

Synthesis and application of styrene/4-hydroxystyrene gradient copolymers made by controlled radical polymerization: Compatibilization of immiscible polymer blends via hydrogen-bonding effects

Jungki Kim^a, Hongying Zhou^b, SonBinh T. Nguyen^b, John M. Torkelson^{a,c,*}

^a Department of Chemical and Biological Engineering, Northwestern University, Evanston, IL 60208-3120, USA

^b Department of Chemistry, Northwestern University, Evanston, IL 60208-3120, USA

^c Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208-3120, USA

Received 10 April 2006; received in revised form 14 June 2006; accepted 14 June 2006

Available online 7 July 2006

Abstract

Styrene (S)/4-hydroxystyrene (HS) copolymers are synthesized by hydrolysis of S/4-acetoxystyrene copolymer precursors; two gradient copolymer precursors are made by semi-batch, nitroxide-mediated controlled radical polymerization, and a random copolymer precursor is prepared by conventional free radical polymerization. Conventional heat curves from differential scanning calorimetry indicate two glass transition temperatures (T_g s) and a broad T_g in well-annealed 59/41 mol% and 25/75 mol% S/HS gradient copolymers, respectively, both of which contain short S end-blocks. In contrast, a narrow T_g is observed in a 57/43 mol% random copolymer. Each S/HS copolymer is added at 5 wt% by solution mixing to an 80/20 wt% polystyrene (PS)/polycaprolactone (PCL) blend and tested for its ability to compatibilize the blend during melt processing; the hydroxyl groups on the HS units can form hydrogen bonds with the PCL ester groups. The S/HS random copolymer fails as a compatibilizer while both gradient copolymers are good compatibilizers. Relative to the blend without copolymer, the blend with 59/41 mol% S/HS gradient copolymer also exhibits a major reduction in initial dispersed-phase domain size and irregularly shaped domains, which are indicators of a sharply reduced interfacial tension. In contrast, the blend with 25/75 mol% S/HS gradient copolymer has an average PCL domain size comparable to the blend without copolymer and a broad domain size distribution. The presence of S/HS copolymers in the blend leads to reduced PCL crystallization and melting temperatures as well as reduced enthalpies of crystallization and melting, consistent with some solubilization of copolymer in the PCL domain interiors.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Gradient copolymer; Compatibilization; Hydrogen bond

1. Introduction

Blending two or more immiscible polymers has the potential to lead to synergistic material properties. A common requirement for this potential to be realized is that the interparticle distance between dispersed-phase domains is maintained below a value called the critical ligament thickness [1,2]. In

turn, this usually means that the average dispersed-phase diameter must be maintained to be less than a few microns [1–4]. Hence, stabilization of the dispersed-phase domain size against melt-state coarsening, taken as the criterion for compatibilization [5], is important in processing immiscible polymer blends.

Accordingly, many compatibilization strategies have been studied. In particular, addition of various types of copolymer (e.g., *block* [3,5–13], tapered *block* [14,15] and *graft* [9,16,17]) during melt processing has been heavily examined and shown to be successful in small-scale (although not large-scale [3]) studies. Addition of *block* copolymer to immiscible blends

* Corresponding author. Department of Chemical and Biological Engineering, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208-3120, USA.

E-mail address: j-torkelson@northwestern.edu (J.M. Torkelson).

during solid-state shear pulverization (SSSP) has recently been shown to achieve compatibilization [18]. Reactive blending involving in situ formation of *block* or *graft* copolymers during melt processing [13,19–21] or SSSP [22,23] has also yielded compatibilization. Regardless of the presence or absence of specific attractive interactions between the added copolymer and any of the blend components, it is well appreciated that interfacial *block* and *graft* copolymers can reduce interfacial tension and provide steric hindrance to dispersed-phase coalescence [3–29].

