

# Compatibilizing Efficiency of Copolymer Precursors for Immiscible Polymer Blends

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**ABSTRACT:** An anhydride-terminated polystyrene (PS-*b*-Anh) as a block copolymer precursor and a copolymer (PS-*co*-TMI) of styrene (St) and 3-isopropenyl- $\alpha,\alpha$ -dimethylbenzene isocyanate (TMI) as a graft copolymer precursor are chosen to investigate the effect of the type of the copolymer precursor on its compatibilizing and stabilizing efficiency for polymer blends. Results show that during the melt blending of the PS and PA6, the addition of PS-*b*-Anh dramatically decreases the size of the dispersed phase domains, irrespective of its molecular weight. This indicates that a diblock copolymer PS-block-PA6 (PS-*b*-PA6) is

formed by a reaction between the terminal anhydride moiety of the PS-*b*-Anh and the terminal amine group of the PA6. When PS/PA6 (30/70) blends are annealed at 230°C for 15 min, their morphologies are much more stable in the presence of the PS-*b*-Anh block copolymer precursor than in the presence of the PS-*co*-TMI graft copolymer precursor. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3392–3398, 2012

**Key words:** *in situ* compatibilization; reactive extrusion; polymer blends

## INTRODUCTION

Polymer blending provides a practice way to produce new polymer materials with specific end-use properties without creating new molecules. However, the vast majority of polymers are mutually immiscible and thermodynamically unstable, which leads to phase separation and yields materials with poor mechanical properties.<sup>1–3</sup> To address this challenge, various kinds of copolymers have been used as compatibilizers in blends to reduce the interfacial tension, promote the dispersion of one phase in another and stabilize resulting morphology.<sup>4–6</sup> Especially, block and graft copolymers whose segments are chemically identical to or have affinity with the polymer components as compatibilizers have gained significant research interest in recent decades. Their efficiencies as compatibilizers are believed to depend on their molecular architecture, composition, and molecular

weight.<sup>7–10</sup> Some authors concluded that the compatibilizing efficiency of tapered diblock copolymers is better than that of the conventional diblock and triblock copolymers.<sup>11,12</sup> Our recent studies have shown that for graft copolymers with the same backbone and the same number of grafts per backbone, the longer the grafts, the higher their compatibilizing and stabilizing efficiency; for a given backbone/graft mass ratio, the longer the grafts and concomitantly the smaller the number of grafts per backbone, the higher the compatibilizing and stabilizing efficiency of the graft copolymer.<sup>1,6,9</sup> These studies are mainly related to the compatibilizing efficiency of premade copolymers. In fact, the prevailing compatibilization method is the so-called *in situ* (or reactive) compatibilization. It consists in reacting two reactive polymers to form a copolymer as compatibilizer. Such reactive polymers are called copolymer precursors or compatibilizer precursors. Formed *in situ* at the interfaces, such a copolymer is believed to have higher compatibilizing efficiency than a premade one.<sup>13–16</sup>

This work aims to compare the compatibilizing efficiency of the molecular architecture of the copolymer precursors for immiscible polymer blends. The blend system is composed of polystyrene (PS) and polyamide 6 (PA6). It is chosen because it facilitates the study. It may also have potential commercial interest.<sup>17</sup> The anhydride terminated polystyrene (PS-*b*-Anh) and copolymer (PS-*co*-TMI) of styrene (St) and 3-isopropenyl- $\alpha,\alpha$ -dimethylbenzene isocyanate (TMI) are used as copolymer precursors. The differences

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**TABLE I**  
Selected Characteristics of the PS, PA6, and PS-co-TMI Used in This Work

Materials	$M_n^a$ (kg/mol)	$M_w^a$ (kg/mol)	Supplier
PS	101.3	228.8	Yangzi-BASF Styrenics, Nanjing, China
PA6	19.4	49.4	UBE Nylon, Thailand
PS-co-TMI <sup>b</sup>	39.8	140.4	Our laboratory

<sup>a</sup> Molar masses measured by SEC using PS standards for the calibration and THF as the eluent. The PA6 was first *N*-trifluoroacetylated before the SEC measurement<sup>1</sup>.

<sup>b</sup> The TMI content in the PS-co-TMI was 8.0 wt %.

between them lie in that the former bears a terminal anhydride group and the latter isocyanate moieties along the PS backbone. Thus the former leads to the formation of a block copolymer and the latter a graft copolymer.

## EXPERIMENTAL

### Materials

St, maleic anhydride (MAH), 4-methylphthalic anhydride, *N*-bromosuccinimide (NBS), and TMI were purchased from Aldrich. St and tetrahydrofuran (THF) were purified over an aluminum oxide column. NBS was purified by recrystallization in ethanol. The formula molar mass and the boiling temperature of TMI are 201 g/mol and 270°C/760 mmHg, respectively. Benzoyl peroxide (BPO) was used as the free radical initiator. It was purified by dissolution in chloroform, precipitation in methanol and was then dried in a vacuum oven at room temperature. Toluene used as the solvent for the copolymerization was purified by boiling in the presence of anhydrous calcium oxide.

