A Novel Reactive Processing Technique: Using Telechelic Polymers To Reactively Compatibilize Polymer Blends

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ABSTRACT Difunctional reactive polymers, telechelics, were used to reactively form multiblock copolymers in situ when melt-blended with a blend of polystyrene and polyisoprene. To quantify the ability of the copolymer to compatibilize the blends, the time evolution of the domain size upon annealing was analyzed by SEM. It was found that the most effective parameter to quantify the ability of the copolymer to inhibit droplet coalescence is $K_{rel}t_{stable}$, the relative coarsening constant multiplied by the stabilization time. These results indicate that intermediate-molecular-weight telechelic pairs of both highly reactive Anhydride-PS-Anhydride/NH$_2$-PI-NH$_2$ and slower reacting Epoxy-PS-Epoxy/COOH-PI-COOH both effectively suppress coalescence, with the optimal molecular weight being slightly above the critical molecular weight of the homopolymer, M_c. The effects of telechelic loading were also investigated, where the optimal loading concentration for this system was 0.5 wt %, as higher concentrations exhibited a plasticizing effect due to the presence of unreacted low-molecular-weight telechelics present in the blend. A determination of the interfacial coverage of the copolymer shows that a conversion of ∼1.5−3.0 % was required for 20 % surface coverage at 5.0 wt % telechelic loading, indicating a large excess of telechelics in this system. At the optimal loading level of 0.5 wt %, a conversion of 15 % was required for 20 % surface coverage. The results of these experiments provide a clear understanding of the role of telechelic loading and molecular weight on its ability to reactively form interfacial modifiers in phase-separated polymer blends and provide guidelines for the development of similar reactive processing schemes that can use telechelic polymers to reactively compatibilize a broad range of polymer blends.

KEYWORDS: polymer blend • interfacial modification • compatibilization • telechelic • multiblock copolymer • coalescence • coarsening constant • plasticization

INTRODUCTION

Polymer blends provide a cost-effective method to tailor the properties of a material (1). However, most polymers are immiscible due to their positive enthalpy of mixing (2), and a sharp interface between the two phases results. This material is invariably inferior than that targeted, as mechanical failure occurs due to poor energy transfer between the unlike polymers which have few entanglements between them. To alleviate this problem, a small amount of copolymer may be incorporated into the blend to compatibilize the two phases (3, 4). Ideally, this copolymer resides at the interface, allowing the homopolymers to entangle with the interfacial modifier (5, 6). The resulting interfacial compatibilization results in smaller dispersed phases, increased energy transfer efficiency, and greater interfacial adhesion (7). When the dispersed minor phase chains can relax in the copolymer, the interfacial tension is reduced (8, 9). This makes droplet breakup by shear forces easier and leads to a finer, more homogeneous dispersion of particles throughout the matrix during the blending process (10). Another role of the copolymer is to inhibit the recombination of the minor-phase droplets by static coalescence. Since the blend is not in a thermodynamically stable state, the droplets reduce the interfacial energy of the system by a recombination process called coalescence (11).

Many polymer blends must be heated above the T_g values of the individual components during processing, during which time droplet coalescence occurs. Droplet coalescence is suppressed with addition of compatibilizer because the copolymer chains that extend into the matrix must be compressed before the droplets are able to coalesce (12, 13). If the elastic repulsive force required for this compression of the copolymer is greater than the attractive van der Waals force between the droplets, coalescence will be inhibited (13).

A very effective way to compatibilize a blend is to form the copolymer in situ using polymers with reactive end groups (12, 14, 15). This forms a diblock via a reaction between the end groups of two chains which can occur only at the interface. In comparison, a premade copolymer may become trapped as a micelle in one of the homopolymer phases of the blend. It must then diffuse through the bulk to the interface, decreasing its efficiency as a compatibilizer (16).

It has been shown that a premade multiblock copolymer offers enhanced compatibilization effects relative to a diblock

copolymer due to the fact that a multiblock copolymer will cross the interface several times, forming loops (4, 17, 18). The interfacial strength is increased as the homopolymer chains become entangled with the loops of the copolymer. We have recently begun to study the formation of loops at interfaces (19–22), including multiblocks at a polymer/polymer interface created in situ by melt-mixing difunctional reactive polymers called telechelics with a blend at high temperature.

In this paper, we report results of our studies which examine the ability of telechelic polystyrene and polyisoprene to compatibilize a polystyrene/polyisoprene blend. To quantify the compatibilization efficiency of this process, the blends are annealed for various times and scanning electron microscopy (SEM) is used to determine the domain size of the dispersed phase. Here, we use Macosko's definition of compatibilization, the stabilization of blends against coalescence (13). Upon annealing, the domain sizes are expected to grow with time by the relationship (11)

$$D^3(t) = D_0{}^3 + Kt \qquad (1)$$

where $D(t)$ is the diameter of the dispersed phase at annealing time t, D_0 is the diameter of the particle at zero minutes of annealing, and K is the coarsening constant. The coarsening constant in polymer blends describes the rate of coalescence of the minor phase. In the coalescence process, Brownian motion first brings two droplets toward each other. The matrix film between the droplets is then drained as the droplets push out the fluid, and the van der Waals attractive force between the droplets causes them to merge together into a larger droplet (12, 23). For coalescence, $K \propto \varphi_d T/\eta_m$, where φ_d is the volume fraction of the dispersed phase, T is the temperature, and η_m is the matrix viscosity (11). It has also been shown that $K \propto A/\eta_m$ (24), where A is the Hamaker constant. The Hamaker constant describes the strength of the van der Waals forces between the droplets and decreases with an increase in the energy barrier between coalescing droplets (24, 25). Thus copolymers located at the interface can suppress coalescence due to steric hindrance, as the chains extending into the matrix result in a large repulsive force when compressed, creating a energy barrier that must be overcome for droplet recombination to occur.

To effectively suppress coalescence, the chains of a copolymer block must become entangled with the homopolymer. A premade multiblock copolymer offers the advantage of crossing the polymer/polymer interface several times, increasing the interfacial strength of the blend. However, premade copolymers must first diffuse to the interface. Since the critical micelle concentration of premade multiblock copolymers is very low, most copolymers remain trapped in the homopolymer phase, where they are ineffective as compatibilizers. If monofunctional reactive polymers are used to form a diblock copolymer in situ with a molecular weight similar to that of the multiblock copolymer, micellization problems can be minimized. However, a diblock copolymer only crosses the polymer/polymer interface one time. In addition, the large size of these monofunctional reactive polymers reduces their effectiveness as compatibilizers. The concentration of reactive end groups is low, and any diblock copolymer that is formed at the interface sterically hinders other reactive polymers from approaching the interface. Using lower molecular weight difunctional reactive polymers to form multiblock copolymers at the interface offers the advantage of multiple interfacial crossings while at the same time minimizing the problems associated with premade multiblock copolymers. When smaller telechelic building blocks are used to create a large multiblock copolymer in situ, compatibilization is made more efficient due to a higher reactive end group concentration and more facile approach to the interface.

The choice of telechelic molecular weight is still quite important. To determine the overall effectiveness of this compatibilization scheme to improve blend properties, the right balance of static and dynamic coalescence suppression must be realized. Lower molecular weight telechelics offer the advantage of a higher concentration of end groups per given volume and the ability to approach the interface quickly, readily forming a copolymer and providing good suppression of dynamic coalescence during mixing (13, 26). However, higher molecular weight telechelics should provide better suppression of static coalescence during annealing, as it is more difficult to compress longer chains between two coalescing droplets (13). An optimal telechelic molecular weight can thus be defined as that which results in a system where the blend will be well compatibilized and the coarsening constant K is small. It is therefore the goal of this study to determine the role of telechelic loading and chain length on its ability to reactively compatibilize a phase-separated polymer blend.