The advent and development of controlled radical polymerization (CRP) have offered the possibility of synthesizing new classes of polymers with well-defined molecular structure [30–39]. Among others, CRP can produce statistical or random copolymers with narrower molecular weight distribution [30,31] than conventional free radical polymerization (ConvFRP) and *block* copolymers that cannot be made by anionic polymerization (e.g., copolymers with 4-acetoxystyrene blocks [39,40]). In contrast to anionic polymerization, CRP can yield gradient copolymers with a gradual change in composition along the chain. The nature of CRP, providing for both long propagating radical lifetimes and a broad array of co-monomers that can cross-propagate, allows for the formation of gradient copolymers by modifying as a function of time the co-monomer composition in a copolymerization reaction mixture [32–38]. (Anionic methods do not yield gradient copolymers with batch or semi-batch polymerization due to the very large differences of reactivity ratios associated with anionic copolymerization.) Gradient copolymers are expected to be highly effective compatibilizers when added to immiscible blends during melt processing due to a much higher critical micelle concentration and better interfacial activity than *block* copolymers of the same composition [41]. A study demonstrating enhanced interfacial activity of gradient copolymers, as compared with random or *block* copolymers, supports these expectations [42]. Using a polystyrene/poly(methyl methacrylate) blend and styrene/methyl methacrylate gradient copolymers, we recently provided the first demonstration that blend compatibilization can be achieved by gradient copolymer addition during melt processing [43].

Here we provide experimental results on the application of gradient copolymers made by nitroxide-mediated controlled radical polymerization (NM-CRP) in compatibilizing a polymer blend in which a favorable thermodynamic interaction, hydrogen bonding, exists between the dispersed phase and one of the repeat units of the added gradient copolymer. In other words, our study involves the compatibilization of an A/B polymer blend by an A/C gradient copolymer where the B and C repeat units can participate in hydrogen bonding [24–26]. We add low levels (5 wt% relative to total blend weight) of styrene/4-hydroxystyrene gradient copolymer to immiscible 80/20 wt% polystyrene/polycaprolactone blends. (The 4-hydroxystyrene repeat units, also called 4-vinyl phenol repeat units, are known to form hydrogen bonds with the oxygen atoms in the ester groups in the polycaprolactone [44–50].) The effects of gradient copolymer addition on initial dispersed-phase domain size and coarsening during

high-temperature static annealing are studied as a function of gradient copolymer composition and are compared to results obtained with addition of S/HS random copolymer. We find that added S/HS gradient copolymers are effective in the suppression of PCL domain coarsening during static, high-temperature annealing, i.e., in achieving compatibilization, while added S/HS random copolymers do not compatibilize PS/PCL blends.

We also present the non-isothermal crystallization and melting behavior of PCL domain in each PS/PCL blend. The added S/HS copolymers exhibit strikingly different degrees of impact on the crystallization and melting behavior of the PCL dispersed phase as a function of the detailed copolymer structure. We also note that irregular, non-spherical dispersed-phase domains are formed in the 80/20 wt% PS/PCL blends compatibilized with low levels of S/HS gradient copolymers and that the irregular interfaces remain stable during high-temperature annealing. Finally, given the multi-step nature of the production of S/HS gradient copolymers via hydrolysis of S/4-acetoxystyrene gradient copolymers, we also provide descriptions of the synthesis and characterization of the gradient copolymers.

2. Experimental section

2.1. Materials and methods

Styrene (Aldrich, 99%) and 4-acetoxystyrene (AS, Aldrich, 96%) were deionized using *tert*-butylcatechol inhibitor remover and dried over CaH₂ before use. The unimolecular initiator A-T (*N*-(α -methylbenzyloxy)-di-*tert*-butylamine) was synthesized as previously reported [37,38,51], and AIBN (Aldrich) was used as received. Polystyrene (Pressure Chemical; nominal $M_w = 30,000$ g/mol) and polycaprolactone (Aldrich; nominal $M_w = 80,000$ g/mol) were used as received for the major and the minor phases of the blends, respectively.

Apparent number-average and weight-average molecular weights (M_n and M_w) of S/AS copolymers were determined by gel permeation chromatography (GPC, Waters Breeze Instrument) relative to PS standards. Tetrahydrofuran (THF) was the eluent and the GPC columns were maintained at 30 °C. The GPC is equipped with a refractive index (RI) detector (Waters 2410 differential refractometer) and a fluorescence (FL) detector (Waters 474 scanning fluorescence spectrometer) in series. Copolymer compositions were measured using ¹H NMR spectroscopy (Varian Inova 500 MHz) using CDCl₃ as solvent. The peak integral values from NMR spectra associated with aromatic hydrogens (m, 9H, 6.2–7.3 ppm) and all other hydrogens (m, 9H, 1.2–2.4 ppm) were compared to determine each S/AS copolymer composition.

