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In situ copolymerization and compatibilization of polyester and polystyrene blends. I. Synthesis of functionalized polystyrenes and the reactions with polyester

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Abstract

The in situ compatibilization process between polystyrene (PS) and polybutylene terephthalate (PBT) is carried out by adding three types of hydroxy functionalized polystyrenes (PS-Fs). The PS-F was used to promote the in situ copolymerization reaction and compatibilization during melt blending in the mixer. The results of different characterization techniques including Fourier transform infrared (FTIR), GPC and the differential scanning calorimetry (DSC) demonstrate that the slow alcoholysis reaction between the PS-F and PBT took place after the 60 min thermal treatment. In order to achieve good mechanical properties of the reactive blends of PS-F and PBT, it is important to control the level of degradation of PBT. On the other hand, the optimum degradation is necessary to promote the in situ reaction to the PS-F. In this paper titanium butoxide (TNBT) and triphenyl phosphite (TPP) were used in order to control the reaction and degradation. The addition of 1% TNBT into the blends of PS-F/PBT enhances the miscibility of the PS-F and PBT as a catalyst for the alcoholysis reaction. It is found that the stabilizer TPP not only prevents the excess thermal degradation of PBT but also promotes the reaction between the PS-Fs and PBT by coupling reaction. The anionic polymerization procedure of three different PS-Fs and the characterization results of the reaction between PS-Fs and PBT are described. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: In situ copolymerization; Compatibilization; Synthesis of functionalized polystyrene

1. Introduction

Most polymeric binary blends are thermodynamically immiscible, and exhibit two phase morphology. The relatively poor adhesion between these separated phases results in poor mechanical properties. In general, a compatibilizer such as a block or graft copolymer is added to improve the poor mechanical properties of immiscible polymer blends [1–4].

In the previous study [5], the new polystyrene–block–polybutylene terephthalate (PS–*b*–PBT) block copolymers with different molecular weight were synthesized by anionic polymerization and blended with the immiscible polymer blend of polystyrene (PS) and polybutylene terephthalate (PBT) as a compatibilizer. The addition of block copolymers in PS/PBT blends drastically reduced the dimension of the dispersed phase as reported in various previous literatures [1,3,6–8]. We concluded that the addition of 10 wt% block copolymer transformed the brittle characteristic of PS/PBT blend to ductile behavior. The addition of block copolymer in order to improve the mechanical properties was limited to 10 wt% [5]. The excess addition of block copolymer tended to yield the brittle behavior instead of improvement to ductile behavior.

Despite adding the block copolymer as a preformed compalibilizer into the immiscible polymer blends, the in situ copolymerization and compatibilization can be conducted during blending the prepolymer and parent polymers. It is an economical and novel route without sophisticated and carefully controlled chemistry. Therefore, the in situ copolymerization and compatibilization process has received more attention to improve the properties of various immiscible polymer blends [8–23].

In this paper, we focused on investigating the in situ compatibilization process between PS and PBT by adding tetra phenol functionalized. Prior to the synthesis of new block copolymers, three functionalized polystyrenes (PS-Fs) including mono, di and tetra were prepared as base polymers by anionic polymerization. Our attempts

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Table 1
The characteristic data of the polymers used in this study

Polymer	M_w	M_n	M_w/M_n	IV
PS	193,249	86,110	2.244	0.689
PS-F4	22,987	20,817	1.104	0.162
PS-F2	18,198	17,328	1.505	0.138
PS-F1	14,706	14,097	1.043	0.118
PBT	–	29,683[a]	–	1.0

[a] From the equation $[\eta] = 2.15 \times 10^{-4} M_n^{0.82}$ (dl/g); Ref. [40].

are to use these functionalized polymers for promoting the in situ copolymerization reaction and compatibilization during blending and thermal treatments. In particular, the tetra PS-F which has the most phenol groups among them is used to investigate the copolymerization and compatibilization in the PS/PBT blends. The synthesis procedure of each PS-F is also described. Various characterization techniques are used to understand the possible mechanism of in situ copolymerization and compatibilization in this blend system.

2. Experimental

2.1. Materials

The materials used in this study were PBT (Hoechst Celanese Corporation, Celanex 2002), PS (Dow Chemical Corporation, Styron 615 APR). The PS-Fs, including tetra, di and monophenol functional group (PS-F4, PS-F2, PS-F1), were prepared by anionic polymerization by Quirk and his co-worker as described in a later section. The chemical

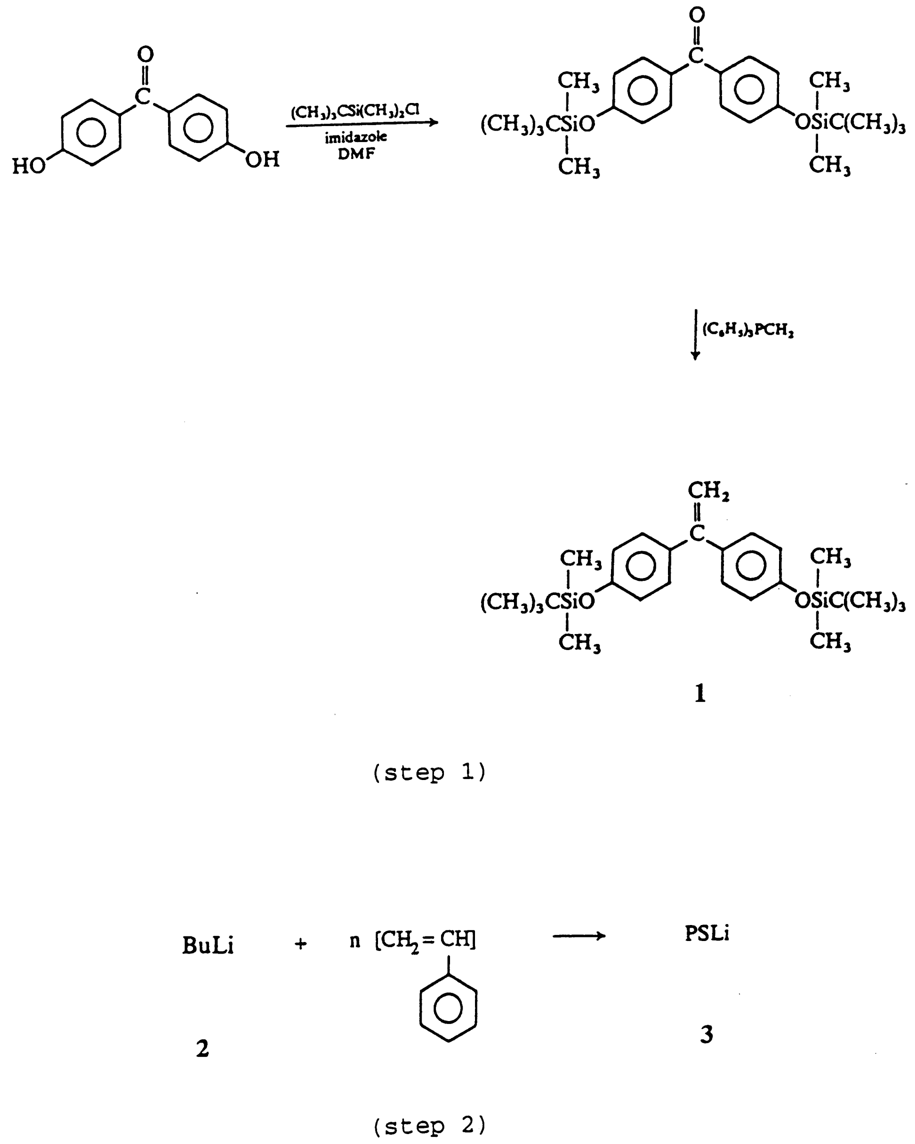
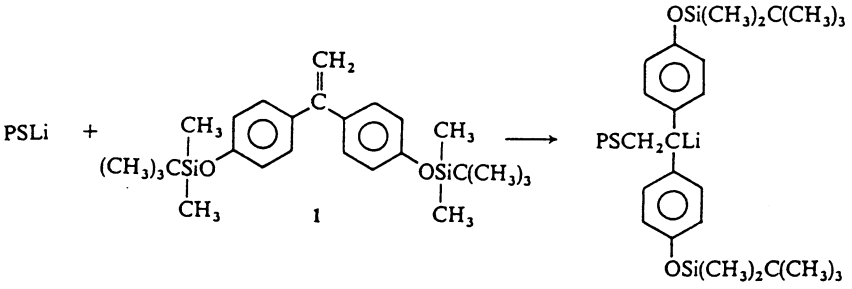
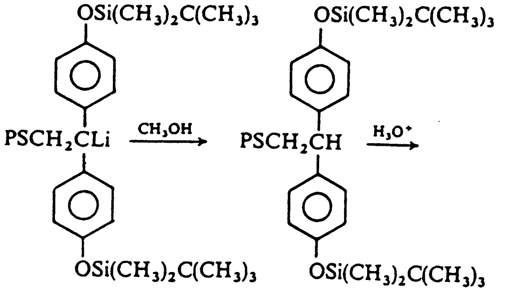