EXPERIMENTAL SECTION

Materials. Polystyrene (PS) (M_n 77 000; M_w 196 000) and polyisoprene (PI) (M_n 191 000; M_w 293 000) were purchased from Aldrich. The PS pellets were first ground up into a coarse powder and placed in a vacuum oven at 130 °C for 1 week to remove any residual solvent and monomer. To prevent thermal degradation of the polyisoprene, 0.25 wt % tris(4-*tert*-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanate (Aldrich, 97 %) and 0.25 wt % tris(2,4-di-*tert*-butylphenyl)phosphate (Aldrich, 98 %) antioxidants were incorporated into homopolymer and telechelic PI by dissolving them in HPLC-grade toluene (Fisher) at room temperature, stirring overnight in an amber-colored jar purged with argon, and then evaporating the solvent and drying in a vacuum oven at 50 °C for 1 week.

The difunctional anionic polymers were synthesized at the University of Tennessee. Reactive pairs used in this study include succinic anhydride terminated polystyrene (Anh-PS-Anh) with primary amine-terminated polyisoprene (NH$_2$-PI-NH$_2$), as well as epoxide-terminated polystyrene (Epoxy-PS-Epoxy) with carboxylic acid-terminated polyisoprene (COOH-PI-COOH) (27–31). The functionality of the Anh-PS-Anh was 1.6, and the functionality of the remaining telechelics was 1.9. In addition, the polyisoprene telechelics were fluorescently labeled with 1-(1-anthryl)-1-phenylethylene (32) (APE) adjacent to each functional group.

Table 1. Number-Average Molecular Weights and Polydispersity Indexes of Difunctional Polystyrene and Polyisoprene Polymers Used in This Study

telechelic	M_n	PDI	telechelic	M_n	PDI
Anh-PS-Anh	16 000	1.11	NH_2-PI-NH_2	16 000	1.28
Anh-PS-Anh	37 000	1.02	NH_2-PI-NH_2	32 000	1.27
Anh-PS-Anh	83 000	1.02			
Epoxy-PS-Epoxy	18 000	1.04	COOH-PI-COOH	18 000	1.14
Epoxy-PS-Epoxy	44 000	1.04	COOH-PI-COOH	54 000	1.18

The number-average molecular weights (M_n) and polydispersity indexes (PDI) of the reactive pairs used in this study are shown in Table 1.

In Figure 1, the reactions between the telechelic end groups at elevated temperatures are shown.

The second-order reaction between the carboxylic acid and epoxy forms an ester (15) and has been shown to be slow, with only 9% conversion after 2 min of mixing Epoxy-PS-Epoxy and COOH-PS-COOH at 180 °C (33, 34). The second order reaction between a cyclic anhydride and an aliphatic amine first yields amic acid after a ring-opening step, and then an imide and water are formed after a condensation step (35). This reaction is very fast, with 99% conversion between Anh-PS-Anh and NH_2−PS-NH_2 after 2 minutes of mixing at 180 °C (33, 34).

Blending and Annealing Procedure. The blends studied contained 5.0% telechelics by weight, while the remaining 95% of the sample consisted of a blend that was 90% PS/10% PI. Stoichiometric amounts of Anh-PS-Anh/NH_2-PI-NH_2 and Epoxy-PS-Epoxy/COOH-PI-COOH constituted the telechelic contribution of the blend. For example, a blend of 90% PS/10% PI + 5.0% 37k Anh-PS-Anh/16k NH_2-PI-NH_2 contains 1026.0 mg of PS, 114.0 mg of PI, 37.8 mg of 37k Anh-PS-Anh, and 22.3 mg of 16k NH_2-PI-NH_2. The ratio of telechelics is determined by the concentration of reactive end groups, which depends on the molecular weight and functionality of the telechelic. The contents were first placed together in an aluminum weighing pan and were premixed by hand. The four components were then placed in an Atlas Laboratory Mixing Molder heated to 180 °C, with a rotor speed of 100 rpm. A stainless steel collar was made to sit on the mixing cup and surround the rotor, where dry argon was purged through the collar to minimize thermal oxidation of the PI. It was observed that samples initially extruded from the mixing molder were inhomogeneous due to poor blending in the pathway between the bottom of the cup and where the blend was extruded. To ensure homogenous samples, the four components were first blended in the mixing molder for the shortest possible time and extruded twice, followed by melt blending for various times. A small aliquot of the blend, approximately 5 mm in diameter, was extruded and then quenched at room temperature, where it was cool to the touch after a few seconds. For SEM, samples were melt-blended for a total of 10 minutes. These small samples were then placed in an argon-purged oven at 150 °C for 15, 30, 60, and 180 min to anneal the samples.

SEM Analysis. Samples for SEM were placed in liquid nitrogen for at least 90 min and then shattered with a hammer. The smallest pieces were placed in HPLC grade n-heptane (Acros) overnight at room temperature to remove the polyisoprene. After they were rinsed with fresh solvent, the samples were dried under vacuum at room temperature for at least 4 h. After the samples were mounted onto grids, they were sputter-coated with gold for 10 s to prevent charge buildup.

A Delong Instruments LV-EM5 low-voltage SEM (5 kV) was used to analyze the samples. Micrographs were analyzed using Image J 1.36b software (NIH) to determine the area of the holes where the polyisoprene once resided. Only hole areas with a circularity greater than 0.7 were considered. From the area of the holes, A, an equivalent diameter of each hole, D_i, was calculated by:=

$$D_i = 2(A/\pi)^{0.5} \qquad (2)$$

Since the center of the holes is not necessarily being observed by SEM, geometric corrections were applied, and the number-average (D_n), weight-average (D_w), and volume to surface area average (D_{vs}) diameters were calculated (36). In this analysis, the diameter is defined as the largest chord on a given circle. This layer chord length, l_i, was used to calculate the weighted chord lengths:

$$l_h = \sum N_i / \sum N_i/l_i$$

$$l_n = \sum N_i l_i / \sum N_i$$

$$l_w = \sum N_i l_i^2 / \sum N_i l_i \qquad (3)$$

where the subscript h refers to the harmonic average, and N_i is the number of chords of size i. Applying geometric corrections gives the weighted diameters:

$$D_n = l_h(\pi/2)$$

$$D_w = l_n(4/\pi)$$

$$D_{vs} = l_w(3\pi/8) \qquad (4)$$

Several micrographs were analyzed, each containing approximately 100−400 domains, and the average weighted diameter and standard deviation were recorded.

RESULTS AND DISCUSSION

SEM images of representative samples melt-blended for 10 min and then annealed at 150 °C under argon for 0 and 180 min are shown in Figure 2. From Figure 2, one can visually observe that the blends with the telechelics have a larger initial droplet size than the uncompatibilized blend.

Coarsening Constant. In Figure 3, D^3, expressed as $D_n D_w D_{vs}$, is plotted as a function of annealing time in order to determine the coarsening constant K.

The results show that the slope of the initial linear portion of the curve is reduced in the compatibilized blends due to the suppression of coalescence by steric hindrance of the copolymer. In addition, the results in Figure 3 agree with the visual results shown in Figure 2, in that the initial droplet size in the compatibilized blends is actually larger than that in the uncompatibilized blend. The initial size of the droplets varies widely in the compatibilized blends. However, the coarsening constant does not depend on the initial size of the particle, only the rate of growth. Thus, it may be more useful to quantify the rate of coalescence of PI droplets using the relative cubed diameter, $D(t)^3/D_0^3$. The data in Figure 3
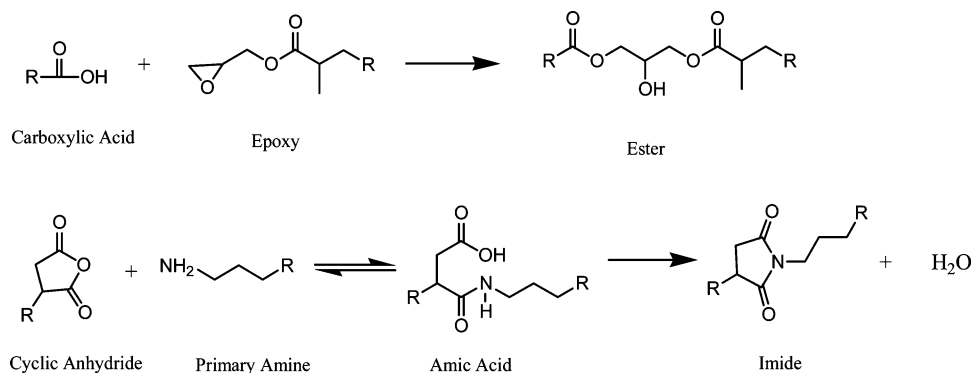
FIGURE 1. Reactions between (top) carboxylic acid and epoxy groups to yield an ester and (bottom) a cyclic anhydride and a primary amine to first yield amic acid and, after condensation, an imide.
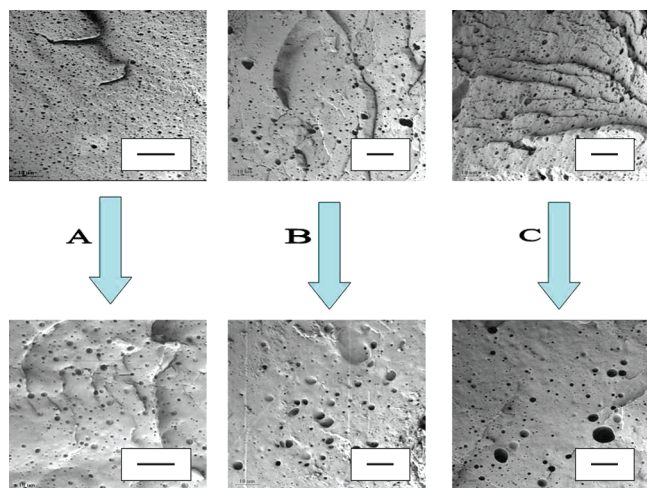