Table I shows selected characteristics of the PS and PA6. The PS-co-TMI was synthesized in the laboratory by copolymerization of St and TMI in toluene using BPO as a free radical initiator. The detailed procedure of the synthesis of PS-co-TMI and its applications can be found elsewhere.<sup>18–25</sup>

### Synthesis and characterization of anhydride-terminated polystyrene (PS-*b*-Anh) by ATRP

4-methylphthalic anhydride (5.0 g, 30 mmol) was dissolved in carbon tetrachloride (CCl<sub>4</sub>; 50 mL). NBS (5.5 g, 30 mmol) and BPO (0.31 g) were added later.<sup>26</sup> After the reaction mixture was refluxed at 90°C for 2 h, the mixture was cooled in an ice bath and then the succinimide was filtered off. Lastly, the organic phase was evaporated under vacuum to remove CCl<sub>4</sub> yielding yellowish oil. The resulting

product was 4-bromomethylphthalic anhydride, which was subsequently used as the ATRP initiator.

CuCl (99.5 mg, 1 mmol), Cu (64 mg, 1 mmol), 2,2-bipyridyl (dpy, 468 mg, 3 mmol), and 4-bromomethylphthalic anhydride (241 mg, 1 mmol) were charged to a 50 mL reactor.<sup>27</sup> Three freeze-thaw cycles were repeated to remove oxygen. St was then transferred to the reactor via an injector and was stirred for 15 min at room temperature. The reactor was then placed in a preheated oil bath at 100°C for 24 h. Figure 1 shows the reaction mechanism. At the end of the polymerization, the mixture was dissolved in THF and stirred with cation exchange resin. The solution was concentrated and PS-*b*-Anh precipitated in cold absolute methanol.

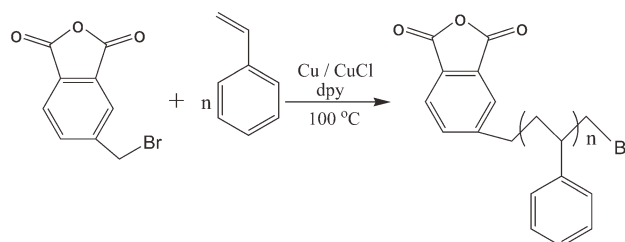
The <sup>1</sup>H nuclear magnetic resonance (NMR) of type Brucker Avance DMX-400 was used to characterize polymer products at room temperature. Chloroform-D was used as the solvent.

Size exclusion chromatography (SEC) was used to measure the molecular weight and molecular weight distribution of polymer products. The SEC measurement was done with an apparatus of type Waters 1525/2414 equipped with a refractometer. THF was the mobile phase and PS standards were used for the calibration.

The glass transition temperatures of the purified PS-*b*-Anh copolymer precursors were measured using a differential scanning calorimeter (DSC) of type DSC7 Perkin-Elmer under nitrogen atmosphere. Samples were subjected to the following thermal cycle. They were heated from 50 to 200°C at 10°C/min and maintained at 200°C for 2 min to erase their previous thermal history. They were then cooled down to 50°C at 10°C/min. Finally, they were heated up again to 200°C at 10°C/min.

### Blend preparation

Polymer blends were prepared by mixing the components in a Brabender mixer equipped with a mixing chamber and two screws inside the mixing chamber. For the compatibilized blend systems, the content of the as-synthesized copolymer precursor in the blends was 1, 3, or 6 wt % with respect to the PS/PA6 blends. Prior to the blending, the PS, PA6,



**Figure 1** Reaction route for the synthesis of PS-*b*-Anh.

**TABLE II**  
Molar Mass and Heating Behavior of PS-*b*-Anh Block Reactive Compatibilizers

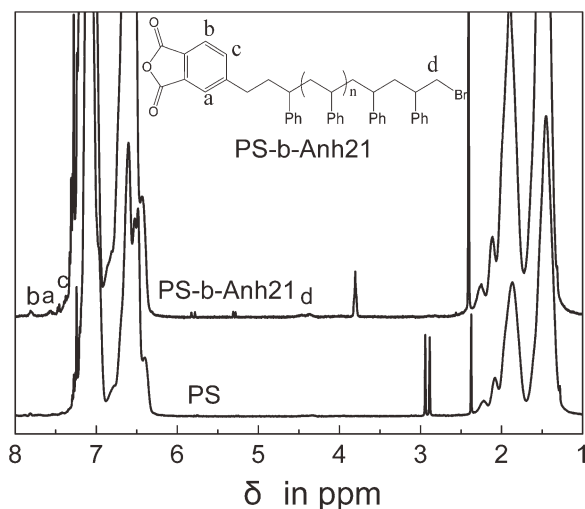
Experimental designation	$M_n$ (kg/mol)	$M_w$ (kg/mol)	$T_g$ (°C)
PS- <i>b</i> -Anh12	11.8	27.5	71.6
PS- <i>b</i> -Anh18	17.6	37.9	84.5
PS- <i>b</i> -Anh21	20.5	34.8	95.3
PS- <i>b</i> -Anh57	56.6	94.8	96.1