Fig. 1. (a) The procedure (Steps 1–3) of PS-F2 synthesis. (b) The procedure (Steps 4–6) of PS-F2 synthesis.



3 **1** **4**

(step 3)



4 **5** **6**

(step 4)

Fig. 1. (*continued*)

structure, molecular weight and intrinsic viscosity (IV) of the polymers in this study are listed in Table 1.

1,1,2,2-Tetrachloroethane (TCE) (Fluka Chemical Company) was used as a solvent for characterization studies, including a Fourier transform infrared spectroscopy (FTIR) and gel permeation chromatography (GPC). Titanium butoxide (TNBT) (Aldrich Chemical Company) and triphenyl phosphite (TPP) (Aldrich Chemical Company) were used as the catalyst and stabilizer, repectively.

2.2. *Synthesis of functionalized polystyrene*

Three PS-Fs were prepared by anionic polymerization technique as follows. First the main procedure of diphenol-functionalized polystyrene (PS-F2) is described as well as the other PS-Fs including PS-F1 and PS-F4.

The synthesis of termination agent was carried out by first silylating 4,4′-dihydroxybenzophenone with *t*-butyldimethylsilylchloride followed by a Wittig reaction to form 1,1-bis(4-*t*-butyldimethylsiloxyphenyl)ethylene as shown in the Step 1 procedure in Fig. 1.

The polymerization of poly(styryl)lithium was carried out in benzene solution at 25°C in all-glass sealed reactors using break seals and standard high vacuum techniques. The reaction of styrene and butyl-lithium is shown in the Step 2 procedure in Fig. 1.

Termination reaction of poly(styryl)lithium was carried out by adding the terminating agent (0.06 M excess for functionalization) in the presence of tetrahydrofuran (THF) ($[\mathrm{THF}]/[\mathrm{Li}^+] = 30$). The extent of the addition reaction was monitored by ultraviolet–visible spectroscopy. After 12 h, the substituted diphenylalkyllithium adduct **4** was formed as shown in the Step 3 procedure in Fig. 1a.

The adduct **4** was isolated by precipitation into excess methanol and formed the functionalized polymer **5**. The PS-F2, **6**, was obtained by hydrolysis of functionalized polymer **5** with 1–3 vol% HCl in THF under reflux for 3 h as shown in the Step 4 procedure in Fig. 1b [24].

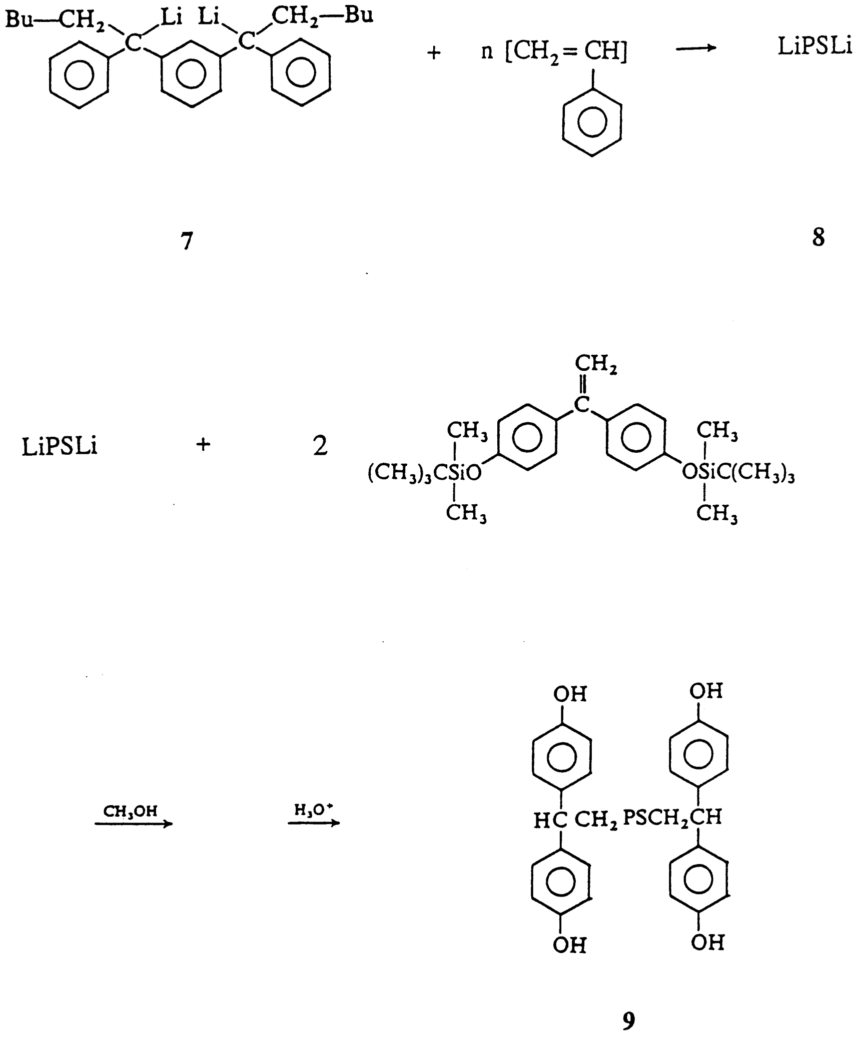


Fig. 2. The procedure (Steps 7–9) of PS-F4 synthesis.

Thin layer chromatographic analysis (TLC) using toluene as a solvent showed only one peak for the PS-F2 **6**, i.e. no spot corresponding to unfunctionalized polystyrene was observed. Analogous TLC analysis of a sample of the functionalized polymer after doping with 1 wt% of unfunctionalized polystyrene base polymer showed two spots, indicating that the functionalized polymer sample has less than 1 wt% of unfunctionalized polymer impurity.

The ^{1}H NMR spectrum exhibited a resonance at $\delta =$ 4.45 ppm, which was assigned to the hydroxyl protons, since it disappeared on shaking with D_2O. The peaks corresponding to the silyl protecting group in functionalized polymer **5** were also absent in the ^{1}H NMR spectrum of the PS-F2 **6**.