FIGURE 2. SEM images of 90% PS/10% PI blends annealed at 150 °C for 0 min (top) and 180 min (bottom): (A) uncompatibilized; (B) 37k Anh-PS-Anh/32k NH$_2$-PI; (C) 44k Epoxy-PS-Epoxy/54k COOH-PI-COOH. The scale of the bar in each image is 10 μm.
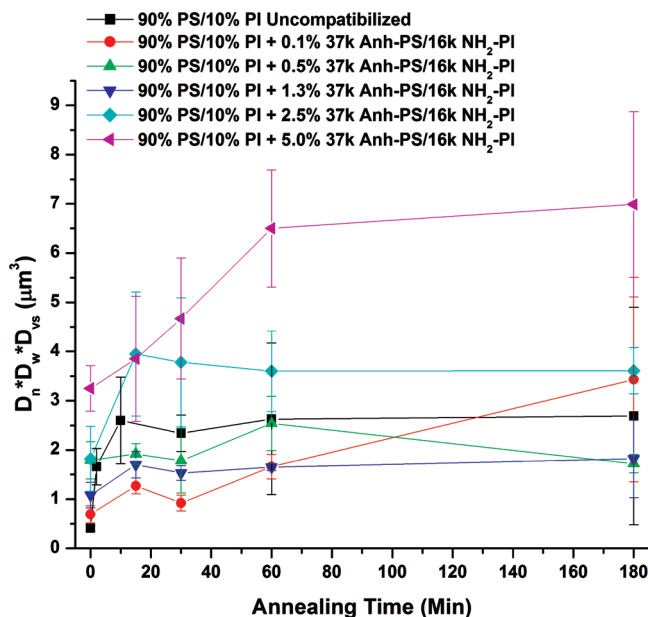

FIGURE 3. D^3 as a function of annealing time for 90% PS/10% PI blends with 5.0 wt % telechelics.
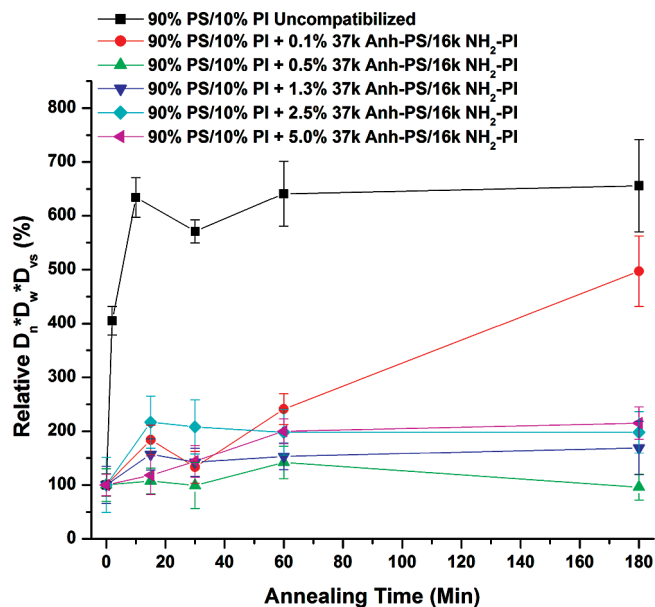

FIGURE 4. Relative D^3 ($D(t)^3/D_0^3$) as a function of annealing time for 90% PS/10% PI blends with 5.0 wt % telechelics.

The results in Figure 4 show that the droplets in the blend without telechelics coalesce rapidly, as the relative size increases by a factor of ~6 after only 10 min of annealing. The 18k Epoxy-PS-Epoxy/20k COOH-PI-COOH telechelics also did not compatibilize the blend, as the domain size increased rapidly for the entire 180 min of annealing and its relative droplet size surpassed that of the uncompatibilized blend. All of the other telechelic pairs suppress coalescence relative to the uncompatibilized blend, as their droplet size increases only by a factor of ~ 2 after 180 min of annealing.

The coarsening constant K in eq 1 was determined from the slope of a linear fit of $D(t)^3 - D_0^3$ as a function of annealing time, with D^3 expressed as $D_n D_w D_{vs}$. The slope of the line was determined by fitting the data from zero time to the stabilization time of the droplets to a line. In a study of polystyrene/poly(dimethylsiloxane) blends by Macosko et al., the system was described as stable to coalescence if the particle size changed less than 25% after 30 min of annealing (37). We use a similar criterion, defining the droplets as stabilized when the D_{vs} increase is less than 25% between annealing time intervals. Table 2 shows the stabilization

are replotted as the relative cubed diameter as a function of annealing time in Figure 4.

Table 2. Coarsening Constant K Determined from a Linear fit of $D(t)^3 - D_0^3$ as a Function of Annealing Time

90% PS/10% PI 5.0 wt % telechelics	stabilization (min)	K (μm^3/min)	Kt_{stable} (μm^3 growth)	R^2
uncompatibilized	10	2.3×10^{-1}	2.3	0.737
16k Anh-PS-Anh/16k NH_2-PI-NH_2	180[a]	2.7×10^{-2}	4.9	0.980
37k Anh-PS-Anh/16k NH_2-PI-NH_2	60	6.6×10^{-2}	3.9	0.988
37k Anh-PS-Anh/32k NH_2-PI-NH_2	60	5.0×10^{-2}	3.0	0.915
83k Anh-PS-Anh/32k NH_2-PI-NH_2	180[a]	1.7×10^{-2}	3.1	0.930
18k Epoxy-PS-Epoxy/20k COOH-PI-COOH	180[a]	3.4×10^{-2}	6.2	0.863
44k Epoxy-PS-Epoxy/20k COOH-PI-COOH	15	5.3×10^{-2}	0.8	1.000
44k Epoxy-PS-Epoxy/54k COOH-PI-COOH	30	4.9×10^{-2}	1.5	0.972

[a] The droplets were not stabilized, and a time of 180 min was used in the calculation.

Table 3. Relative Coarsening Constant K_{rel} Determined from a Linear Fit of $(D(t)^3/D_0^3) - 1$ as a Function of Annealing Time

90% PS/10% PI 5.0 wt % telechelics	stabilization (min)	K_{rel}	$K_{rel}t_{stable}$ (% growth)	R^2
uncompatibilized	10	5.7×10^1	570	0.737
16k Anh-PS-Anh/16k NH_2-PI-NH_2	180[a]	9.0×10^{-1}	162	0.980
37k Anh-PS-Anh/16k NH_2-PI-NH_2	60	1.6	96	0.988
37k Anh-PS-Anh/32k NH_2-PI-NH_2	60	2.3	138	0.915
83k Anh-PS-Anh/32k NH_2-PI-NH_2	180[a]	4.8×10^{-1}	86	0.930
18k Epoxy-PS-Epoxy/20k COOH-PI-COOH	180[a]	6.5	1170	0.863
44k Epoxy-PS-Epoxy/20k COOH-PI-COOH	15	5.7	86	1.000
44k Epoxy-PS-Epoxy/54k COOH-PI-COOH	30	3.5	106	0.972

[a] The droplets were not stabilized, and a time of 180 min was used in the calculation.

time, absolute coarsening constant K, total growth expressed as Kt_{stable}, and R^2 of the linear fit of the data.