and copolymer precursor were dried in a vacuum oven at 80°C for 12 h. The dried blend components were charged simultaneously to the mixing chamber and mixed at 100 rpm and 230°C for 10 min. Samples were taken from the mixing chamber and then quenched in liquid nitrogen to freeze-in their morphologies within 0.5 min.

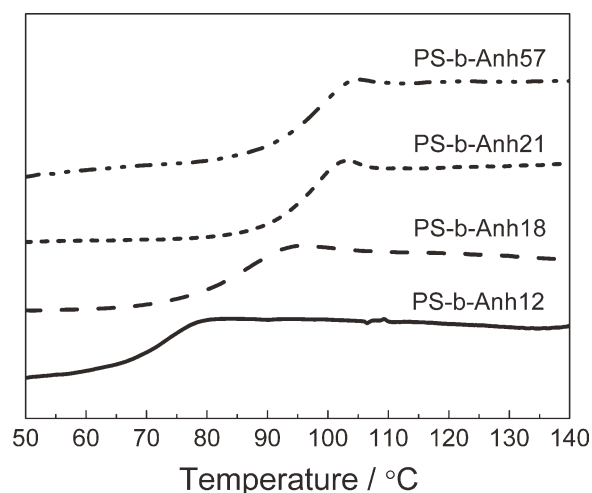
The resulting blend was extracted in HCl (6 mol/L) for 2 days to remove the PA6. Its insoluble fraction was then extracted in THF for 2 days to remove the PS. The extraction operation was repeated several times till the amount of the insoluble material did not decrease anymore. Finally, it was dried in a vacuum oven at 80°C for 12 h and assessed by  $^1\text{H}$  NMR with Chloroform- $D$  as the solvent. The residues were also characterized by DSC subjecting to the following thermal cycle. They were heated from 50 to 260°C at 10°C/min and maintained at 260°C for 2 min to erase their previous thermal history. They were then cooled down to 50°C at 10°C/min. Finally, they were heated up again to 260°C at 10°C/min.

### Quiescent annealing

Pieces of blend samples of about 20 mm thick were warped with coppery netting and then annealed in a



**Figure 2**  $^1\text{H}$  NMR spectra of the pure PS and PS-*b*-Anh21.



**Figure 3** DSC thermograms of PS-*b*-Anh.

silicon oil bath at 230°C. After various annealing times (from 5 to 15 min), they were taken out from the oil-bath and quenched immediately in liquid nitrogen to freeze-in the morphologies.

### Characterization of blend morphologies

A scanning electron microscope (SEM) of type ZEISS ULTRA55 was used to characterize the blend morphologies. Before the SEM observations, samples were first fractured in liquid nitrogen. The fractured surfaces were immersed in THF at room temperature for 2 days in order to remove the dispersed PS phase domains. They were dried in the vacuum oven at 80°C for 12 h and gold sputtered. The voltage for the SEM was 3.0 or 5.0 kV.

The diameter of the dispersed phase domains was determined using a semi-automatic image analysis method. It was characterized by a volume average particle diameter,  $d_v$ , defined as:

$$d_v = \frac{\sum n_i d_i^4}{\sum n_i d_i^3} \quad (1)$$

For each blend at least 500 particles were counted for statistically meaningful values of  $d_v$ .

## RESULTS AND DISCUSSION

### Characterization of PS-*b*-Anh

Four PS-*b*-Anh copolymer precursors are synthesized. Based on their number-average molar mass, they are denoted as PS-*b*-Anh12, PS-*b*-Anh18, PS-*b*-Anh21, and PS-*b*-Anh57, as shown in Table II. They correspond to a number-average molar mass of about 12, 18, 21, and 57 kg/mol, respectively. Figure 2 compares the  $^1\text{H}$  NMR spectra between the pure PS and PS-*b*-Anh21. The absorption peaks at 7.44