2.3. Preparation of tetraphenol-functionalized polystyrene (PS-F4)

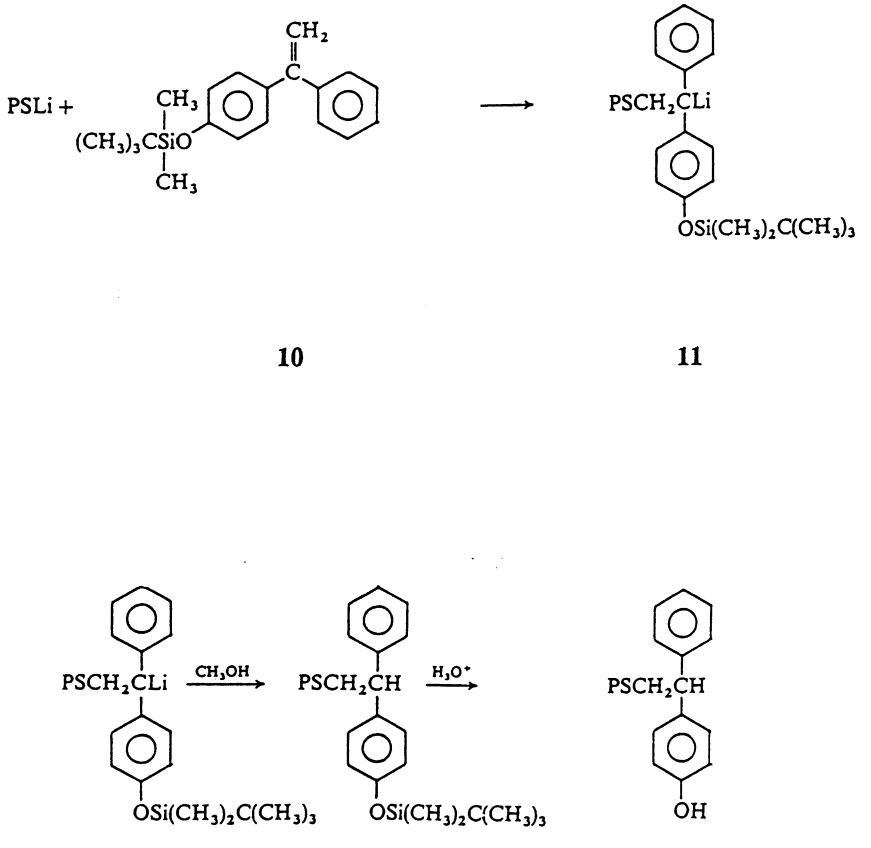
The synthesis procedure of PS-F4 is the same as that of PS-F2. It was carried out by dilithium initiator **7** instead of monolithium **2** [25]. The polymerization of poly(styryl)dilithium **8** is shown in Fig. 2. Then steps 3 and 4 in Fig. 1a were followed, the PS-F4 **9** was prepared as shown in Fig. 2.

2.4. Preparation of monophenol-functionalized polystyrene (PS-F1)

The synthesis procedure of PS-F1 is also the same as that for PS-F2. But the termination agent was changed from 1,1-bis(4-*t*-butyldimethylsiloxyphenyl)ethylene **1** to 1-[4-(*tert*-butyldimethylsiloxy)phenyl]-1-phenylethylene **10** [26]. The substituted diphenylalkyllithium adduct **11** was formed as shown in Fig. 3. Then after the Step 4 procedure shown in Fig. 1, PS-F1 **12** was prepared.

2.5. Blends

Binary blends of PS/PBT and PS-F/PBT were prepared in the Mini-Max injection molder (Model CS-183 MMX, Custom Scientific Instruments Inc.). The blending conditions including composition and temperature are listed in



10

11

12

Fig. 3. The procedure (Steps 10–12) of PS-F1 synthesis.

Table 2. Prior to blending, the pellets of PS and PBT were dried in a vacuum oven for 24 h at 60 and 110°C, respectively. After placing the polymer in the barrel of the Mini-Max injection molder, 1 wt% of TNBT or TPP was added by a syringe as a catalyst or stabilizer.

2.6. *Differential scanning calorimetry*

Differential scanning calorimetry (DSC) measurements of parent polymers and various blends were conducted by a DuPont 9900 thermal analyzer system at a heating rate of 20°C/min. The glass transition temperature (T_g), melting temperature (T_m), and enthalpy change of melting (ΔH) were determined.

Table 2
The compositions and temperatures for the blending process

Blends	Composition (wt%)	Temperature (°C)
PS/PBT	10/90, 25/75	250, 270
PS-F4/PBT	25/75	270
PS/PBT/PS-F4	10/90/5, 10/90/10	250, 270
PS/PBT/PS-F2	10/90/5, 10/90/10	250, 270
PS/PBT/PS-F1	10/90/5, 10/90/10	250, 270
PS/PBT/PS-F4	25/75/5, 25/75/10, 25/75/25	250, 270

2.7. *Scanning electron microscopy*

The phase morphology of the blends and parent polymers was observed by a scanning electron microscope (SEM, ISI model SX-40). Each fracture surface of the blends and parent polymers was prepared in liquid nitrogen and coated with gold–palladium alloy by a vacuum coating machine (Polaron E5400).

2.8. *Fourier transform infrared spectroscopy*

The chemical reaction in various polymer blends were investigated by FTIR (Perkin Elmer 16 PC). The samples of various blends were ground to powder and then immersed into TCE solvent for 24 h at room temperature. The solution was filtered to obtain the dissolved fraction of the blends. The thin film was cast by dropping the solution on the sodium chloride window, and then drying it in the hood at room temperature. The studies of spectroscopy were carried out in the wavelength range of 600–2000 cm^{-1} at a resolution of 4 cm^{-1}.

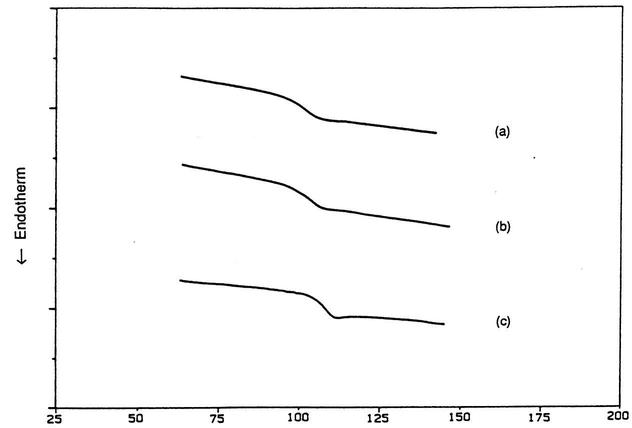


Fig. 4. DSC curves of: (a) PS, (b) PS/PS-F4 50/50, and (c) PS-F4.

2.9. Gel permeation chromatography

The molecular weight of the solute extracted from the TCE solution was determined by GPC (Waters Associates) by using the universal calibration curves. The solution was prepared by the same procedure as the sample for FTIR. It was precipitated in the excess methanol, and then dried. The dried solute was dissolved in THF.

2.10. Transmission electron microscopy

The phase morphology of the PS/PS-F4 50/50 blend was studied by a transmission electron microscope (TEM, JEOL JEM-1200EX II). The blend was dissolved in THF at room temperature for 24 h. The solution concentration was 0.3 wt%. The thin cast film was made on a mesh which was pre-coated with carbon. The magnification of 20K was used.

3. Results and discussion

We begin with describing two fundamental studies of the miscibility of PS with PS-Fs and the characterization of possible reaction between PS-F and PBT. We focused on studying the particular PS-F such as PS-F4, which has more functional groups than the other PS-Fs. The experiments were carried out at 270°C. We presume that the experiments at 270°C may promote the faster reaction than that at 250°C. Additionally, DSC, FTIR, GPC, SEM are used to determine the miscibility between PS-F4/PS and PS-F4/PBT.

