6 and the SAN₂₇-PAR block copolymer. These model compounds were melt mixed with the SAN₂₇-PAR block copolymer (run 2050) or the PA-6 in the same way as aforementioned for 10 min with weight ratios of 1/20 and 10/20 to the polymer components. Each of these model compounds has relatively low volatility, even at the melt mixing temperature of 260°C. If the reaction of Figure 7 actually proceeds, the molecular weight of the SAN₂₇-PAR block copolymer should shift to the smaller side because of chain scission.

Figure 8 shows the molecular weight distribution profiles after the melt mixing. To eliminate the effect of heat decomposition during the melt mixing, the molecular weight distribution profiles of the polymer components melt mixed under the same conditions were plotted together. When the SAN₂₇-PAR block copolymer was melt mixed with *N,N'*-diacyl-1,6-diaminohexane with a 1/20 ratio, the molecular weight distribution was almost the same as that of the unreacted one. Even

1) ester-amide exchange



2) ester-amine exchange



3) amide-phenol exchange

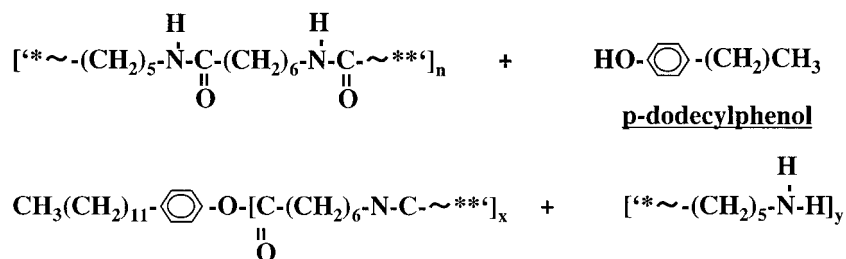


Figure 7 The model reaction schemes for $x + y = m$.

when melt mixed with a 10/20 ratio, the degree of shift in the molecular weight was very small. When the PA-6 was melt mixed with *p*-dodecylphenol even at the weight ratio of 10/20, the molecular weight distribution was almost the same as that of the unreacted PA-6. When the SAN₂₇-PAR block copolymer was melt mixed with stearylamine, one can see clear shifts to the smaller side and the shoulder appeared at around $M = 1000$. The degree of shift in the molecular weight distribution increased with the increase of the fed model compound ratio. Especially when melt mixed with stearylamine in a weight ratio of

10/20 (the ester ratio to the amine was 1.5 mol), the shoulder peak at around $M = 1000$ was extremely increased.

To confirm the reaction in part 2 in Figure 7 more clearly, Figures 9 and 10 show the ¹³C-NMR and FTIR spectra of the SAN₂₇-PAR block copolymer, respectively. The ¹³C-NMR spectra between 160 and 170 ppm, which were attributed to the carbons of the carbonyl units, are shown in Figure 9. This is because the chemical shifts of these carbons are very sensitive to the difference between the ester and amide linkage. The spectrum at around 164.5 ppm was attributed to the car-