Table 2 shows that the blends have various stabilization times. The coarsening before the stabilization time nearly fits the linear model of eq 1. The uncompatibilized blend fit poorly to eq 1 due to a rapid slowdown in coarsening between 2 and 10 min. On comparison of the data in Table 2 with Figures 3 and 4, it is clear that the lowest K value does not describe the best compatibilized blend, as the 83k Anh-PS-Anh/32k NH_2-PI-NH_2 blend has the lowest K value but is not stabilized after annealing. Since all the blends have various stabilization times, it may be more instructive to use Kt_{stable}, the coarsening constant multiplied by the stabilization time, as a measure of the telechelics' ability to compatibilize the blends. This provides a measure of the total growth, so that different stabilization times are accounted for. The Kt_{stable} value for 18k Epoxy-PS-Epoxy/20k COOH-PI-COOH has the largest value in the table, agreeing with the data in Figure 4. 44k Epoxy-PS-Epoxy/20k COOH-PI-COOH and 44k Epoxy-PS-Epoxy/54k COOH-PI-COOH have the smallest Kt_{stable} values, which also agrees with the results in Figures 3 and 4. However, the uncompatibilized blend has a smaller Kt_{stable} value than the remaining Anh/NH_2 telechelic pairs, which undoubtedly suppresses coalescence. Thus, it is clear that this analysis of the data in Figure 3 does not provide a quantifiable measure of the ability of the telechelics to compatibilize these blends.

Inspection of Figure 3 shows that the blends have different initial droplet sizes, and all compatibilized blends have an initial D^3 value greater than that of the uncompatibilized blend, which may explain the failure of the analysis of the data in Figure 3 to accurately describe the effectiveness of the telechelics as compatibilizers. For instance, if the drop-

lets are large to begin with, annealing will lead to even larger droplets being formed, and the absolute K values of these blends will be larger than that of the uncompatibilized blend. Therefore, accurately quantifying the effectiveness of the compatibilizers will require the analysis of the relative size increase of the droplets, as shown in Figure 4. If D^3/D_0^3 is plotted as a function of annealing time, the slope is the relative coarsening constant, K_{rel}, in units of percent growth/min. The value $K_{rel}t_{stable}$ then provides a measure of the total percent growth up to stabilization. The results of these analyses are shown in Table 3.

Table 3 shows that 44k Epoxy-PS-Epoxy/20k COOH-PI-COOH, 44k Epoxy-PS-Epoxy/54k COOH-PI-COOH, 37k Anh-PS-Anh/16k NH_2-PI-NH_2, and 37k Anh-PS-Anh/32k NH_2-PI-NH_2 exhibit the lowest $K_{rel}t_{stable}$ values of stabilized blends, in agreement with the data in Figure 4. The results show that the slower reacting Epoxy/COOH pair produced sufficient copolymer in the 10 min mixing time to suppress coalescence as effectively as the highly reactive Anh/NH_2 pair.

It is also interesting to note that the low-molecular-weight pairs of both the Anh/NH_2 and Epoxy/COOH systems both suppress coalescence poorly relative to the intermediate molecular weight telechelic pairs. Since this is the case for both the high- and low-reactivity pairs, this observation can be explained as a molecular weight effect, where the blocks of the copolymer formed from the telechelic are too short to effectively entangle with the homopolymer chains as a compatibilizer. For entangled chains, the polymer viscosity is proportional to $M_w^{3.4}$ when $M_w > M_c$, where M_c is the critical molecular weight (38). M_c is approximately equal to twice the entanglement weight, M_e (39). At a temperature of 140 °C, the M_e value of polystyrene is ~13 000, whereas the M_e value of polyisoprene is only ~6000 (40). For the 16k Anh-

PS-Anh/16k NH_2-PI-NH_2 and 18k Epoxy-PS-Epoxy/20k COOH-PI-COOH blends, the PS telechelic molecular weight is below M_c, which results in poor entanglement between the PS block of the copolymer and the PS matrix. The PS copolymer blocks therefore have significant mobility and can be readily squeezed out of the way of the recombining droplets (13, 37), leaving the concentration of copolymer at the interface too low to effectively suppress coalescence.

This observation agrees with our previous compatibility studies using premade multiblock copolymers. In this work, premade diblock, triblock, pentablock, and heptablock opolymers with a similar overall molecular weight and composition but different block size were examined as compatibilizers of PS and PMMA bilayers (4). It was found that the interfacial strength of the compatibilized interface ranked as pentablock > triblock > diblock > heptablock. This was interpreted as a manifestation of an increase in the number of crossings per chain with the number of blocks within the chain, where an increased number of crossings increases the strength of the interface. The behavior of the heptablock copolymer was ascribed to the fact that that the block size in this copolymer was below the entanglement molecular weight of the homopolymers. Therefore, the blocks could not entangle well with the homopolymers, resulting in a decrease in the ability of these compatibilizers to effectively strengthen the interface. The effect of telechelic molecular weight found in this study agrees very well with this previous work, emphasizing that the most effective multiblock copolymer compatibilizers are those where each copolymer block size is larger than the entanglement weight of the homopolymer. Otherwise the copolymer will not as effectively modify the interface, regardless of how many times it crosses the interface. In this study, the suppression of droplet coalescence for blends that were mixed for 10 min was studied. However, an interesting and useful expansion of this work could examine blends mixed for different times to further determine the importance of mixing time on coalescence suppression, as the telechelics first form diblock copolymers and then triblock copolymers on their way to longer multiblock copolymers.

Specific Interfacial Area. The change in specific interfacial area (interfacial area per unit volume) as a function of annealing time also provides a method to quantify the effectiveness of telechelic pairs to compatibilize a polymer blend. As the blend anneals, smaller droplets coalesce into larger ones, reducing the surface area of the droplets, causing the volume to surface area ratio to increase. Therefore, a well-compatibilized blend will lose less specific surface area during annealing than a poorly compatibilized blend. The specific surface area of the droplets in the blend can be calculated by (13)

$$S_{sp} = 6\phi_{minor}/D_{vs} \qquad (5)$$

where φ_{minor} is the volume fraction of the minor phase in the blend and D_{vs} is the volume to surface area droplet diameter as determined by SEM.

The interpretation of these results (Supporting Information) show that the uncompatibilized blend loses more than half of its specific surface area as the droplets coalesce during annealing. When the 18k Epoxy-PS-Epoxy/20k COOH-PI-COOH telechelic pair is used, only one third of the original specific surface area remains after annealing, showing these telechelics mainly act as plasticizers that make coalescence easier. The most effective telechelic pairs, which have the lowest $K_{rel}t_{stable}$ values shown in Table 3, only lose $\sim$15−25% of their specific surface area before stabilization is achieved.

Another point of interest is that the droplets in the blends compatibilized with 44k Epoxy-PS-Epoxy/20k COOH-PI-COOH and 44k Epoxy-PS-Epoxy/54k COOH-PI-COOH rapidly grow and lose specific surface area in the first 15 min of annealing but then become stabilized. On the whole, the blends stabilized with the Anh/NH_2 telechelics do not lose a significant amount of specific surface area until after 30 min of annealing. This suggests that the slower conversion of telechelics into multiblock copolymers for the less reactive Epoxy/COOH pair impacts the morphology development. Because of the lower initial copolymer concentration at the interface for the slow Epoxy/COOH reaction, the droplets can initially coalesce quickly and reduce the droplet surface area. As the droplets grow and their surface area decreases, the local copolymer concentration increases until a critical copolymer surface coverage has been reached, stabilizing the droplets against further coalescence. The Epoxy/COOH reaction is known to be slower than the Anh/NH_2 reaction, which allows initial morphology coarsening; however, our results clearly show that it produces sufficient copolymer to ultimately stabilize the blends, as the blends remain stabilized after short annealing times.