3.1. Thermal properties of binary blends

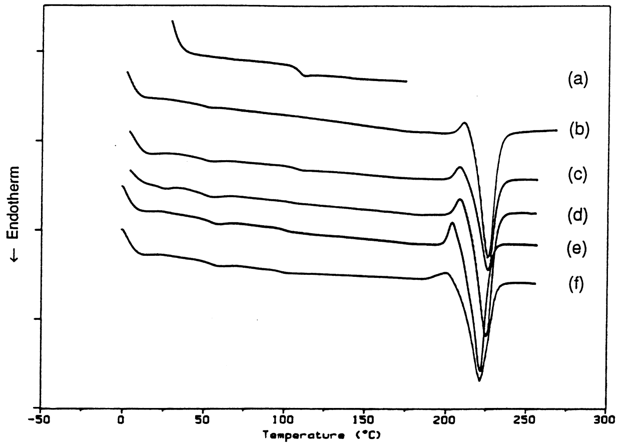


Fig. 5. DSC curves of PS-F4/PBT 25/75 blends prepared at 270°C: (a) PS-F4, (b) PBT, (c) 10 min, (d) 10 min with 1% TNBT, (e) 60 min, (f) 60 min with 1% TNBT.

The DSC curves of neat PS, neat PS-F4 and PS/PS-F4 50/50 blend at 270°C are shown in Fig. 4. The T_gs of PS and PS-F4 appear at 101.8 and 108.7°C, respectively. The PS/PS-F4 50/50 blend shows only one T_g at 104°C in Fig. 4. This shift of T_g of PS/PS-F blend suggests the possible miscibility of PS with PS-F4, which corresponds to the additivity rule of mixture.

Figs. 5 and 6 show the DSC curves of PS-F4/PBT 25/75 and 50/50 blends prepared at 270°C with and without TNBT as well as thermal treatments. The blend prepared with 10 min thermal treatment did not show any change in the T_g or T_m positions. However, in the blends of PS/PBT with TNBT and 10 min thermal treatment, their T_g and T_m positions exhibit a slight shift toward lower temperature. Furthermore, for the blends with long thermal treatment, i.e. 60 min, both of T_g and T_m positions demonstrate significant shifts. In particular, the shifts of T_g and T_m of the blends with TNBT and 60 min thermal treatment are most significant among the blends. This result suggests that the reaction-induced miscibility may occur in the blends prepared even for a short thermal treatment period. We speculate that TNBT promotes the reaction between PS-F4/PBT and thus results in the miscibility between PS-F4 and PBT.

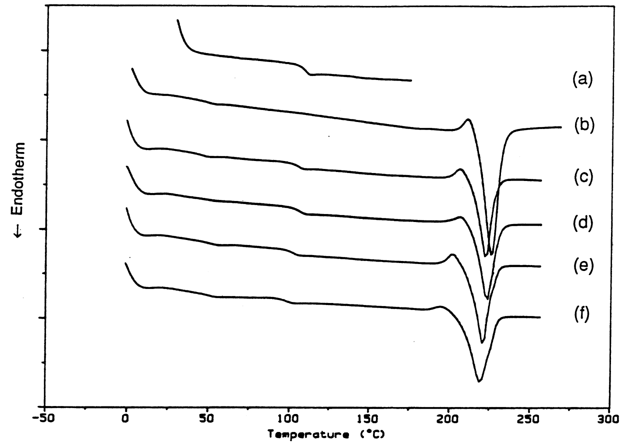


Fig. 6. DSC curves of PS-F4/PBT 50/50 blends prepared at 270°C: (a) PS-F4, (b) PBT, (c) 10 min, (d) 10 min with 1% TNBT, (e) 60 min, (f) 60 min with 1% TNBT.

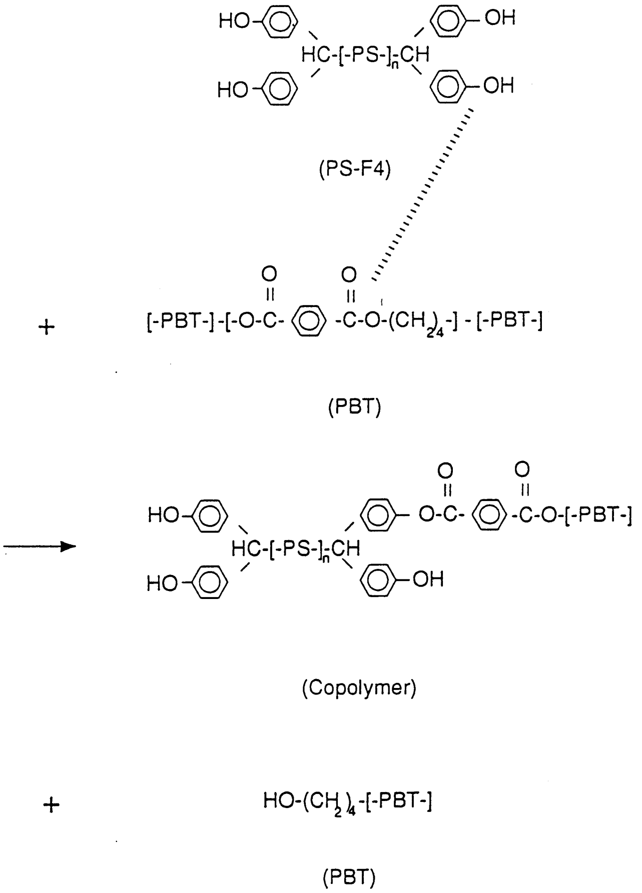


Fig. 7. The mechanism of alcoholysis reaction in PS/PBT blends.

The reaction between PS-F4/PBT might be associated with the alcoholysis (Fig. 7). It is a kind of transesterification, between the hydroxyl (proton donor) in the PS-F4 and carbonyl (proton acceptor) in the PBT [27–30]. The possible mechanism of alcoholysis reaction between PS-F4 and PBT as shown in Fig. 8 is similar to the reaction suggested by Robeson [27] and Mondragon [30] for the phenoxy/PBT and phenoxy/PC blends.

The changes in T_gs of the PS component, T_ms and ΔH data of the PBT component in PS-F4 25/75, 50/50 and 75/25 blends prepared at 270°C for 60 min thermal treatment with 1% TNBT as a function of the content of PS-F4 are shown in Fig. 8a and b. The T_ms decrease from 226.2 to 217.9°C with increasing the content of PS-F4 as seen in Fig. 9a. On the other hand, the T_g of the PS component decreases from 108.7 to 98.3°C with increasing the content of PS-F4 as seen in Fig. 8b. Furthermore, the heat of fusion of PBT phase exhibits the upper bound deviation from the linear additivity of the heat of fusion as shown in Fig. 8c. The curve of ΔH shows a maximum at 75 wt% of PBT. The overall heat of fusion is above the straight line connecting the extreme points for the entire composition. Paul and Altamirano [31] and Nishi et al. [32] reported that the heat of fusion of the partially miscible blends of amorphous and crystalline polymers were decreased, i.e. the value of heat of fusion will be below the straight line. They suggested that mobility of the crystalline polymer was restricted by the other amorphous material, resulting in lower crystallinity of the blends of PVF_2 and PMMA. Roberson and Furtek [27] and Paul coworkers [33] also reported the similar results of phenoxy/PBT blend and PC/PBT blend.