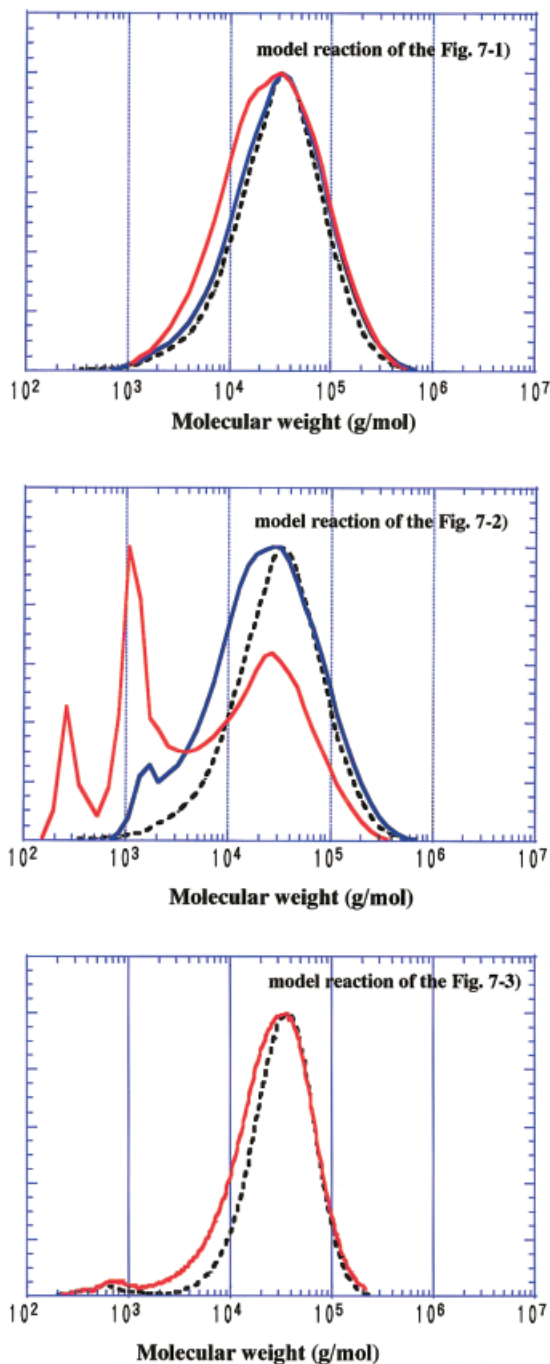


Figure 8 The molecular weight distribution after the model reaction of Figure 7. (—) the molecular weight distribution when the polymer component alone was melt mixed. The blue and red solid lines show the molecular weight distribution when 20 g of the polymer components were melt mixed with 1 and 10 g of the model compound, respectively.

bonyls of the ester linkage in both terephthalic and isophthalic residues.^{41,45–47} If the amide linkage was generated, these carbon spectra should

be shifted to lower magnetic fields.^{41,45,46,48} Clear peaks between 166 and 168 ppm appeared in the ¹³C-NMR spectrum after melt mixing of the SAN₂₇-PAR block copolymer with stearylamine. Furthermore, in the FTIR spectrum after the melt mixing, one can see the novel peaks at around 1540 and 1640 cm⁻¹, although they could not be found before the melt mixing. These peaks were from the N—H in the plane mode (amide II)⁴⁹ and the C=O stretching in the amide linkages (amide I).⁴⁹ These changes in the ¹³C-NMR and FTIR indicated that the reaction in Figure 7 (part 2) actually occurred, and as a result amide linkages were generated between stearylamine and the terephthalic and isophthalic residues.

From these results it may be concluded that the most probable reaction among the reactions in Figure 5 (parts 1–3) was that in part 2, which is the transreaction between the esters of the PAR chain and the terminal amine of the PA-6.

Hydrogen Bonds between C=O in PAR Chains and N—H in PA-6

To confirm the hydrogen bonds between the C=O in the PAR chains and the N—H in the PA-6, the FTIR spectra of the 70/30 and 50/50 blends of the PA-6/SAN₂₇-PAR block copolymer (run 2050) were analyzed. Because the C=O stretching peaks^{50,51} in the PAR chains appear at around 1740 cm⁻¹ and apart from those in PA-6 (at around 1640 cm⁻¹ for amide I)⁴⁹ in the FTIR spectrum, the C=O peaks in the PAR chain could be used as a tracer of the hydrogen bonds in part 4 in Figure 5. If the PAR chains interacted with the PA-6 via the hydrogen bonding, the C=O stretching in the PAR chains should be shifted to lower frequency⁵¹ because of the electron drawing effects of the hydrogen bonds. As a result, some spectra peaks or shoulders should appear between 1641 and 1740 cm⁻¹. However, neither clear peaks nor shoulders could be found in the FTIR spectrum of either blend. Thus, we could not conclude that the PAR chain interacted with the PA-6 via hydrogen bonds from the results of the FTIR measurements. Considering the sensitivity of the FTIR spectrum to hydrogen bonds, another analyses such as solid-state NMR measurements or quantum chemical calculation should be added in the future to discuss the existence of hydrogen bonds in an exact manner.