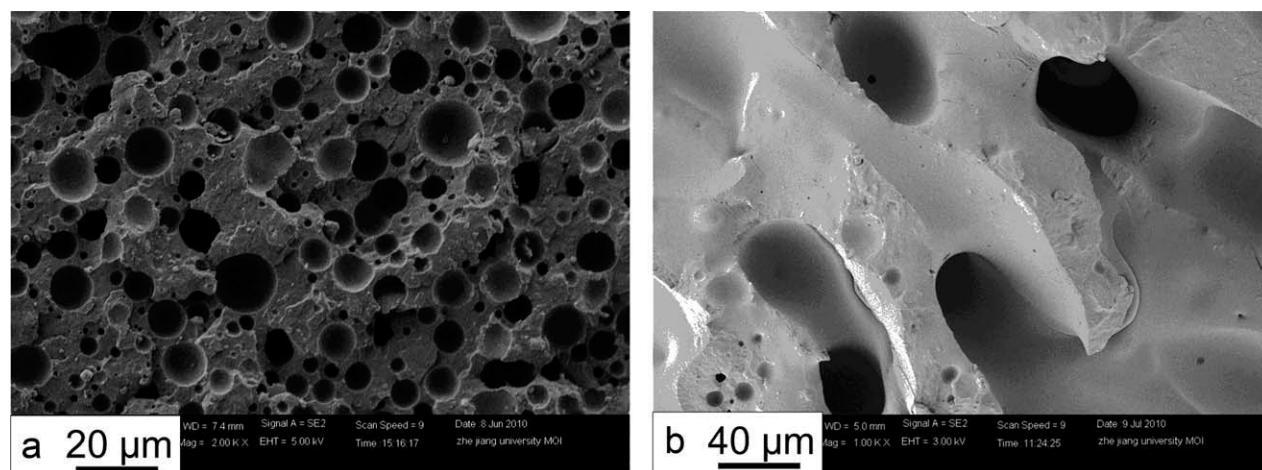


Figure 4 SEM micrograph of (a) PS/PA6 (30/70 by mass) and (b) PS/PA6 (50/50 by mass) blends.

and 7.52 ppm can be assigned to the phthalic anhydride moiety of the PS-*b*-Anh,<sup>26</sup> indicating that the anhydride group is indeed attached to the PS chain.

Figure 3 shows the DSC traces of the melting behavior of the four PS-*b*-Anh block copolymer precursors. It can be seen that  $T_g$  of the PS-*b*-Anh

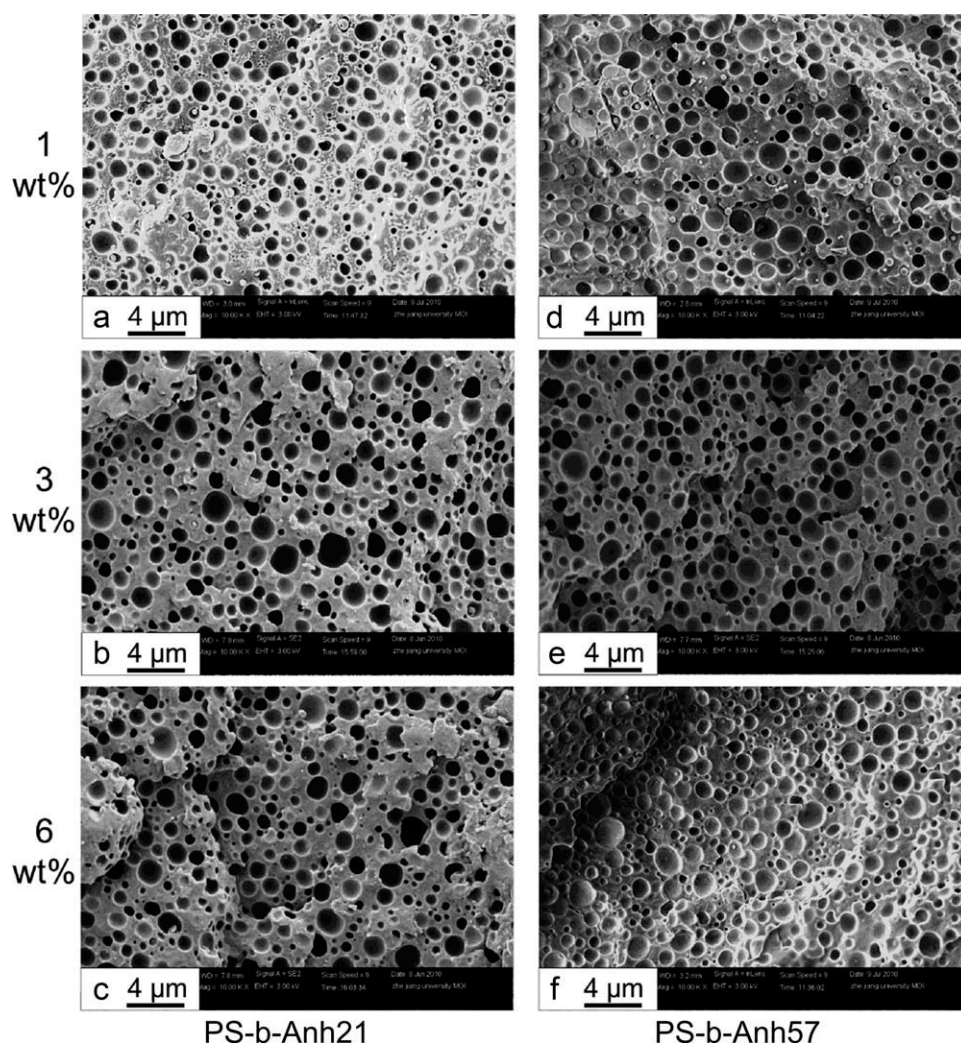
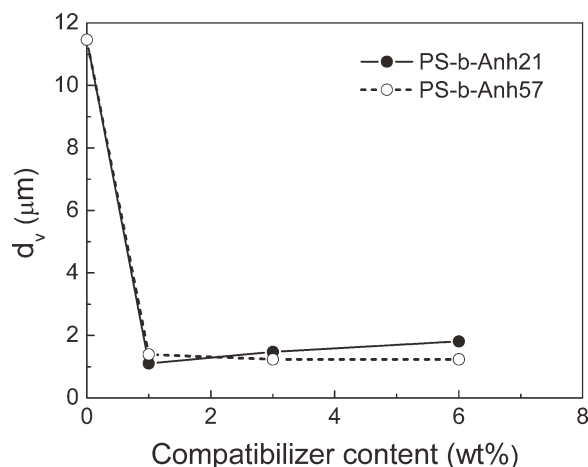