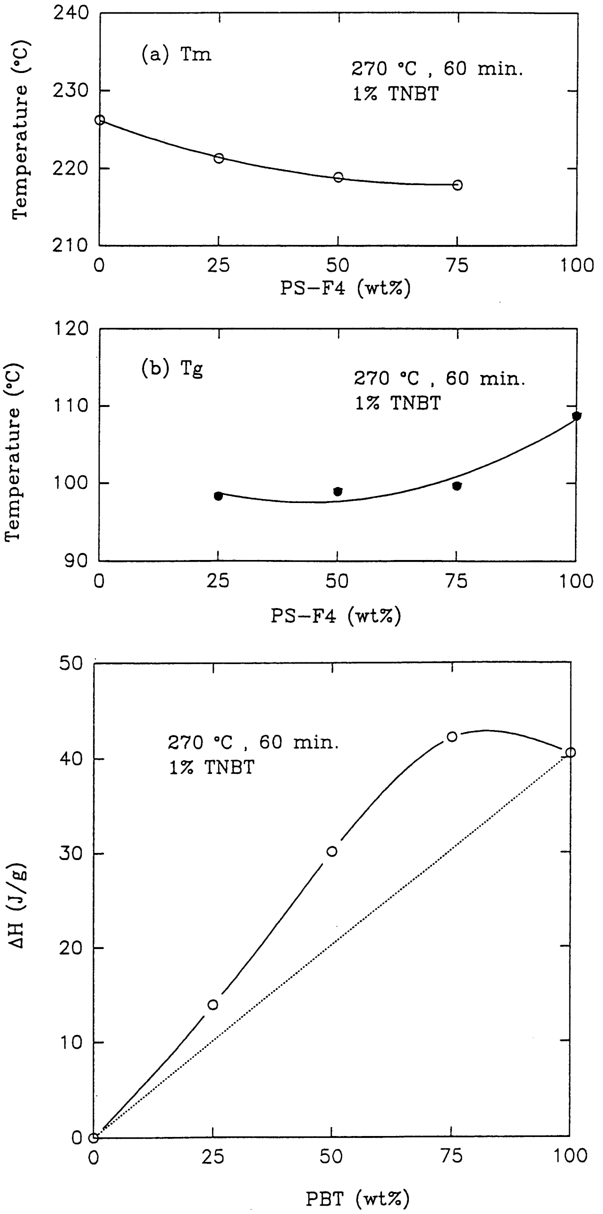


Fig. 8. The T_ms (a), T_gs (b) and the heat of fusion of PS-F4/PBT blends with 1% TNBT as a function of PS-F4 and PBT contents. (c) The heat of fusion of PS-F4/PBT blends with 1% TNBT as a function of PBT content.

Based on these DSC results, we surmise that the blends of PS-F4/PBT become miscible due to the long heat treatment period with 1% TNBT at 270°C. However, this long thermal treatment at 270°C is detrimental to the mechanical properties associated with excess thermal degradation as we describe later. Therefore, our efforts were made to induce fast reaction in PS-F4/PBT without the excess degradation.

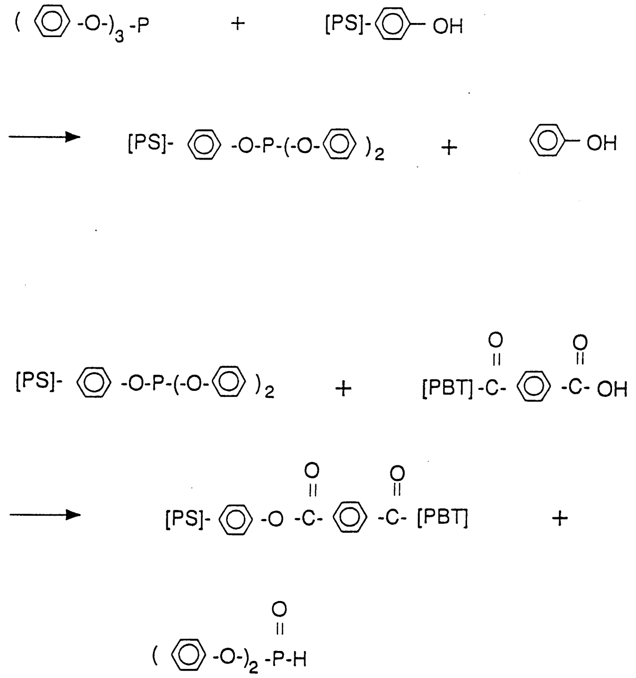


Fig. 9. Mechanism of coupling reaction induced by TPP in PBT.

Aharoni et al. [34] suggested the chain extension mechanism of PET with TPP. Similarly, we conclude that the addition of TPP will act as a stabilizer that prevents the excess degradation. In addition to that, it will promote the reaction between PS-F4 and PBT. The possible mechanism of coupling reaction induced by TPP between PS-F4 and PBT is shown in Fig. 9. In the first step, TPP reacts with the hydroxyl end group in PS-F4. Secondly, the alkyldiphenyl phosphite reacts with the carboxylic chain end of PBT. Then PS–PBT block copolymer is formed from the coupling reaction in addition to the alcoholysis reaction proposed in Fig. 7.

The effects of TPP on the thermal properties of PS-F4/PBT blends were carried out by using DSC at 270°C with 10 min thermal treatment with and without 1% TPP. The thermal treatment was limited to 10 min in order to minimize the thermal degradation. The significant shifts of T_g and T_m in PS-F4/PBT blends with 1 wt% TPP were observed in comparison to those without TPP. Although the shifts are less significant than those with long thermal treatment and TNBT, the T_g moves from 108.7 to 102.9°C and the T_m moves from 226.2 to 219.4°C by adding TPP. Fig. 10a–c shows the T_gs, T_ms and ΔH as a function of PS-F4 and PBT contents. The blends without the addition of TPP exhibit the scattered values of their T_gs in comparison with the monotonic change of T_ms from 226.2 to 220°C. The heat of fusion of the PBT component in the blends is still higher than the straight line connecting the extreme points; but it demonstrates a smaller deviation from the straight line than that of blends with 1% TNBT shown in Fig. 10c.

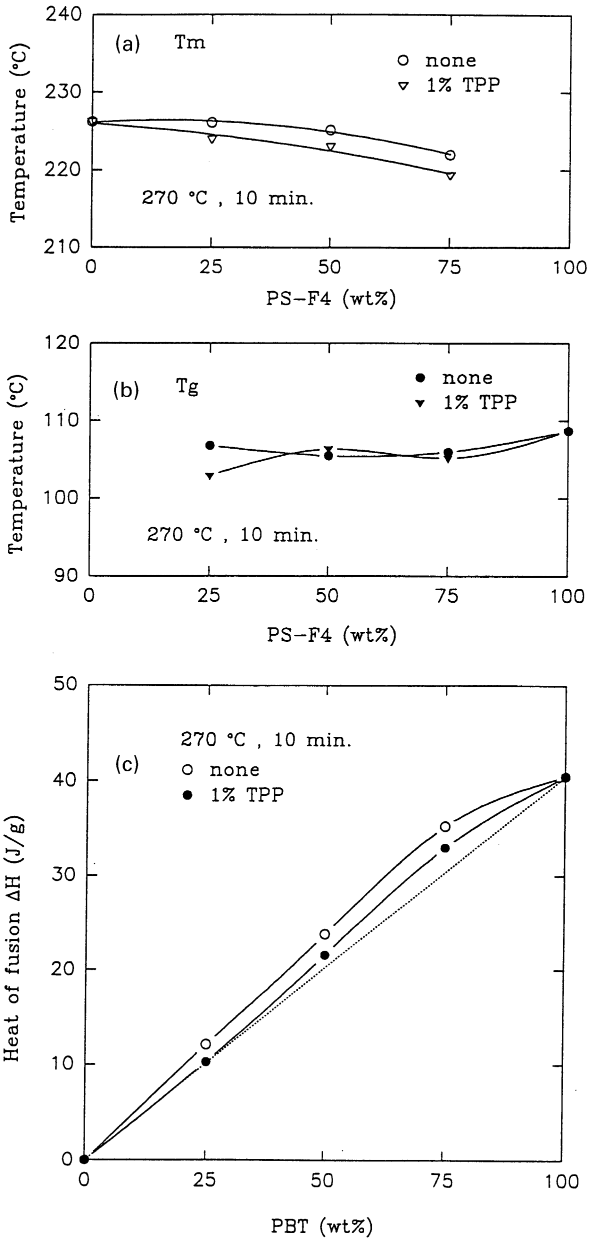


Fig. 10. The T_ms (a) and T_gs (b) and the heat of fusion of PS-F4/PBT blends with 1% TPP as a function of PS-F4 and PBT contents. (c) The heat of fusion of PS-F4/PBT blends with 1% TPP as a function of PBT content.