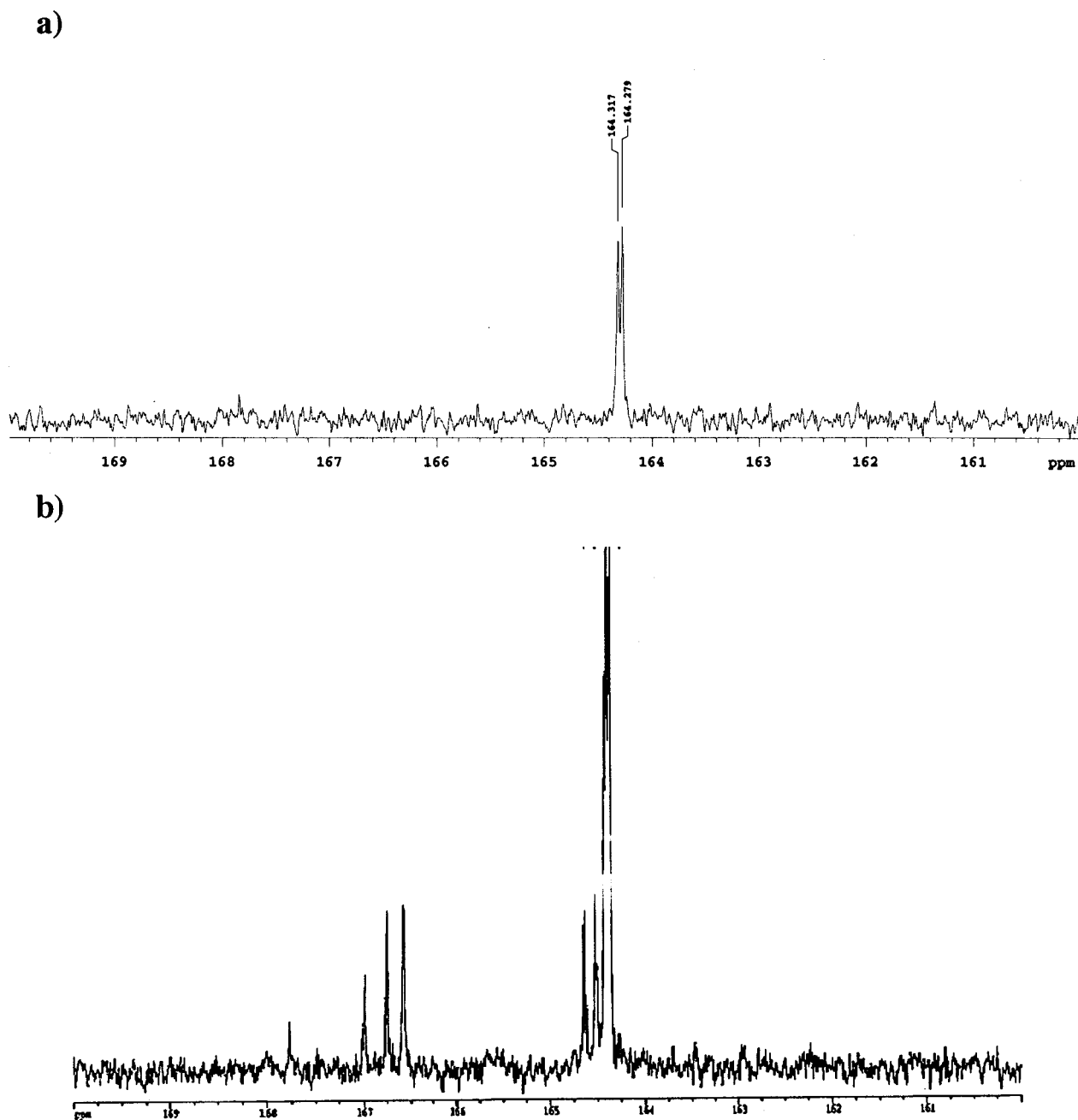


Figure 9 The ^{13}C -NMR spectrum (a) before and (b) after the reaction in part 2 of Figure 7.

Most Probable Compatibilization Mechanism of PA-6/ABS Blends by SAN₂₇-PAR Block Copolymer

Considering these results, the most probable compatibilization mechanism of the PA-6/ABS blends by the SAN₂₇-PAR block copolymer was as follows. The SAN₂₇-PAR block copolymer reacted with the PA-6 via the *in situ* reaction shown in part 2 of Figure 5, and those SAN₂₇-PAR/PA-6 block copolymers were generated during the melt mix-

ing process. The SAN₂₇-PAR block copolymer compatibilized the PA-6 and ABS blend by anchoring the PAR/PA-6 and the SAN₂₇ chains to the PA-6 and ABS phase, respectively.

CONCLUSIONS

A SAN₂₇-PAR block copolymer was applied as a reactive compatibilizer for a PA-6/ABS blend sys-