2.2. Synthesis of pyrene-labeled PS macroinitiator (*PS)

In a test tube, S (25 ml; 0.219 mol) and pyrene-labeled methacrylate monomer [23,52,53] (1-pyrenylmethyl methacrylate; 0.14 mol% relative to S monomer) were combined with A-T (0.03 g; 5.0×10^{-3} mol/l). The test tube was sealed

with a rubber stopper and paraffin film, then placed in an oil bath at 90 °C for 180 min after being purged with N₂. The resulting pyrene-labeled PS (*PS) was washed via several cycles of dissolution in THF and precipitation with methanol. After drying under vacuum for a day, *PS was found via GPC to have $M_n = 8400$ g/mol, $M_w/M_n = 1.27$ (RI detector) and $M_n = 8700$ g/mol, $M_w/M_n = 1.25$ (FL detector; $\lambda_{ex} = 335$ nm, $\lambda_{em} = 395$ nm for pyrene detection). The *PS was used as the macroinitiator for subsequent chain extensions to produce S/AS gradient copolymers.

2.3. Synthesis of S/AS copolymers

Semi-batch chain extension of *PS was employed to synthesize S/AS gradient copolymers. For the gradient copolymer with 0.59 cumulative S mole fraction (F_S), *PS (0.1099 g) was combined with S (10 ml; 0.0874 mol) in a test tube, purged with N₂ for 30 min, and then AS was added at a constant rate of 0.05 ml/min into the test tube. The reaction temperature was maintained at 90 °C, and dry N₂ was blown into the test tube throughout the reaction. The reaction was quenched after 240 min. Aliquots (~1 ml) of the reaction mixture were taken at 60 and 150 min of reaction time for GPC and ¹H NMR analyses. The final copolymer was washed by several cycles of dissolution (THF) and precipitation (methanol) and dried under vacuum.

The S/AS gradient copolymer with $F_S = 0.25$ was synthesized using a similar method; *PS (0.1073 g) was dissolved in the mixture of S (7 ml; 0.0808 mol) and AS (3 ml; 0.0196 mol) in a test tube and purged with N₂ for 30 min. A constant flow rate of 0.07 ml/min of AS was introduced via a syringe pump into the test tube placed in an oil bath at 90 °C. The reaction was conducted at 90 °C for 240 min. Aliquots were taken at 60 and 150 min of reaction time and the final product was washed and dried as described above.

A S/AS random copolymer ($F_S = 0.57$) was made by conventional, batch free radical polymerization. A mixture of S (10 ml; 0.0874 mol) and AS (7.2 ml; 0.0471 mol) was combined with the initiator AIBN (0.040 g) in a test tube. Following a 30 min N₂ purge, reaction was carried out at 80 °C for 10 min to maintain low conversion (3.7% by gravimetry), thereby preventing drift in copolymer composition. The copolymer was washed and dried as described above.

2.4. Hydrolysis of S/AS copolymers

All S/AS copolymers were hydrolyzed to obtain S/HS copolymers following procedures in Ref. [54]. Each copolymer was dissolved in a flask containing a 9:1 v/v 1,4-dioxane/hydrazine hydrate mixture, which was stirred under N₂ for 6–7 h at room temperature. Hydrolyzed product was collected after washing several times with deionized water and placed under vacuum at room temperature for 3 days [38,40,54]. Complete hydrolysis of each copolymer was verified by NMR analysis, which revealed the disappearance of the acetoxy hydrogen peak near 2.28 ppm.

2.5. Thermal characterization of S/HS copolymers

Differential scanning calorimetry (DSC, Mettler-Toledo DSC 822e) was used to characterize the T_g s of the S/HS copolymers. Each copolymer (2–5 mg) was placed in a sealed aluminum pan. Dry N₂ was purged (50–55 ml/min) through the DSC cell during measurements. The copolymer samples were heated at a rate of 10 °C/min to 210 °C and held at this temperature for 15 min to erase thermal history. The samples were then cooled to 25 °C at a rate of 40 °C/min and reheated to 210 °C (10 °C/min; second heat) at which temperature the samples were annealed for 180 min. After annealing, samples were cooled to 25 °C at a rate of 40 °C/min before being reheated to 210 °C (10 °C/min; third heat).