Similar DSC studies were conducted to confirm the similar effect of addition of TPP on PS/PBT blends prepared at 270°C for 10 min thermal treatment with and without TPP. When the PS content increases to 75 wt%, the T_m of PBT component decreases from 226.2 to 222.4°C. Similarly, Fig. 11a–c exhibits the plots of T_g, T_m and ΔH as a function of PS and PBT contents. In Fig. 11a and b, the T_gs and T_ms of PS/PBT blends at 270°C for 10 min mixing time exhibit a little change. For the PS/PBT blends with 1% TPP, the T_ms demonstrate a little shift from 226.2 to 222.4°C with increasing the component of PBT. These results lead us to conclude that the addition of TPP may promote the miscibility of both PS-F4/PBT and PS/PBT blends. The heat of fusion curve (Fig. 11c) demonstrates a small deviation from

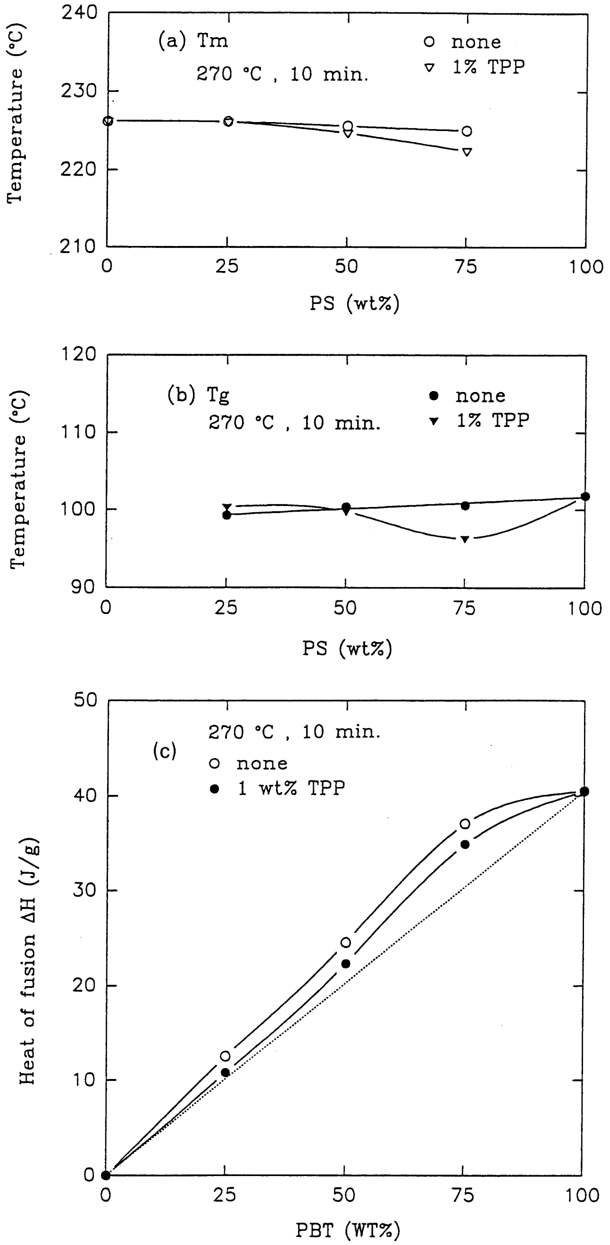


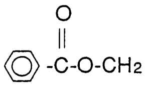
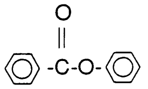
Fig. 11. The T_ms (a) and T_gs (b) and the heat of fusion of PS/PBT blends as a function of PS contents. (c) The heat of fusion of PS/PBT blends as a function of PBT content.

the straight line connecting the extreme points. The deviation is slightly larger than that of PS-F4/PBT blends in Fig. 10c; but much less significant than that of the PS-F/PBT blends with 1% TNBT (Fig. 8c).

3.2. Fourier transform infrared spectroscopy

The FTIR spectra of various blends were studied to find out the reaction between PS-F4 and PBT blend. All the samples of FTIR were extracted from TCE solvent that is a good solvent for PS but not for PBT. If the copolymerization reaction takes place with degradation during blending and thermal treatment, a small amount of copolymerized PBT or degraded PBT may dissolve in the TCE solvent and the characteristic peaks of PBT will appear in the FTIR spectra. Table 3 shows the characteristic infrared absorption wave number of ester and benzene group during PS-F4/PBT reaction. PBT is identified with two characteristic bands at 1720 and 730 cm^{-1}. The former band indicates the C=O stretching of the aliphatic ester in PBT, while the latter band indicates the carbon–hydrogen bending of substituted benzene in PBT. PS-F4 is characterized by the 700 cm^{-1} band corresponding to the carbon–hydrogen bending of non-substituted benzene in PS-F4 and the 1604 cm^{-1} band corresponding to the carbon–carbon stretching of benzene in PS-F4. If the alcoholysis takes place during blending as suggested in Fig. 7, new infrared absorption peaks at 1070 and 1740 cm^{-1} will appear. The peaks at 1070 and 1740 cm^{-1} are characteristic of an aromatic ester, which indicates the copolymer formed from the reaction of PS-F4 and PBT.

Table 3
The characteristic infrared absorption wave numbers of the ester and benzene groups (Ref. [35])

Groups	Wave number (cm^{-1})
	1720^a
	1740^a 1070^b
	1604^c 700^d 730^e

As shown in Fig. 12, the C=O stretching band (1740 cm^{-1}) appeared as a new peak in the blend of PS-F4/PBT 50/50 with the reaction time of 60 min and 1% TNBT catalyst. Therefore, the spectra in Fig. 12f exhibits the reaction associated with the in situ copolymerization by alcoholysis. It also shows that the reaction rate between PS-F4/PBT is very slow because the peak appears only after the 60 min treatment. In comparison to the spectra of PS-F4/PBT 25/75, the peak intensity at 1740 cm^{-1} in the spectra of PS-F4/PBT 50/50 is more significant than that of PS-F4/PBT 50/50. However, it is difficult to distinguish the reaction from the peak position or intensity at 1070 cm^{-1} because this peak overlaps with the peak of para-distributed phenyl coupled to the oxygen atom of PS-F4. Thus, the estimation of the extent of reaction was not successful because the intensity ratio of A_{1070}/A_{730} would indicate the content of ester change [35–38]. Instead, the reaction content is determined by using the intensity ratios of A_{1720}/A_{1604} of various PS/PBT and PS-F4/PBT blends, which the 1604 cm^{-1} band corresponds to the PS-F concentration and

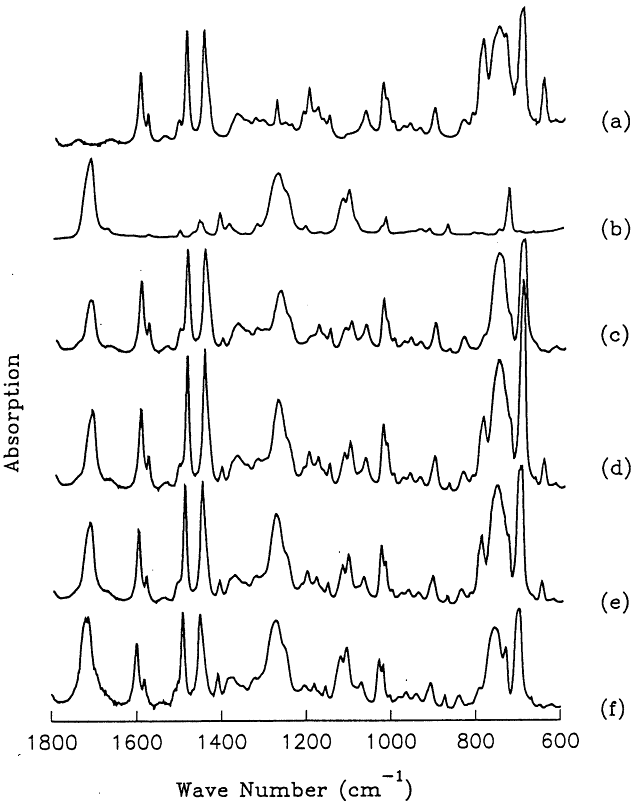


Fig. 12. FTIR spectra of PS-F4/PBT 50/50 blends prepared at 270°C for various treatments: (a) PS-F4, (b) PBT, (c) 10 min, (d) 10 min with 1% TNBT, (e) 60 min, (f) 60 min with 1% TNBT.