Effects of Telechelic Loading. It is important to understand why the initial droplet size is not reduced with addition of telechelics. As discussed in the Introduction, one role of the copolymer is to reduce the interfacial tension of the minor-phase droplets and assist in their breakup by shear forces into a finer dispersion. However, our results show that the initial droplet size is actually larger in the 90% PS/10% PI blends with telechelics than in the uncompatibilized blend. One explanation for this is that the telechelics, except for 83k Anh-PS-Anh, have lower molecular weights than the homopolymers, 77k M_n for PS and 191k M_n for PI. This results in a decrease of the viscosity of the sample, which alters droplet formation during melt blending, where there is an equilibrium between the rate of droplet breakup by shear forces and recombination by coalescence. The final droplet size is predicted to be (41)

$$\frac{1}{R} = A\frac{\eta_a G}{\varphi_d \sigma} + \frac{B}{\sigma} \qquad (6)$$

where R is the droplet radius, η_a is the apparent blend viscosity, G is the shear rate, φ_d is the volume fraction of the dispersed phase, σ is the interfacial tension, A is a constant related to the coalescence probability, and B is a constant related to the macroscopic bulk breaking energy. Thus, even
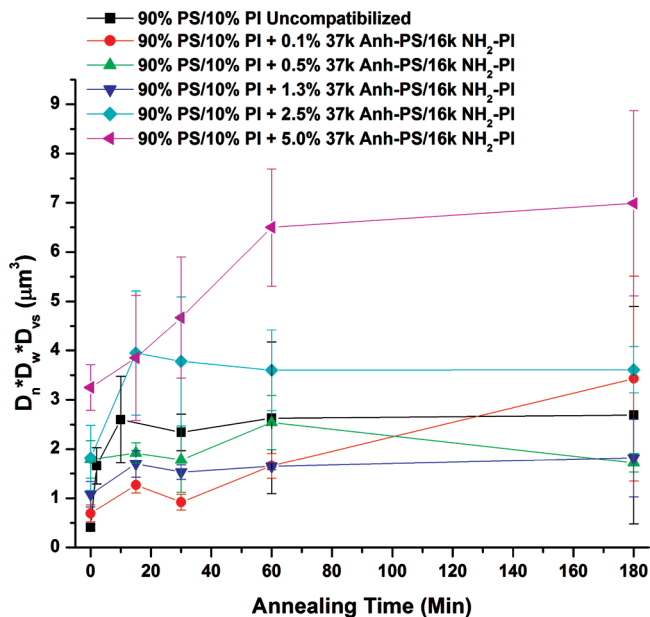
FIGURE 5. SEM results of $D_nD_wD_{vs}$ as a function of annealing time for 90% PS/10% PI polymer blends compatibilized with various amounts of 37k Anh-PS-Anh/16k NH$_2$-PI-NH$_2$ telechelics.

FIGURE 6. SEM results of the relative $D_nD_wD_{vs}$ as a function of annealing time for 90% PS/10% PI polymer blends compatibilized with various amounts of 37k Anh-PS-Anh/16k NH$_2$-PI-NH$_2$ telechelics.

though high-molecular-weight multiblock copolymers are being formed during mixing, any remaining unreacted telechelics remain in the homopolymers lowering η_a, acting as plasticizers. Equation 6 shows that lowering the viscosity makes coalescence easier, increasing droplet size.

A telechelic loading of 5.0 wt % was chosen as an initial loading for this study; however, the plasticizing effect of the unreacted telechelic chains can be reduced by lowering the amount of telechelics in the blend. Thus, a blend of 90% PS/ 10% PI compatibilized with 37k Anh-PS-Anh/16k NH$_2$-PI-NH$_2$ with a range of telechelic loadings (5.0, 2.5, 1.3, 0.5, and 0.1 wt %) was examined. The results of the compatibilization of this blend, melt-mixed at 180 °C for 10 min, are shown in Figure 5 as a plot of $D_nD_wD_{vs}$ as a function of annealing time and in Figure 6 as a plot of the relative D^3 as a function of annealing time.

Figure 5 shows that the initial size of the droplets is reduced as the telechelic loading decreases, as fewer unreacted telechelics acting as plasticizers are present in the blend. Figure 6 clearly demonstrates that reducing the telechelic loading to 1.3 and 0.5 wt % retains its ability to compatibilize the blend, as a large reduction in the growth of the droplets still occurs, yet the initial droplet size decreases. At these loading levels, there are sufficient telechelics present in the system for interfacial coverage of the droplets to prevent coalescence but also not enough to significantly plasticize the blend. When the telechelic loading is further reduced to 0.1 wt %, however, the coalescence is not suppressed, presumably because too few telechelics are available to saturate the interface and inhibit coalescence. The coarsening constants were determined for the data in Figures 5 and 6 and are shown in Table 4.

As previously discussed, $K_{rel}t_{stable}$ best quantifies the effectiveness of the compatibilizers. With the exception of the 0.1 wt % blend, which never achieved stabilization, Kt_{stable}
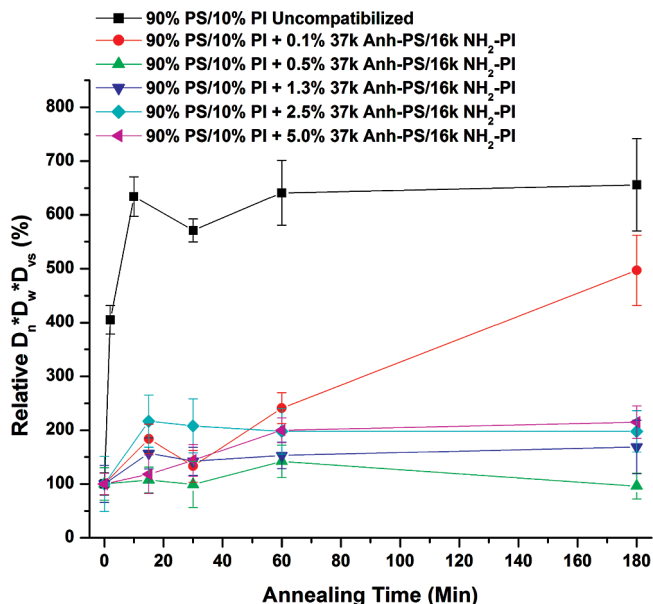
decreases as the telechelic loading is reduced. Since reducing the telechelic loading reduces the plasticization effect, the initial size of the droplets is also smaller. Thus, the increase in absolute size is also reduced. In relative terms, there was no significant difference between $K_{rel}t_{stable}$ for telechelic loadings of 5.0 and 2.5 wt %. When the loading was further reduced to 1.3 and 0.5 wt %, a significant decrease in absolute and relative size growth is observed, with the 0.5 wt % loading clearly showing the slowest growth. These results demonstrate the significant plasticization effects of the unreacted telechelics when large excesses are used. Figure 6 and Table 4 show that the optimal telechelic loading for 90% PS/10% PI with the 37k Anh-PS-Anh/16k NH$_2$-PI-NH$_2$ telechelic pair is 0.5 wt %.

At this loading level, the telechelics reduce the $K_{rel}t_{stable}$ value by a factor of approximately 80 and the absolute K value by a factor of approximately 25 relative to that of the uncompatibilized blend. In a study by Tao et al. (42), in a 90% PS/10% HDPE blend compatibilized with 3.5 wt % styrene–ethylene butylene–styrene (SEBS) triblock copolymer, the coarsening constant was reduced by a factor of only 1.7, and significant coarsening was still observed. When an 80% PS/20% HDPE blend was compatibilized with 10 wt % SEBS triblock copolymer, the K value was reduced by a factor of 45. Although we cannot make direct comparisons, our results show that multiblock copolymers formed in situ are very effective in suppressing droplet coalescence, as lower loading levels are required to achieve a similar reduction in K. This might be explained by the fact that a multiblock copolymer has a larger surface area at the biphasic interface than a di- or triblock copolymer, requiring lower loading levels to achieve the same interfacial coverage.