2.6. PS/PCL blends – preparation and characterization of coarsening

Blend compositions were fixed at 80 wt% overall styrene content regardless of the presence or absence of S/HS copolymer. A total of 0.8 g of dry polymer mixture was dissolved in 1,4-dioxane followed by precipitation into rapidly stirred methanol. The powdery precipitate was isolated by filtering and dried under vacuum at 60 °C for a day and then further dried at 120 °C under vacuum for a few hours to remove any residual solvent. Melt processing of each pre-mixed and precipitated blend was done at 210 °C in a cup-and-rotor mixer (Atlas Electronic Devices MiniMAX molder) for 5 min at 120 rpm rotor speed with three steel balls [5,43] in the cup. Samples were collected by spatula and rapidly quenched in liquid N₂. Static annealing of blend samples (30–40 mg) was done using DSC by raising the temperature from 25 °C to 210 °C (40 °C/min) and holding at temperature for 30, 90 or 240 min.

Scanning electron microscopy samples were obtained by cryo-fracture in liquid N₂ and dipping into acetic acid to remove the dispersed PCL phase. A 3 nm layer of Au/Pd was coated onto the sample surface, and the morphology was observed using a Hitachi S3500N SEM. A total of 260–720 particles (dispersed-phase domains) per sample were analyzed using Scion Image Beta 4.0.2 software to determine the number-average dispersed-phase diameter. In those cases in which the dispersed-phase domain was non-spherical, the diameter value corresponds to that of a circle with same area, as calculated from 2-dimensional image analysis by the software.

2.7. Thermal analysis of blend samples

For crystallization and melting characterization of PCL domains in all PS/PCL blend sets, the sample of each blend (5–10 mg) was heated using DSC to 210 °C and held for 30 min to erase thermal history. Then samples were cooled to –20 °C at a rate of 20 °C/min to obtain non-isothermal crystallization curves and held at this temperature for 3 min before being reheated to 210 °C at a rate of 10 °C/min to obtain melting curves.

3. Results and discussion

3.1. Gradient and random copolymer characterization

Table 1 provides the characterization of apparent molecular weight (MW) and overall styrene mole fraction for the S/4-acetoxystyrene and S/HS gradient and random copolymers synthesized in this study. One gradient copolymer and the random copolymer have nearly identical overall styrene mole fractions ($F_S = 0.59$ for SgradHS1 and $F_S = 0.57$ for SranHS); a second gradient copolymer has a much lower styrene mole fraction ($F_S = 0.25$ for SgradHS2). The apparent M_n and M_w values are roughly similar in the several copolymers. These materials allow for a determination of the effects of copolymer type and overall styrene composition on the effectiveness of S/HS copolymers as compatibilizers in PS/PCL blends where hydrogen-bonding effects are possible between the HS units in the copolymer and the ester groups in the PCL.

The proof of gradient structure of SgradHS1 is provided in Fig. 1(a) and that of SgradHS2 is provided in Fig. 1(b). In each figure, the cumulative styrene mole fraction of each aliquot is determined by ^1H NMR; one data set (given by squares) uses GPC with refractive index detection while a second data set (given by circles) uses GPC with fluorescence detection (set to be sensitive to the pyrene label on the short PS macroinitiator used as the starting point for gradient copolymer synthesis) to determine apparent normalized chain length. The gradient structure of each copolymer is proven by the fact that the value of cumulative styrene mole fraction decreases as the normalized chain length (calculated from the apparent M_n of each aliquot and final copolymer) increases, regardless of the choice of GPC detector. Since the fluorescence detector of the GPC senses only the pyrene moieties covalently attached at low levels to the PS macroinitiator, the discrepancy between the data from the refractive index and fluorescence detectors reflects contributions from copolymer chains that may arise from thermal initiation [55] and/or copolymer chains that may have experienced free radical termination [55–57] during the semi-batch chain extension process in which the copolymer is made by continuous addition of 4-acetoxystyrene monomer. While these non-ideal effects do not interfere significantly with the formation of a gradient structure in the copolymers, they likely contribute to the polydispersity of the resulting copolymers.