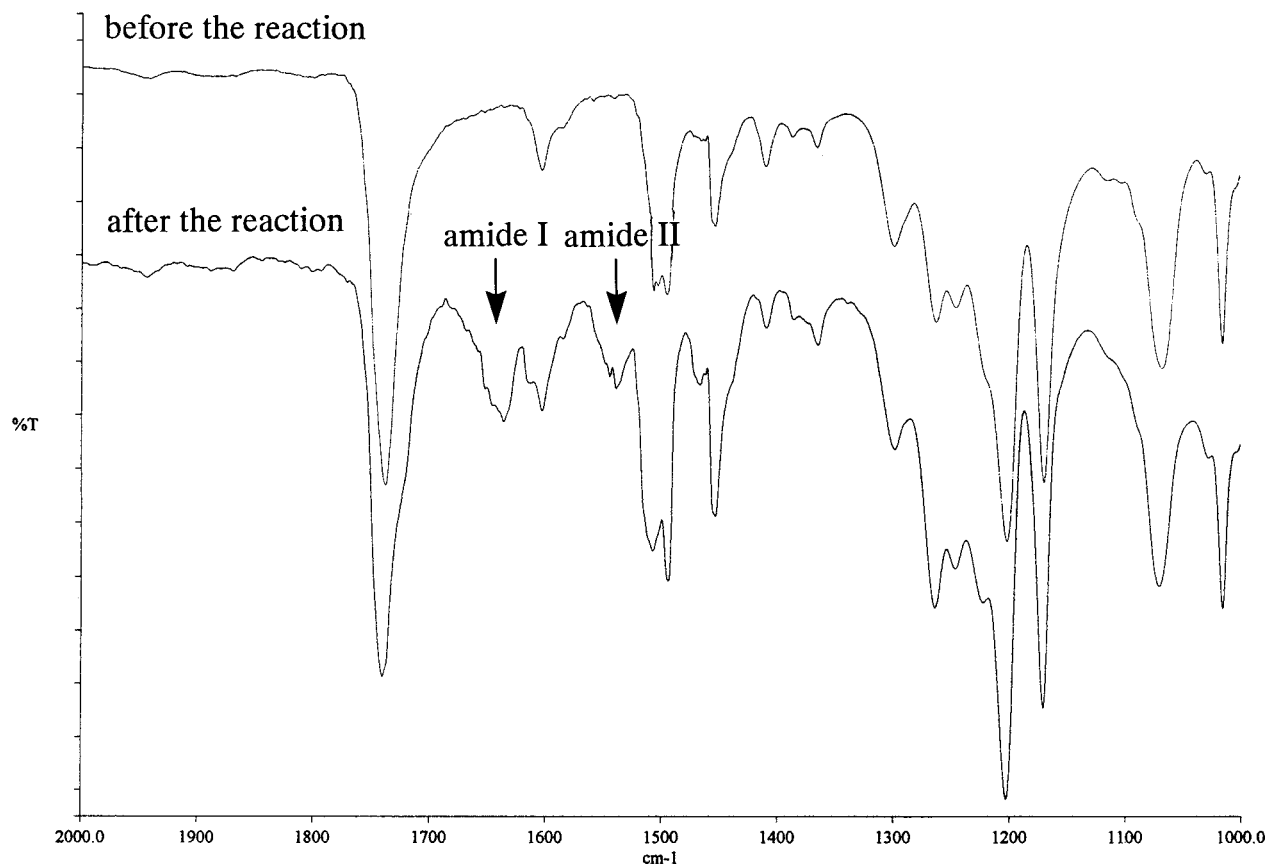


Figure 10 The FTIR spectrum of the SAN₂₇-PAr block copolymer before and after the reaction in part 2 of Figure 7.

tem. The SAN₂₇-PAr block copolymer was found to be effective for compatibilization of PA-6 and ABS blends.

1. The addition of 3.0–5.0 wt % SAN₂₇-PAr block copolymer reduced the size of the ABS-rich phase to <1.0 μm for 70/30 and 50/50 PA-6/ABS blends. In the uncompatibilized blends the size of the ABS-rich phase was larger than several microns.
2. The impact energy absorption of the PA-6/ABS blend was sensitive to the size of the ABS-rich phase. When the size of the ABS-rich phase was <1.0 μm, the impact energy absorption could reach the super toughness region for the 70/30 and 50/50 PA-6/ABS compositions. A necessary condition for the super toughness in our experimental analysis was to mix 3.0–5.0 wt % SAN₂₇-PAr block copolymer for the 70/30 or 50/50 blend of PA-6 and ABS.
3. From THF extraction it may be concluded that almost all of the fed SAN₂₇-PAr block

copolymers could react with PA-6 by melt mixing for only 10 min.

4. The model experiments between low molecular weight compounds and the SAN₂₇-PAr block copolymer or PA-6 was carried out to establish what reaction actually occurred during the blend preparation process. The results of the analysis of the molecular weight distribution shifts and chemical shifts after the model reactions indicated the following facts. The most probable reaction occurring between the PAr chain and the PA-6 was the reaction in part 2 of Figure 5, which was the transreaction between the esters of the PAr chain and the terminal amine of PA-6. As a result, SAN₂₇-PAr/PA block copolymer was generated during the melt process.
5. From conclusions 3 and 4, the SAN₂₇-PAr block copolymer was supposed to compatibilize the PA-6 and ABS blend by anchoring these PAr/PA-6 and SAN₂₇ chains to the PA-6 and ABS phase, respectively.

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