Figure 5 SEM micrographs of the PS/PA6(30/70 by mass) blend with various amounts of PS-*b*-Anh21 or PS-*b*-Anh57: (a) PS-*b*-Anh21 (1 wt %); (b) PS-*b*-Anh21 (3 wt %); (c) PS-*b*-Anh21 (6 wt %); (d) PS-*b*-Anh57 (1 wt %); (e) PS-*b*-Anh57 (3 wt %); (f) PS-*b*-Anh57 (6 wt %).



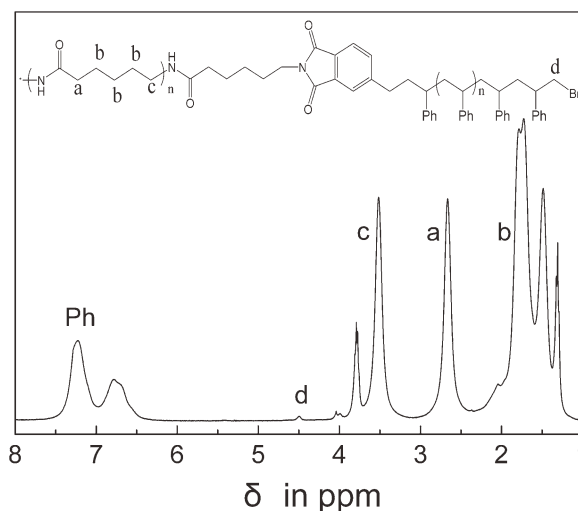
**Figure 6** Diameter of the PS dispersed phase domains ( $d_v$ ) vs. the content of the PS-*b*-Anh copolymer precursor in the PS/PA6/PS-*b*-Anh (30/70/ $x$ ) blend after mixing at 100 rpm for 10 min at 230°C.

increases from 71.6 to 96.1°C when its molar mass increases from 11.8 to 56.6 kg/mol (also see Table II).

#### Formation of PS-*b*-PA6 during reactive blending

Figure 4 shows that the morphologies of the PS/PA6 (30/70 by mass) and PS/PA6 (50/50 by mass) blends are of dispersed and co-continuous types, respectively. Figures 5 and 6 show that when the PS-*b*-Anh block copolymer precursor is added to PS/PA6 (30/70 by mass) blends, a significant reduction in the size of the dispersed phase is observed relative to that of the uncompatibilized blend, whatever the molar mass of the precursor. For example, the dispersed phase size of the uncompatibilized PS/PA6 (30/70 by mass) blend is 11.5  $\mu\text{m}$ . It is reduced to 1.8  $\mu\text{m}$  upon the addition of 1 wt % PS-*b*-Anh21. This is a strong indirect indication of the formation of a PS-*b*-PA6 copolymer during the reactive polymer blending process.

To further confirm the formation of the PS-*b*-PA6, the PS/PA6/PS-*b*-Anh blends are subjected to successive extraction in HCl (6 mol/L) to remove the PA6 phase domains and then in THF to remove the PS phase domains. The residues that cannot be dissolved in HCl and THF are analyzed by  $^1\text{H}$  NMR and DSC. Figure 7 shows that the  $^1\text{H}$  NMR spectrum has two broad resonances at 6.7 and 7.2 ppm characteristic of the PS chain and another three at 1.8, 2.7, and 3.6 ppm corresponding to PA6. This