By using a pyrene-labeled, low MW PS macroinitiator (abbreviated as *PS) for gradient copolymer syntheses, we

Table 1
Apparent molecular weight and cumulative styrene mol fraction (F_S) data for S/HS copolymers

Copolymers	Apparent M_n^a	M_w/M_n^a	F_S^b
SranHS	48,000	1.79	0.57
SgradHS1	60,100	1.70	0.59
SgradHS2	65,600	1.77	0.25

^a Analysis by GPC refractive index detector on S/AS copolymer precursors.

^b Analysis by ^1H NMR on S/AS copolymer precursors.

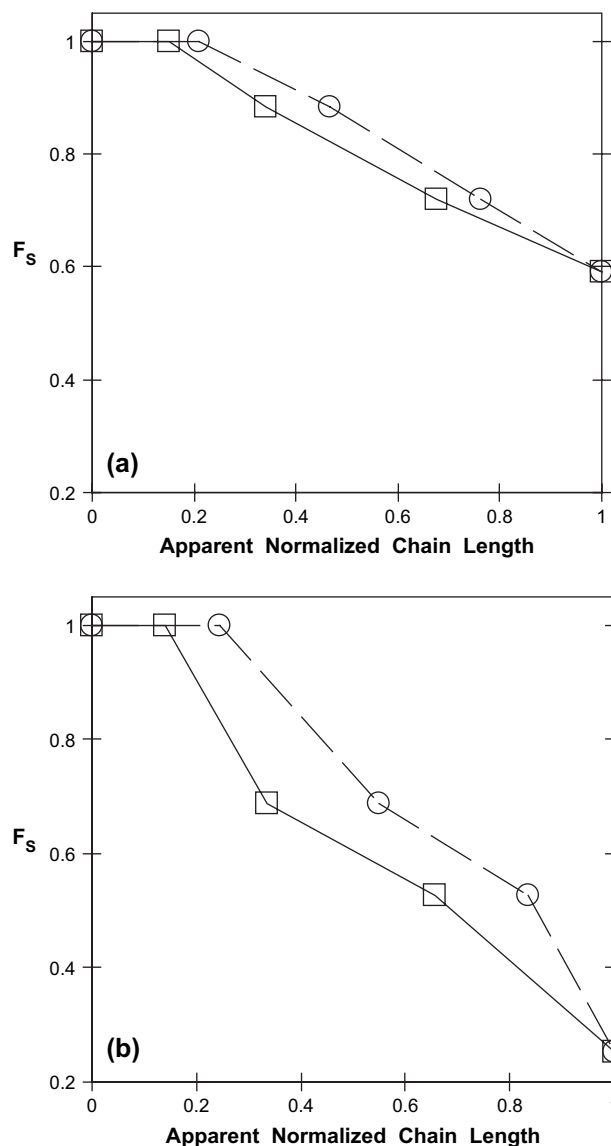


Fig. 1. Evolution of cumulative styrene mole fraction, F_S , of gradient copolymers as a function of normalized chain length (squares: GPC with refractive index detection; circles: GPC with fluorescence detection set to the pyrene label) for (a) SgradHS1 and (b) SgradHS2. F_S and GPC data are taken from the S/AS precursor copolymers which undergo 100% hydrolysis of acetoxy functionalities to yield S/HS copolymers.

are also able to quantify approximately the portion of inactive (dead) macroinitiator and/or chains terminated early during the semi-batch chain extension. Fig. 2 compares the GPC chromatograms of *PS (results from the refractive index and fluorescence detectors are nearly indistinguishable) with the GPC chromatogram of SgradAS1 (from which SgradHS1 was made via hydrolysis) using the refractive index detector and the GPC chromatogram of SgradAS1 using the fluorescence detector with sensitivity set to pyrene. (As SgradHS copolymer is made directly by hydrolysis of SgradAS copolymer, comparisons made on SgradAS copolymers yield comparisons of SgradHS copolymers.)