Surface Coverage. Additional insight into the process of coalescence suppression can be gained by determining the percent of the interface covered with multiblock copoly-

Table 4. Stabilization Time, Absolute Coarsening Constant Kt_{stable}, Relative Coarsening Constant $K_{rel}t_{stable}$, and R^2 of the Linear Fit of the Data for 90% PS/10% PI Blends with Various 37k Anh-PS-Anh/16k NH$_2$-PI-NH$_2$ Telechelic Loading

90% PS/10% PI 37k Anh-PS-Anh/16k NH$_2$-PI-NH$_2$ (%)	stabilization (min)	K (min)	Kt_{stable} (μm^3/min)	K_{rel} (%/min)	$K_{rel}t_{stable}$ (%)	R^2
5.0	60	6.6×10^{-2}	3.9	2.0	122	0.946
2.5	15	1.4×10^{-1}	2.1	7.8	117	1.000
1.3	15	4.1×10^{-2}	0.6	3.8	57	1.000
0.5	15	8.7×10^{-03}	0.1	4.7×10^{-1}	7	1.000
0.1	180[a]	1.5×10^{-2}	2.8	2.2	398	0.948
uncompatibilized	10	2.3×10^{-1}	2.3	5.7×10^1	572	0.737

[a] The blend was not stabilized, and values at 180 min were used in the calculations.

mers and this parameter's role in the compatibilization process. For a blend to be compatibilized, complete saturation of the interface is not required; there only need to be sufficient chains present at the interface to sterically hinder the droplets from recombining. Macosko reported that an interfacial coverage of ~20% by a 85k PS/PMMA diblock copolymer was sufficient to stabilize a blend of 70% PS/30% PMMA (13). Lyu reported that 80% interfacial coverage by a 20k PS/20k PE diblock copolymer, 40% interfacial coverage by a 50k PS/50k PE diblock copolymer, and 20% interfacial coverage by a 100k PS/100k PE diblock copolymer were needed to stabilize a system of 87% PS/13% HDPE (43).

Similar data for this system will further aid in using this process to compatibilize other systems. To determine the number of chains at the interface, it is assumed that all of the copolymer is located at the interface. With this assumption, the number of copolymer chains per nm^2 of interfacial area, Σ, can be calculated as (13)

$$\Sigma = \frac{\text{chains/vol}}{\text{interfacial area/vol}} = \frac{N_A \rho_{cop} \phi_{cop}}{M_{n,cop} S_{sp}} = \frac{N_A \rho_{cop} \phi_{cop} D_{vs}}{M_{n,cop} 6 \phi_{minor}} \quad (7)$$

where N_A is Avogadro's number, ρ_{cop} is the density of the copolymer, φ_{cop} is the volume fraction of the copolymer, $M_{n,cop}$ is the number average molecular weight of the copolymer, S_{sp} is the specific interfacial area, D_{vs} is the volume to surface area diameter, and φ_{minor} is the volume fraction of the minor phase. The density of the copolymer is calculated using the temperature-dependent density of PS (44)

$$1/\rho_{PS} = 0.9199 + (5.098 \times 10^{-4})T +$$
$$(2.354 \times 10^{-7})T^2 + [32.46 + 0.1017(T)]M_{w,PS} \quad (8)$$

and the temperature-dependent density of PI (45)

$$1/\rho_{PI} = 1.0771 + (7.22 \times 10^{-4})T + (2.346 \times 10^{-7})T^2 \quad (9)$$

where T is the temperature in °C and $M_{w,PS}$ is the weight-average molecular weight of polystyrene. The copolymer

molecular weight and the volume fraction of copolymer in the blend are determined by GPC with fluorescence detection.

The copolymer volume fraction is calculated as

$$\varphi_{cop} = \frac{\text{vol}_{\text{Anh-PS-Anh}} + \text{vol}_{\text{NH}_s\text{-PI-NH}_2}}{\text{total blend vol}} \quad (10)$$

where $\text{vol}_{\text{Anh-PS-Anh}}$ and $\text{vol}_{\text{NH}_2\text{-PI-NH}_2}$ are the volume of telechelics which have reacted to form the copolymer. The volume of the fluorescently labeled NH$_2$−PI-NH$_2$ in the copolymer is

$$\text{vol}_{\text{NH}_2\text{-PI-NH}_2} = Cm_{\text{NH}_2\text{-PI-NH}_2} \frac{1}{\rho_{PI}} \quad (11)$$

where C is the conversion of NH$_2$-PI-NH$_2$ into copolymer, $m_{\text{NH}_2\text{-PI-NH}_2}$ is the total mass of NH$_2$-PI-NH$_2$ in the blend, and ρ_{PI} is the density of PI at 180 °C. As the system is designed to contain stoichiometric amounts of equally reactive end groups, the number of moles of Anh-PS-Anh in the copolymer is equal to the moles of NH$_2$-PI-NH$_2$ in the copolymer. The volume of Anh-PS-Anh in the copolymer is therefore

$$\text{vol}_{\text{Anh-PS-Anh}} =$$
$$Cm_{\text{NH}_2\text{-PI-NH}_2} \frac{1}{M_{n,\text{NH}_2\text{-PI-NH}_2}} \frac{1.9 \text{ end groups NH}_2}{\text{mol of NH}_2\text{-PI-NH}_2} \times$$
$$\frac{1.6 \text{ end groups Anh}}{1.9 \text{ end groups NH}_2} \frac{1 \text{ mol Anh-PS-Anh}}{1.6 \text{ end groups Anh}} \times$$
$$M_{n,\text{Anh-PS-Anh}} \frac{1}{\rho_{\text{Anh-PS-Anh}}} \quad (12)$$

GPC with fluorescence detection (Supporting Information) can be used to determine the conversion of the PI telechelic into a multiblock copolymer. By calculation of the expected molecular weight and polydispersity index of the multiblock copolymers (46), the chromatogram can be deconvoluted and the conversion obtained. To prove the change in the chromatogram is not simply due to PI degradation, a sample of PI was melt-mixed under argon at 180 °C for times up to 60 min, the results of which (Supporting Information) indicate no significant degradation occurs.

To determine the percent of the interface that is covered by in situ formed copolymer, the maximum amount of interface that can be covered with the copolymer must be determined. The maximum interfacial coverage, Σ^*, expressed as number of copolymer chains per square nanometer of interfacial area (13), is given by

$$\Sigma^* = \frac{\text{thickness of copolymer monolayer}}{\text{vol/chain}} = \frac{h}{M_{n,cop}/\rho_{cop}N_A} \quad (13)$$

where h is the height of the copolymer across the interface. With maximum coverage, the copolymer will be in a stretched state to allow more chains to pack at the interface. In previous studies, the thickness of a diblock or graft copolymer layer in the stretched state is estimated to be half of the lamellar spacing of a symmetric diblock copolymer (13, 16, 47, 48), which is proportional to $M_n^{2/3}$. This calculation assumes the copolymer aligns perpendicular to the interface. However, Noolandi has shown that multiblock copolymers lie mostly flat in the interfacial plane, forming a pancake structure (17). Monte Carlo simulations have also shown that block copolymers have a larger radius of gyration (R_g) along the interfacial axis than across it, forming flat cylinder-shaped structures (3).

To the best of our knowledge, no experimental results of the maximum interfacial coverage using multiblock copolymers have been reported. To a first approximation, the copolymer can be treated as an isotropic chain (3), similar to PS. The height of a PS chain, h, is $2R_g$, where the radius of gyration of PS in the bulk, given in nm, is (49)

$$R_{g,PS} = 0.029M_w^{0.5} \quad (14)$$

This approximation places no restriction on the chain conformation. In order to account for the cylindrical shape of the copolymer at the interface, the extension of a chain across the interface is restricted such that half of each block expands into its respective bulk phase. Half of a PS block and half of a PI block (one diblock equivalent) are therefore used to estimate R_g using eq 14, which is the corresponding height of the flat cylinder that the copolymer occupies at the interface. A pictorial depiction of this structure is shown in Figure 7.

This geometric restriction decreases Σ^* and conversely increases $1/\Sigma^*$, the surface area per chain. Since the chain is more compressed in a cylindrical shape along the interfacial plane, each copolymer chain occupies a larger interfacial area. Thus fewer multiblock copolymers are needed to saturate an interface relative to di- and triblock copolymers.