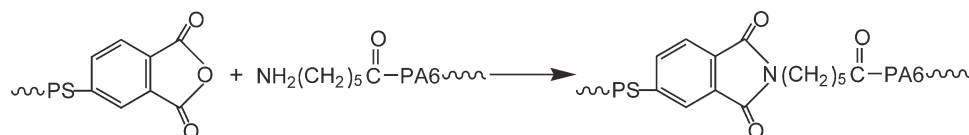


**Figure 7**  $^1\text{H}$  NMR spectrum of PS-*b*-PA6.

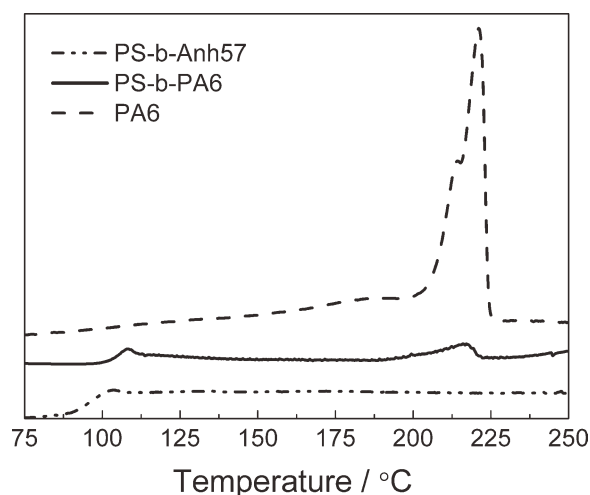
suggests that the chemical reaction between the anhydride of PS-*b*-Anh and amine of PA6 has indeed occurred and that a block copolymer PS-*b*-PA6 is indeed formed. Figure 8 is a schematic of the formation of the PS-*b*-PA6 block copolymer. The formation of this copolymer is corroborated by a peak at 108°C corresponding to the glass transition temperature of the PS and 218°C corresponding to the melting temperature of PA6 appeared in the DSC traces of the melting behavior of the PS-*b*-PA6 (see Figure 9).

#### Comparison of compatibilizing efficiency between block and graft copolymer precursors

In the case of PS-*b*-Anh, the copolymer formed is a PS-*b*-PA6 block copolymer. In the case of the PS-*co*-TMI, it is a PS-*g*-PA6 graft copolymer with the PS as the backbone and the PA6 as the grafts. Figure 10 compares the SEM micrographs of the PS/PA6 (30/70 by mass) blends before and after the annealing at 230°C among the following three cases: without copolymer precursor, with 1 wt % PS-*b*-Anh and with 1 wt % PS-*co*-TMI. Figure 11 shows the diameter of the dispersed phase domains of these blends as a function of the annealing time. For the blends without compatibilizer precursor, the dispersed phase size drastically increases with increasing annealing time, indicating that a significant coarsening process has taken place. In the case of the PS-*co*-TMI, the dispersed phase hardly changes in size for the first 5

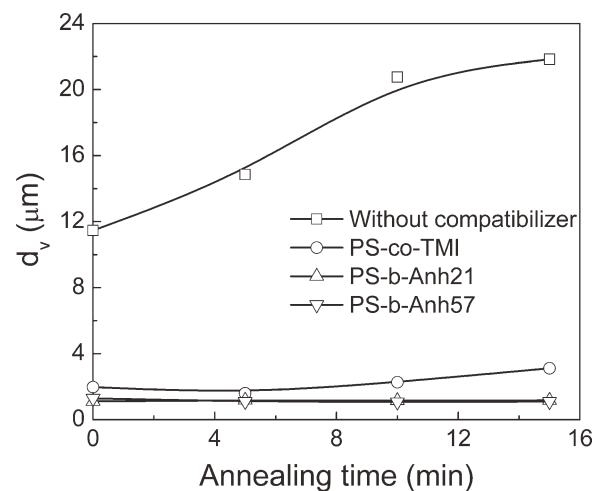


**Figure 8** Schematic of the formation of PS-*b*-PA6 block copolymer by *in situ* reaction between the terminal anhydride group of the PS-*b*-Anh and the terminal amine group of the PA6.