The growth of the macroinitiator during the production of gradient copolymer via chain extension is manifested from

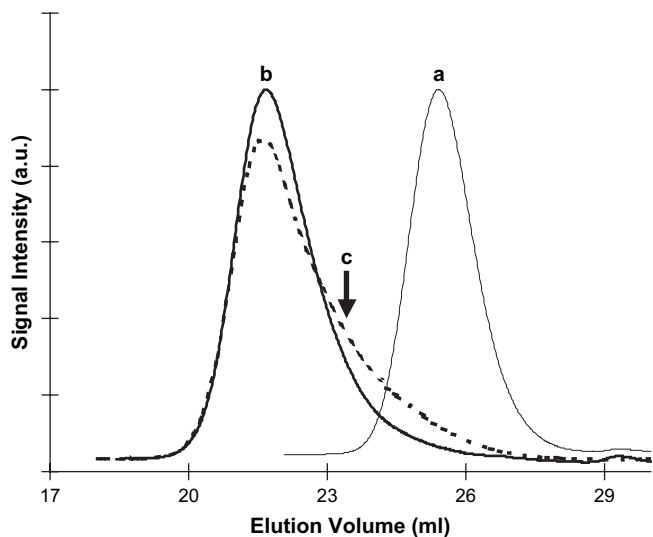


Fig. 2. GPC chromatograms of (a) *PS (macroinitiator) (data from refractive index detector and fluorescence detector are virtually indistinguishable), (b) SgradHS1 using refractive index detection, and (c) SgradHS1 using fluorescence detection set to the pyrene label. GPC data are taken from the S/AS precursor copolymers which undergo 100% hydrolysis of acetoxy functionalities to yield S/HS copolymers.

the shift of the chromatogram to lower elution volume. However, the shape and breadth of GPC chromatograms of the final gradient copolymer are different when obtained by refractive index and fluorescence detectors. The chromatogram obtained by fluorescence exhibits a longer tail at higher elution volume than that obtained by refractive index, suggesting that a small portion of the PS macroinitiator chains is not ‘living’ during the entire chain extension process. A peak-area analysis indicates that less than 10% of copolymer chains are responsible for the lower MW tail; thus, the vast majority of the copolymer chains is extended from the PS macroinitiator. Similar results are obtained with the other gradient copolymer upon comparing the chromatograms from refractive index and fluorescence detection.

The thermal properties of the S/HS copolymers are analyzed by DSC. Fig. 3 compares the heating curves of the two gradient copolymers and the random copolymer. Two curves are provided for each S/HS copolymer: one from the second heat (after erasing thermal history), and the other from the third heat (after the sample had been annealed for 180 min at 210 °C followed by quenching to low temperature). As expected, the random copolymer exhibits a single, narrow T_g regardless of annealing, consistent with the absence of microphase separation (or ordering). In contrast, the gradient copolymer (SgradHS1) with a cumulative styrene mole fraction similar to that of the random copolymer shows evidence of microphase separation after being annealed at 210 °C for 180 min. Specifically, while the second heat curve of SgradHS1 (Fig. 3c) exhibits a single discernable T_g , the third heat curve exhibits two T_g s (Fig. 3d). In Fig. 3d, the transition near 105 °C likely corresponds to nearly pure S domains in the copolymer which may be able to order upon long-term, high-temperature annealing due to the presence of the short PS macroinitiator that forms one end of the gradient copolymer