The value Σ/Σ^* represents the percent of interface that is covered. As the samples are annealed, the PI droplets coalesce, decreasing the amount of surface area present. Thus, there is less available interfacial area to cover as the droplets recombine and, correspondingly, Σ/Σ^* increases
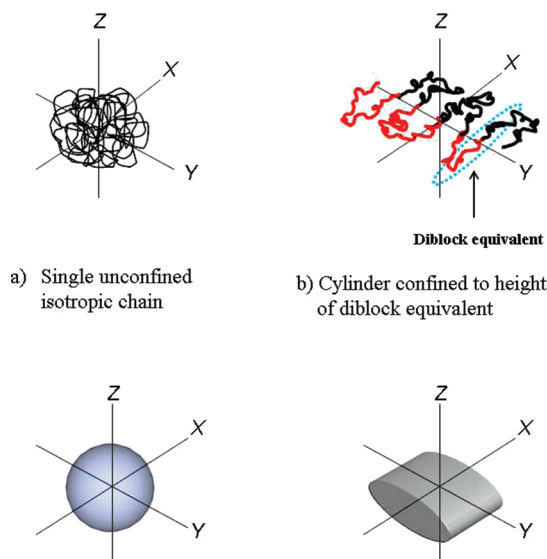

FIGURE 7. When a multiblock copolymer is treated as a single isotropic chain without geometric confinement, its shape is spherical, similar to that depicted in (a). Restricting the width to twice the R_g value of one diblock equivalent in the chain will result in a flattened cylindrical shape, as seen in (b).

with annealing time. The accurate determination of the conversion of telechelics into copolymer and their corresponding molecular weight is currently problematic. The extraction of the copolymer with a selective solvent (n-hexane) was attempted; however, the results were not reproducible for different samples of the same blend. However, the conversion required for stabilization can be determined, which provides insight into this process. The copolymer molecular weight in the equation for Σ and Σ^* cancel each other out, and this value is therefore not required. Using Macosko's results as a guide, we can estimate that 20% interfacial coverage is required for stabilization, and we can calculate the conversion necessary for this coverage. The conversion required at 5.0 wt % telechelic loading for 20% surface coverage of both the initial droplet size and stabilized droplet size are shown in Table 5.

Table 5 shows that, in order to stabilize the droplets at their initial size, a conversion of $\sim 1.5 - 2.5\%$ is required for the Anh/NH$_2$ blends and $\sim 3\%$ is required for the Epoxy/COOH reactive pairs. A larger conversion is required for the latter pair because the initial droplet size is smaller, yielding a larger interfacial area that must be covered. As the blends are annealed, the PI droplets coalesce, reducing their surface area. That is, less copolymer is needed to cover the interfacial area because the area itself has been reduced and Σ/Σ^* increases. The results show a conversion of $\sim 1 - 1.5\%$ is sufficient to stabilize the Anh/NH$_2$ blends, and about 2% conversion is required for the stabilization of the Epoxy/COOH blends. Since the latter pair is of lower reactivity than the former, these results indicate that the stabilized blends have a conversion greater than 2%.

The conversion required for 20% coverage at various loading levels of 37k Anh-PS-Anh/16k NH$_2$-PI-NH$_2$ has also been calculated, and the results are shown in Table 6.

The results in Table 6 show that, even for telechelic loading as low as 0.5 wt %, only a moderate level of

Table 5. Conversion at 5.0 wt % Telechelic Loading Required for a Surface Coverage of 20% of the Initial Droplet Size and Stabilized Droplet Size

90% PS/10% PI 5.0 wt % telechelics	D_{vs}(0 min) (μm)	C needed for 20% coverage (%)	stabilization time (min)	D_{vs}(stable) (μm)	C needed for 20% coverage (%)
16k Anh-PS-Anh/16k NH$_2$-PI-NH$_2$	1.92	1.3	180[a]	2.88	0.9
37k Anh-PS-Anh/16k NH$_2$-PI-NH$_2$	1.88	1.3	60	2.38	1.0
37k Anh-PS-Anh/32k NH$_2$-PI-NH$_2$	1.54	2.3	60	2.06	1.7
83k Anh-PS-Anh/32k NH$_2$-PI-NH$_2$	1.72	2.7	180[a]	2.59	1.8
18k Epoxy-PS-Epoxy/20k COOH-PI-COOH	0.84	3.0	180[a]	2.61	1.0
44k Epoxy-PS-Epoxy/20k COOH-PI-COOH	1.11	2.8	15	1.34	2.3
44k Epoxy-PS-Epoxy / 54k COOH-PI-COOH	1.25	3.0	30	1.71	2.4

[a] The blend was never stabilized, and D_{vs} at 180 min of annealing was used in the calculation.

Table 6. Conversion at Various 37k Anh-PS-Anh/16k NH$_2$-PI Telechelic Loading Required for a Surface Coverage of 20% of the Initial Droplet Size and Stabilized Droplet Size

90% PS/10% PI 37k Anh-PS-Anh/16k NH$_2$-PI-NH$_2$ (%)	D_{vs}(0 min) (μm)	C needed for 20% coverage (%)	stabilization time (min)	D_{vs}(stable) (μm)	C needed for 20% coverage (%)
5.0	1.88	1.3	60	2.38	0.9
2.5	1.34	3.3	30	1.86	2.3
1.3	1.12	7.4	15	1.35	6.1
0.5	1.39	14.5	15	1.43	14.1
0.1	0.93	117.5	180[a]	2.02	54.1

[a] The blend was never stabilized, and D_{vs} at 180 min of annealing was used in the calculation.

conversion is required for 20% surface coverage. It is evident that the 0.1 wt % loading sample cannot stabilize the blend, since the amount of telechelics required for stabilization is ~20% more than is present. The conversion required decreases as the blend is annealed and the droplets coalesce. The 0.1 wt % sample was not stable even after 180 min of annealing, so this calculation shows that the conversion is less than the 54% required for stabilizing a droplet of that size. At 0.5 wt % loading, the conversion required for 20% coverage of the stabilized blend is virtually the same as the initial droplet size. This shows the droplets can be rapidly stabilized due to the high reactivity of the Anh/NH$_2$ pair and the reduced plasticization effect of lower loading levels discussed earlier. This also implies that the 37k Anh-PS-Anh/16k NH$_2$-PI-NH$_2$ system can achieve over 15% conversion in 10 min of melt blending at 180 °C and 100 rpm. The results show that the initial 5.0 wt % telechelic loading was excessive; only ~1% of the telechelics was required to react for 20% coverage, while the rest acted as plasticizers that decreased the viscosity of the blend, leading to a larger initial droplet size. Decreasing the telechelic loading decreased the initial droplet size as the plasticization effect was reduced. A concentration of 0.5 wt % telechelics provides the optimal loading level for this system. At this amount, the plasticization effect is minimized while enough telechelics are present for sufficient conversion.

CONCLUSION

We have proven that difunctional reactive polymers with Anh/NH$_2$ and Epoxy/COOH complementary end groups form multiblock copolymers in situ at the interface between immiscible PS and PI homopolymers via melt blending. By using SEM to measure the minor phase domain size upon sample annealing, we have shown that these copolymers compatibilize the blend by sterically hindering droplet coalescence. To quantify the copolymer's ability to inhibit coalescence, the coarsening constant K for a variety of blends composed of 5.0 wt % telechelic pairs of various molecular weights was determined. The most accurate way to quantify the effectiveness of the telechelics is to analyze $K_{rel}t_{stable}$. Both reactive pairs suppressed coalescence similarly at 5.0 wt % loading, with the optimal molecular weight pairs being slightly above the critical molecular weight of the polymer, M_c. When the telechelic molecular weight is slightly above M_c, the analogous copolymer blocks can become well entangled with the homopolymer and sterically hinder coalescence. Concomitantly, this chain length is low enough to exhibit favorable characteristics of low-molecular-weight telechelics: namely, a high end group concentration and the ability to quickly approach the interface.