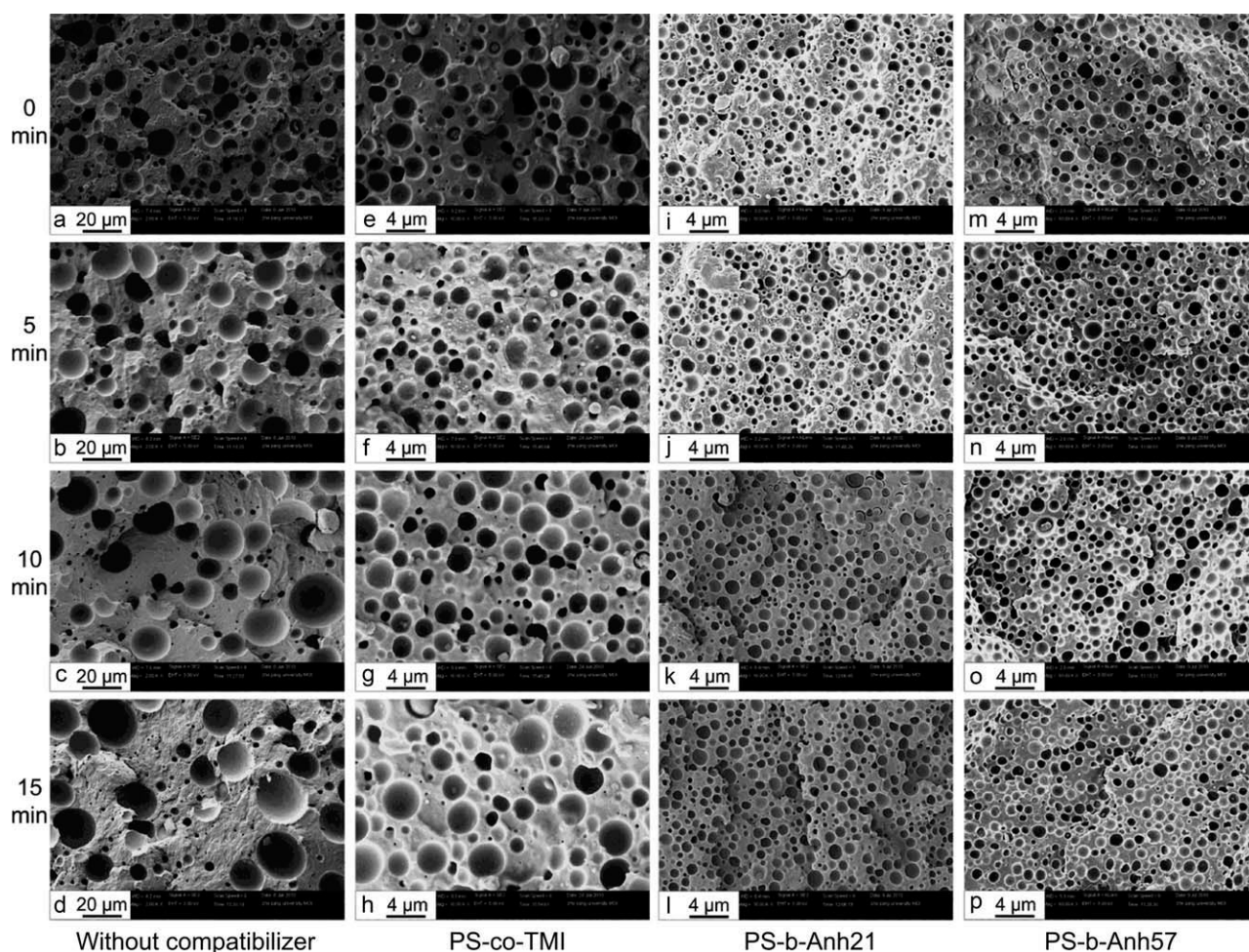
**Figure 9** DSC thermogram of PS-*b*-PA6 in comparison with those of the PS-*b*-Anh57 and PA6.

min and starts increasing in size thereafter. As for PS-*b*-Anh21 and PS-*b*-Anh57, the dispersed phase domain size does not increase at all over the entire



**Figure 11** Diameter of the PS phase domains ( $d_v$ ) vs. annealing time for the PS/PA6 (30/70 by mass) blend at an annealing temperature of 230°C.

annealing time (15 min). Moreover, the dispersed phase domain size of these polymer blends after the annealing follows the order: Without compatibilizer



**Figure 10** Effect of adding 1 wt % compatibilizer precursor on the morphology of the PS/PA6 (30/70 by mass) blend after mixing at 100 rpm for 15 min at 230°C followed by annealing at 230°C. (a–d) without compatibilizer precursor, (e–h) PS-*co*-TMI, (i–l) PS-*b*-Anh21, (m–p) PS-*b*-Anh57.

precursor  $\gg$  PS-*co*-TMI  $>$  PS-*b*-Anh21  $\approx$  PS-*b*-Anh57.

The above results show that the compatibilizing and stabilizing efficiency follows the order: PS-*co*-TMI  $<$  PS-*b*-Anh21  $\approx$  PS-*b*-Anh57. This could be explained as follows. In the case of PS-*b*-Anh, the copolymer formed is a PS-*b*-PA6 block copolymer whereas in the case of PS-*co*-TMI, it is a PS-*g*-PA6 graft copolymer. The difference in molecular architecture might be responsible, at least in part, for the difference in compatibilizing and stabilizing efficiency between PS-*b*-Anh and PS-*co*-TMI. Moreover, from Tables I and II, the molar mass of PS-*b*-Anh is close to that of PA6. Thus the molecular architecture of the resulting PS-*b*-PA6 is expected to be much more symmetrical than that of the PS-*g*-PA6. As a result, the PS-*b*-PA6 is expected to have higher tendency to be located at the interfaces between the PS and PA6 than the PS-*g*-PA6 does. Therefore, the compatibilizing and stabilizing efficiency of PS-*b*-Anh is higher than that of PS-*co*-TMI. Lyatskaya et al.<sup>28</sup> concluded that symmetrical copolymers are more efficient at decreasing the interface tension of immiscible polymer blend.