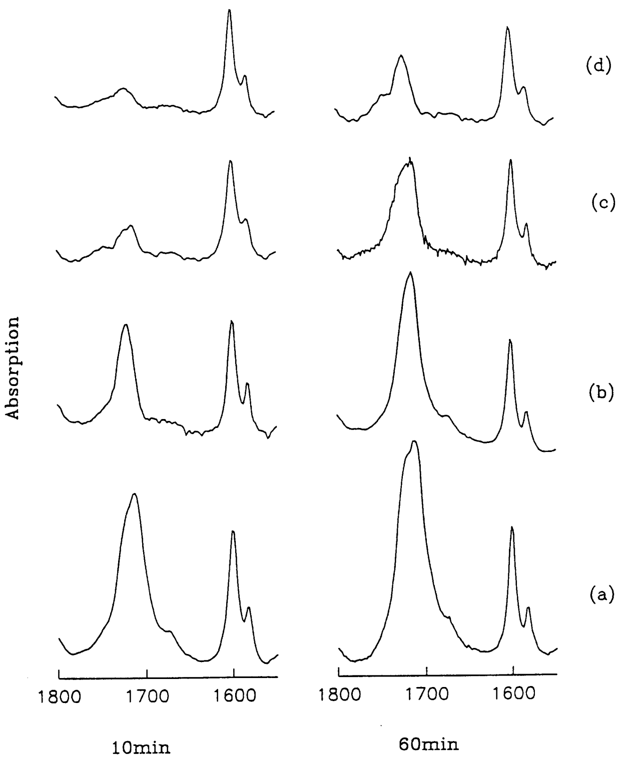


Fig. 13. FTIR spectra of blends prepared at 270°C with different thermal treatments and additives: (a) PS-F4/PBT 25/75 with 1% TNBT; (b) PS-F4/PBT; (c) PS-F4/PBT 25/75 with 1% TPP; (d) PS/PBT 25/75 with 1% TPP.

the 1720 cm^{-1} band corresponds to the PBT concentration in the extracted solution.

Fig. 13 shows the absorption peaks at 1720 cm^{-1} band and 1604 cm^{-1} band for various PS-F4/PBT and PS/PBT blends prepared at 270°C for 10 and 60 min in the extracted portion of TCE solution. In the curve a, the intensity of 1720 cm^{-1} band is stronger than 1604 cm^{-1} band. We speculate that both copolymerization and degradation of PBT take place, and resulting in more intense carbonyl stretching peak. This phenomenon is significant especially in thermal treatment for 60 min. In the spectrum c, the intensity of 1720 cm^{-1} band drastically decreased. It indicates that the stabilizer TPP prevents the thermal degradation of PBT during blending. However, when the thermal treatment time is increased, the intensity of 1720 cm^{-1} band still shows a significant increase. The PS/PBT blend with stabilizer TPP (the spectrum d) shows less 1720 cm^{-1} band intensity than any other blends. The addition of TPP does not show any effect to promote the copolymerization between PS and PBT. Furthermore, it stabilizes PBT. Fig. 14 shows the various intensity ratios of A_{1720}/A_{1604} by varying thermal treatment periods. The intensity of the spectrum d indicates the contribution of carbonyl stretching originated from the thermal degradation of PBT. The intensity difference between the spectra c and d may be associated with the copolymerization of PS-F4 and PBT since both blends are stabilized by TPP.

3.3. Gel permeation chromatography

The extracted fraction of the blends in the TCE solution is prepared for the GPC measurement. In general, PBT is unable to be dissolved in the TCE solvent, unless the short segments of PBT are formed by the thermal degradation. As shown in the GPC curves of PS-F4/PBT and PS/PBT blends (Fig. 15), one small shoulder in the higher range of molecular weight at an elution volume of 38 ml appears. It is especially significant in the blends prepared with 60 min thermal treatment and TNBT catalyst. This indicates that the shoulder may be originated from the extracted part of PBT that is dissolved in the TCE solvent due to the degradation or copolymerization. At an elution volume of 43 ml, there also appears a small shoulder in the range of the low molecular weight. It originates from the molecules of low molecular weight PS-F4, which yields from the termination of the initiator by the impurities in the anionic polymerization process. The results of GPC measurements agree with the explanation of the FTIR results.

3.4. Phase morphology

Fig. 16 shows the SEM micrographs of fracture surface of

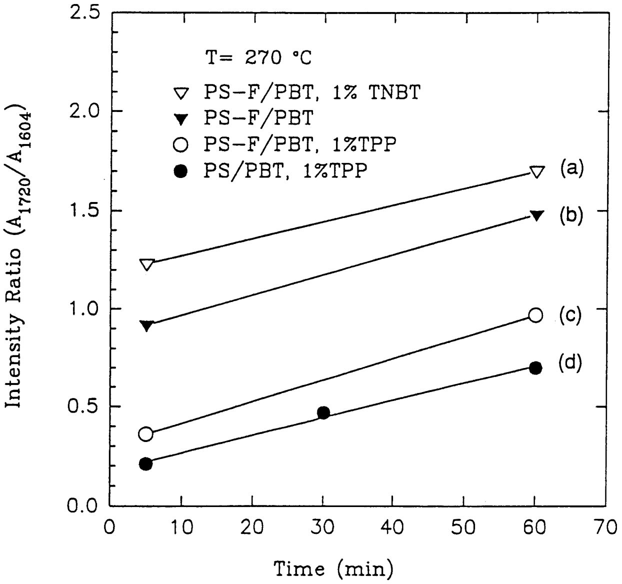


Fig. 14. Intensity ratio of absorption in FTIR spectra for various blends as a function of thermal treatment.

PS/PBT 25/75 and PS-F4/PBT 25/75 blends with 1% TNBT prepared by Mini-Max molder at 270°C. As described in the previous section, the fracture surfaces were prepared in liquid nitrogen. The dispersed phase of PS and PS-F4 in the matrix of PBT were observed in Fig. 16a and b. The size of the PS-F4 phase dispersed in the PBT matrix is much larger than that of PS dispersed in the PBT matrix. As reported in our paper [39], the shear viscosity of PBT blended with 1%TNBT became much lower than that of PBT without TNBT and there was very little effect of 1% TNBT on the viscosity of PS. Therefore, the reduction of viscosity of the matrix attributed to the larger dispersed phase. After the longer thermal treatment for 60 min with the TNBT catalyst, the dispersed phase of PS-F4 reduced significantly as shown in Fig. 16c. This demonstrates that the copolymerization and compatibilization between PS-F4 and PBT may take place by this long thermal treatment with the catalyst. Fig. 16d shows the SEM micrograph of the fractured surface of the PS-F4/PBT blend with 1% TPP. In comparison with the size of the dispersed phase shown in Fig. 16b, the size of dispersed phase of PS-F4 drastically reduced by adding TPP with the 10 min thermal treatment. Furthermore, Fig. 16d shows an interesting feature in the fracture surface of PS/PBT 25/75 blend with 1% TPP, in which all the cracks seem to propagate through the dispersed particles. It suggests that the adhesion between the dispersed phase and matrix became better, thus resulting in the crack through the dispersed particle.