The larger initial droplet size observed in the compatibilized blends is due to the plasticization effect of the unreacted telechelics. The blend viscosity is reduced by adding these low-molecular-weight telechelics, making coalescence easier. Variable telechelic loading experiments on the 37k Anh-PS-Anh/16k NH$_2$-PI-NH$_2$ pair showed that 0.5 wt % telechelics yielded the lowest $K_{rel}t_{stable}$ value. At this loading level, there is a sufficient quantity of telechelics to react and form multiblock copolymers, but the concentration is low enough to minimize plasticization effects.

The absolute and relative specific interfacial area of blends provided complementary data to the coarsening constant calculations. These results show that the four most effective pairs lose ~15−25% of their interfacial area before stabilization. The telechelic loading studies on the 37k Anh-PS-Anh/16k NH$_2$-PI-NH$_2$ system show that 0.5 wt % loading results in a relative specific interfacial area loss of only 3%.

Further analysis indicates that only ~1.5−3.0 % conversion was required to attain 20 % interfacial coverage of multiblock copolymers at 5.0 wt % telechelic loading, indicating that a large excess of telechelics was used. In the reduced loading experiments, a conversion of ~15 % was required for the optimal 0.5 wt % loading.

Supporting Information Available: Graphs of the specific surface area (SA) and relative SA of blends containing 5.0 wt % telechelics, a table of the relative SA at t_{stable} for blends with 5.0 wt % telechelics, a graph of GPC with fluorescence detection of blend components, and a graph of GPC with fluorescence detection of the PI melt mixed for various times. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES

(1) Koning, C.; van Duin, M.; Pagnoulle, C.; Jerome, R. *Prog. Polym. Sci.* **1998**, *23*, 707.
(2) Paul, D. R. Background and Perspective. In *Polymer Blends*; Paul, D. R., Newman, S., Eds.; Academic Press: New York, 1978; Vol. 1.
(3) Dadmun, M. *Macromolecules* **1996**, *29*, 3868.
(4) Eastwood, E. A.; Dadmun, M. D. *Macromolecules* **2002**, *35*, 5069.
(5) Molau, G. E. *J. Polym. Sci. Part A: Polym. Chem.* **1965**, *3*, 4235.
(6) Hu, W.; Koberstein, J. T.; Lingelser, J. P.; Gallot, Y. *Macromolecules* **1995**, *28*, 5209.
(7) Leibler, L. *Makromol. Chem., Macromol. Symp.* **1988**, *16*, 1.
(8) Anastasiadis, S. H.; Gancarz, I.; Koberstein, J. T. *Macromolecules* **1989**, *22*, 1449.
(9) Favis, B. D. *Polymer* **1994**, *35*, 1552.
(10) Karam, H. J.; Bellinger, J. C. *Ind. Chem. Eng. Fundam.* **1968**, *7*, 576.
(11) Crist, B.; Nesarikar, A. *Macromolecules* **1995**, *28*, 890.
(12) Sundararaj, U.; Macosko, C. W. *Macromolecules* **1995**, *28*, 2647.
(13) Macosko, C. W.; Guegan, P.; Khandpur, A. K.; Nakayama, A.; Marechal, P.; Inoue, T. *Macromolecules* **1996**, *29*, 5590.
(14) Orr, C. A.; Adedeji, A.; Hirao, A.; Bates, F. S.; Macosko, C. W. *Macromolecules* **1997**, *30*, 1243.
(15) Guegan, P.; Macosko, C. W.; Ishizone, T.; Hirao, A.; Nakahama, S. *Macromolecules* **1994**, *27*, 4993.
(16) Jeon, H. K.; Zhang, J.; Macosko, C. W. *Polymer* **2005**, *46*, 12422.
(17) Noolandi, J. *Makromol. Chem., Theor. Simul.* **1992**, *1*, 295.
(18) Balazs, A. C.; Siemasko, C. P.; Lantman, C. W. *J. Chem. Phys.* **1991**, *94*, 1653.
(19) Smith, G. D.; Zhang, Y.; Yin, F.; Bedrov, D.; Dadmun, M. D.; Huang, Z. *Langmuir* **2006**, *22*, 664.
(20) Alonzo, J.; Huang, Z.; Liu, M.; Mays, J. W.; Toomey, R. G.; Dadmun, M. D.; Kilbey, S. M., II *Macromolecules* **2006**, *39*, 8434.
(21) Huang, Z.; Ji, H.; Mays, J. W.; Dadmun, M. D. *Macromolecules* **2008**, *41*, 1009.
(22) Huang, Z.; Alonzo, J.; Liu, M.; Ji, H.; Yin, F.; Smith, G. D.; Mays, J. W.; Kilbey, S. M., II; Dadmun, M. D. *Macromolecules* **2008**, *41*, 1745.
(23) Lyu, S.-P. *Macromolecules* **2003**, *36*, 10052.
(24) Fortelny, I.; Zivny, A. *Polymer* **1998**, *39*, 2669.
(25) Hsu, J.-P.; Lin, D.-P.; Tseng, S. *Colloid Polym. Sci.* **1995**, *273*, 271.
(26) Yin, Z.; Koulic, C.; Jeon, H. K.; Pagnoulle, C.; Macosko, C. W.; Jerome, R. *Macromolecules* **2002**, *35*, 8117.
(27) Cernohous, J. J.; Macosko, C. W.; Hoye, T. R. *Macromolecules* **1997**, *30*, 5213.
(28) Quirk, R. P.; Lee, Y. *Macromol. Symp.* **2000**, *157*, 161.
(29) Quirk, R. P.; Zhuo, Q. *Macromolecules* **1997**, *30*, 1531.
(30) Ji, H.; Nonidez, W. K.; Advincula, R. C.; Smith, G. D.; Kilbey, S. M., II; Dadmun, M. D.; Mays, J. W. *Macromolecules* **2005**, *38*, 9950.
(31) Ji, H. N.; Farmer, B. S.; Nonidez, W. K.; Advincula, R. C.; Smith, G. D.; Kilbey, S. M., II; Dadmun, M. D.; Mays, J. W. *Macromol. Chem. Phys.* **2007**, *208*, 807.
(32) Yang, J.; Lu, J.; Winnik, M. *J. Polym. Sci. Part A: Polym. Chem.* **2003**, *41*, 1225.
(33) Orr, C. A. Reactive Compatibilization of Polymer Blends; University of Minnesota, 1997.
(34) Orr, C.; Cernohous, J.; Guegan, P.; Hirao, A.; Jeon, H.; Macosko, C. *Polymer* **2001**, *42*, 8171.
(35) Padwa, A.; Sasaki, Y.; Wolske, K.; Macosko, C. *J. Polym. Sci. Part A: Polym. Chem.* **1995**, *33*, 2165.
(36) Mirabella Jr, F. M. *J. Polym. Sci. Part B: Polym. Phys.* **1994**, *32*, 1205.
(37) Maric, M.; Macosko, C. W. *J. Polym. Sci. Part B: Polym. Phys.* **2002**, *40*, 346.
(38) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, U.K., 1986.
(39) Creton, C.; Kramer, E. J.; Hadziioannou, G. *Macromolecules* **1991**, *24*, 1846.
(40) Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirkel, A. *Macromolecules* **1994**, *27*, 4639.
(41) Zhang, Z.; Qiao, J. *Polym. Eng. Sci.* **1991**, *31*, 1553.
(42) Tao, Y.; Lebovitz, A. H.; Torkelson, J. M. *Polymer* **2005**, *46*, 4753.
(43) Lyu, S.-P.; Jones, T. D.; Bates, F. S.; Macosko, C. W. *Macromolecules* **2002**, *35*, 7845.
(44) Richardson, M. J.; Savill, N. G. *Polymer* **1977**, *18*, 3.
(45) Han, C. D.; Kim, J.; Kim, J. K. *Macromolecules* **1989**, *22*, 383.
(46) Shiau, L.-D. *Macromol. Theory Simul.* **2001**, *10*, 179.
(47) Yin, Z.; Koulic, C.; Pagnoulle, C.; Jerome, R. *Langmuir* **2003**, *19*, 453.
(48) Charoensirisomboon, P.; Inoue, T.; Weber, M. *Polymer* **2000**, *41*, 4483.
(49) *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1989.

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