### CONCLUSIONS

This work is focused on the compatibilizing efficiency of compatibilizer precursors for immiscible polymer blends. The blend system is composed of PS and PA6. An PS-*b*-Anh and a copolymer (PS-*co*-TMI) of St and 3-isopropenyl- $\alpha,\alpha$ -dimethylbenzene isocyanate (TMI) are used as compatibilizer precursors. They are synthesized by ATRP and free radical polymerization.

The compatibilizing and stabilizing efficiency of the PS-*b*-Anh block copolymer precursor is significantly higher than that of the PS-*co*-TMI graft copolymer. This difference mainly results from the difference in the molecular architectures of the resulting copolymers. During the reactive blending process, the PS-*b*-Anh leads to the formation of a PS-*b*-PA6 block copolymer while the PS-*co*-TMI a PS-*g*-PA6 graft copolymer.

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### References

- Zhang, C. L.; Feng, L. F.; Gu, X. P.; Hoppe, S.; Hu, G. H. *Polymer* 2007, 48, 5940.
- Cartier, H.; Hu, G. H. *Polym Eng Sci* 1999, 39, 996.
- Hu, G. H.; Kadri, I. *J Polym Sci Part B: Phys Ed* 1998, 36, 2153.
- Li, H. X.; Hu, G. H. *J Polym Sci Part B: Polym Phys* 2001, 39, 601.
- Li, H. X.; Hu, G. H.; Sousa, J. A. *J Polym Sci Part B: Polym Phys* 1999, 37, 3368.
- Zhang, C. L.; Feng, L. F.; Gu, X. P.; Hoppe, S.; Hu, G. H. *Polym Eng Sci* 2010, 50, 2243.
- Fortelny, I.; Mikesova, J.; Hromadkova, J.; Hasova, V.; Horak, Z. *J Appl Polym Sci* 2003, 90, 2303.
- Hu, G. H.; Scaffaro, R.; La Mantia, F. *J Macromol SciPure Appl Chem A* 1998, 35, 457.
- Zhang, C. L.; Feng, L. F.; Zhao, J.; Huang, H.; Hoppe, S.; Hu, G. H. *Polymer* 2008, 49, 3462.
- Cartier, H.; Hu, G. H. *J Mater Sci* 2000, 35, 1985.
- Matos, M.; Favis, B. D.; Lomellini, P. *Polymer* 1995, 36, 3899.
- Cigana, P.; Favis, B. D. *Polymer* 1998, 39, 3373.
- Milner, S. T.; Xi, H. W. *J Rheol* 1996, 40, 663.
- Sundararaj, U.; Macosko, C. *Macromolecules* 1995, 28, 2647.
- Nakayama, A.; Inoue, T.; Guegan, P.; Macosko, C. *Polym Prepr* 1993, 34, 840.
- Jeon, H. K.; Zhang, J. B.; Macosko, C. W. *Polymer* 2005, 46, 12422.
- Pei, A. H.; Liu, A. D.; Xie, T. X.; Yang, G. S. *J Appl Polym Sci* 2007, 105, 1757.
- Hu, G. H.; Li, H. X.; Feng, L. F. *Macromolecules* 2002, 35, 8247.
- Zhang, C. L.; Feng, L. F.; Hu, G. H.; Xu, Z. B. *J Appl Polym Sci* 2006, 101, 1972.
- Zhang, C. L.; Feng, L. F.; Hoppe, S.; Hu, G. H. *J Polym Sci Part A: Polym Chem* 2008, 46, 4766.
- Zhang, C. L.; Feng, L. F.; Gu, X. P.; Hoppe, S.; Hu, G. H. *Polym Test* 2007, 26, 793.
- Hu, G. H.; Kadri, I. *Polym Eng Sci* 1999, 39, 299.
- Hu, G. H.; Kadri, I. *Polym Eng Sci* 1999, 39, 930.
- Zhang, X. M.; Xu, Z. B.; Feng, L. F.; Song, X. B.; Hu, G. H. *Polym Eng Sci* 2006, 46, 510.
- Hu, G. H.; Feng, L. F.; Pessan, L. A. *J Appl Polym Sci* 2003, 88, 1799.
- Malz, H.; Komber, H.; Voigt, D.; Hopfe, I.; Pionteck, J. *Macromol Chem Phys* 1999, 200, 642.
- Ji, S. X.; Hoye, T. R.; Macosko, C. W. *Polymer* 2008, 49, 5307.
- Lyatskaya, Y.; Jacobson, S. H.; Balazs, A. C. *Macromolecules* 1996, 29, 1059.