The SEM micrographs of the fracture surface of PS-F4/PS 50/50 blend at 270°C for 10 min shows only smooth surface with the crack hesitation lines. In addition to this observation, the thin cast film of the PS/PS-F4 50/50 blend at room temperature was characterized by a transmission electron microscope under 20K magnification. We did not observe the heterogeneous phase morphology in this blend. This observation is consistent with the results of single T_g in the DSC results of the PS-F4/PS 50/50 (Fig. 4b). Thus, we conclude that PS-F4 may be miscible with PS.

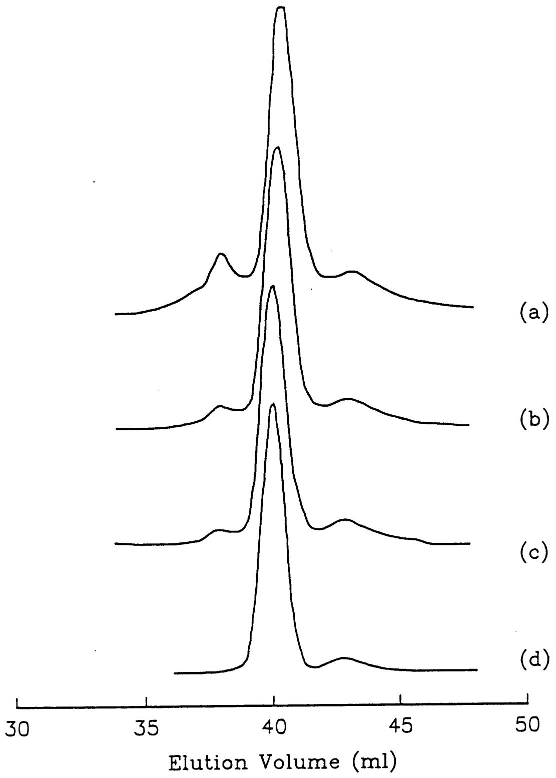


Fig. 15. GPC curves of PS-F4/PBT 25/75 blends prepared at 270°C for various treatments: (a) 60 min with 1% TNBT, (b) 60 min, (c) 10 min with 1% TNBT, (d) PS-F4.

4. Conclusions

Three PS-Fs were synthesized by anionic polymerization. PS-F4, which has the most functional groups among them, was used to investigate the miscibility and copolymerization with PS and PBT.

The results of FTIR, GPC, and DSC demonstrate that the reaction occurs between PS-F4 and PBT, but it is not significant until the samples are subjected to the long thermal treatment (over 60 min). We presume that the slow alcoholysis reaction may occur.

The shift of glass transition temperature and the melting temperature depression in DSC thermograms suggest that the addition of 1% TNBT into the blends of PS-F4/PBT enhances the miscibility of PS-F4 and PBT. It is believed that the alcoholysis reaction that is catalyzed by TNBT takes place between PS-F4 and PBT.

The heat of fusion of PS-F4/PBT blends in the DSC thermograms exhibits higher value than the straight line connecting the extreme points.

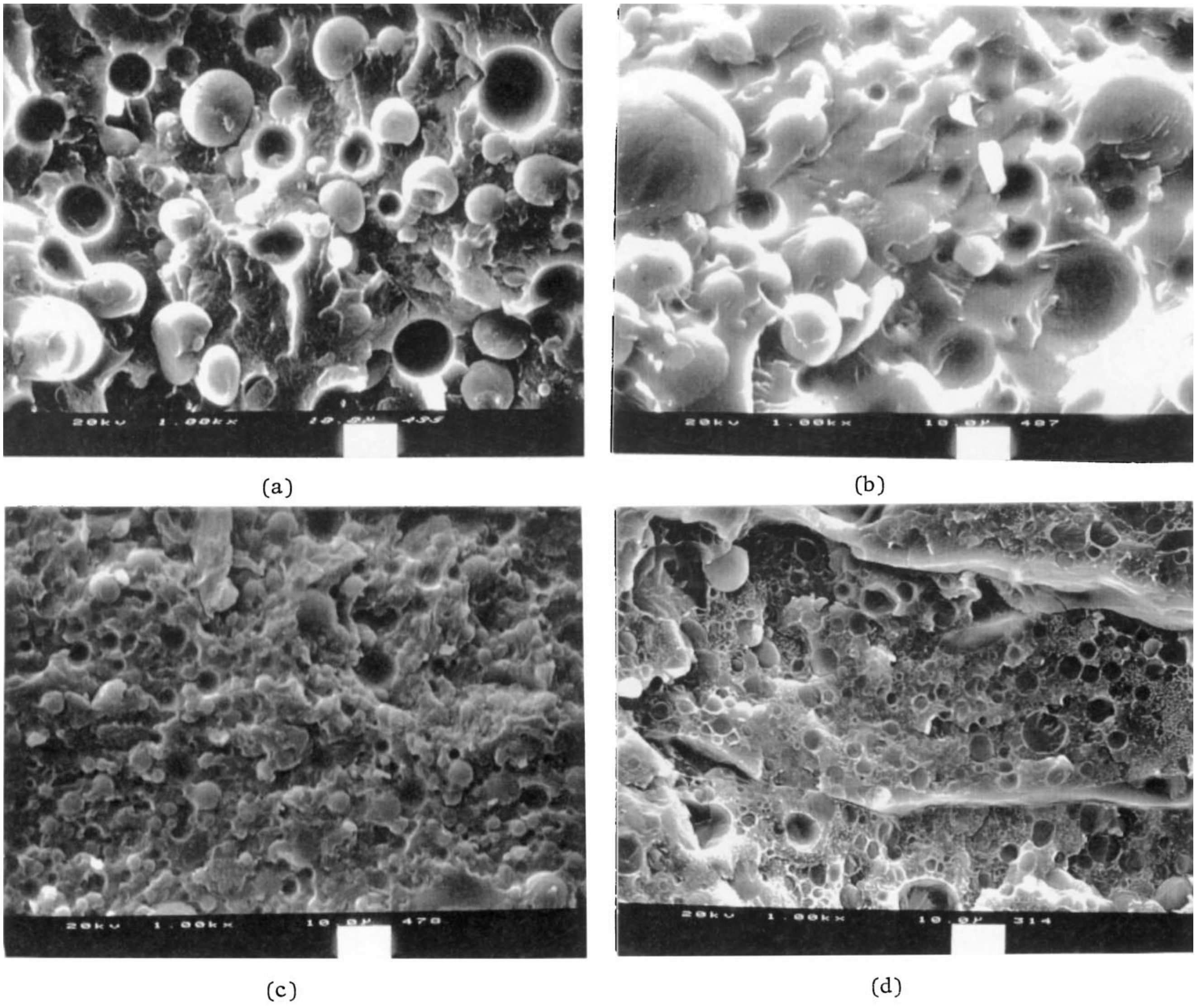


Fig. 16. SEM micrographs of various blends prepared at 270°C with different mixing time and additives: (a) PS/PBT 25/75 for 10 min mixing; (b) PS-F4/PBT 25/75 for 10 min mixing with 1% TNBT; (c) PS-F4/PBT 25/75 for 60 min mixing with 1% TNBT; (d) PS-F4/PBT 25/75 for 10 min mixing with 1% TPP.

The PS-F4/PBT blends with 1% TPP for 10 min thermal treatment period at 270°C show the significant melting temperature depression in comparison with those blends without TPP. It suggests that the stabilizer TPP not only prevents excess thermal degradation of PBT but also promotes the reaction between PS-F4 and PBT by coupling reaction.

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