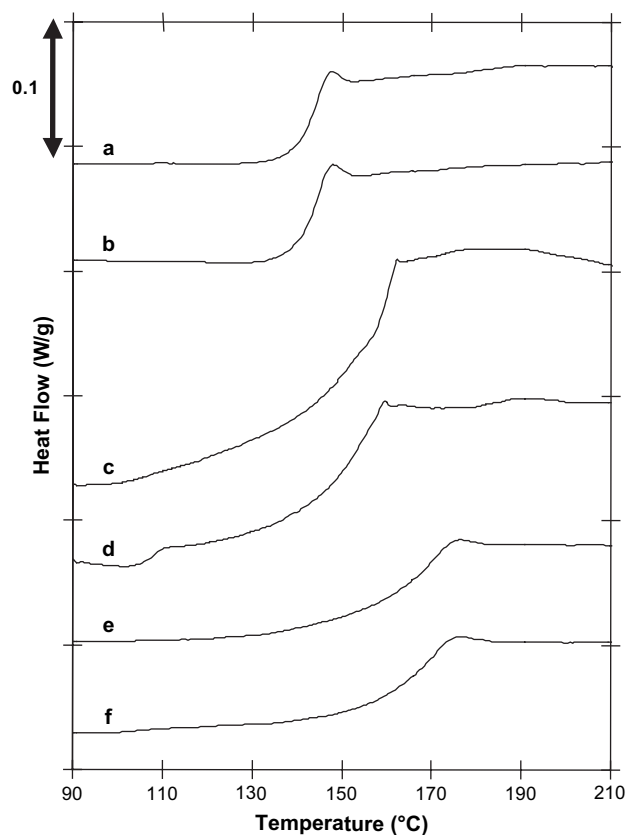


Fig. 3. Comparison of DSC heat curves taken from S/HS copolymers: (a) SranHS – second heat, (b) SranHS – third after 180 min annealing at 210 °C, (c) SgradHS1 – second heat, (d) SgradHS1 – third heat after 180 min annealing at 210 °C, (e) SgradHS2 – second heat, and (f) SgradHS2 – third heat after 180 min annealing at 210 °C.

chain. The second, higher T_g exhibits significant breadth, suggestive of a broad interfacial region that is consistent with the smooth composition gradient in the interior portions of each gradient copolymer chain. In the case of the low S content gradient copolymer, only one broad T_g is evident regardless of annealing.

Qualitatively similar phenomena were reported by Gray et al. [38], who performed thermal analysis on various S/HS gradient copolymers made by NM-CRP. Based on resolution of enthalpy recovery peaks after physical aging, their study indicated that a minimum cumulative styrene mole fraction (0.55 in their study) was needed for S/HS gradient copolymers to exhibit evidence of microphase separation. (This was inferred from the presence of two T_g s and/or enthalpy relaxation peaks after physical aging.) It should be noted that Matyjaszewski et al. [32,33] previously reported thermal-history dependent T_g behavior of styrene–methyl acrylate gradient copolymers, which exhibited two T_g s by DSC only after long-term, high-temperature annealing.

3.2. Compatibilization of PS/PCL blends by S/HS copolymer addition during melt processing

The goal of this section of the study is to determine how the overall composition and distribution of repeat

units in a copolymer that can undergo hydrogen bonding with a homopolymer in an immiscible blend affect blend compatibilization. The model blend system employed here is an 80/20 wt% PS/PCL blend. When S/HS copolymers are added to this blend, hydrogen-bond formation can occur between the hydroxyl functionality in the S/HS copolymer and the ester functionality in the PCL repeat unit [46–50].

Fig. 4a and b shows that the PS/PCL blend without copolymer exhibits largely spherical dispersed-phase PCL domains that undergo coarsening after static, high-temperature annealing for 240 min. The evolution of the number-average dispersed-phase diameter, D_n , as a function of annealing time, t , is expected to obey the following relation [58–60]:

$$D_n^3 = D_n^3(0) + Kt \quad (1)$$

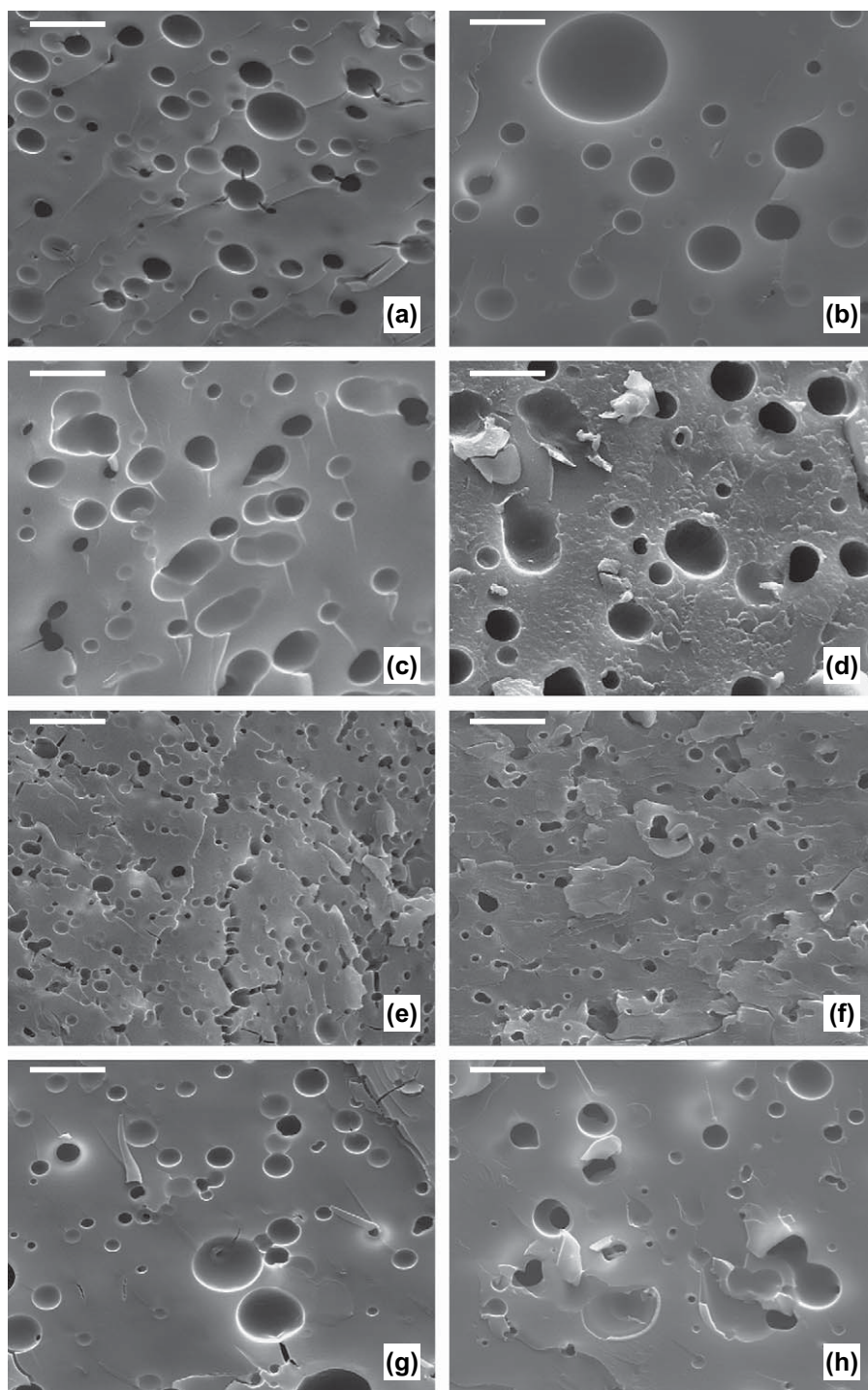


Fig. 4. Scanning electron micrographs of 80/20 wt% PS/PCL blend sets before and after annealing for 240 min at 210 °C: without copolymer before (a) and after (b) annealing, with SranHS before (c) and after (d) annealing, with SgradHS1 before (e) and after (f) annealing, with SgradHS2 before (g) and after (h) annealing. Note: size bars represent 10 μm.

where $D_n(0)$ is the value D_n of the blend upon removal from the mini-max mixer (and before static annealing) and K the coarsening rate parameter. (We note that our K value differs from that described by Crist and Nesarikar [58] by a factor of 8 because our equation involves the cube of the average diameter while their equation involved the cube of the average radius.) Eq. (1) is valid whether the coarsening mechanism is coalescence, Ostwald ripening, or some combination of the two mechanisms. Assuming the simplest of pictures (Brownian motion only) responsible for coarsening by coalescence [58], K is proportional to the quantity Tf/η , where T is absolute temperature, f is the volume fraction of the dispersed phase, and η is matrix viscosity. Assuming the simplest of pictures responsible for coarsening by Ostwald ripening [58], K is proportional to the quantity $\mathcal{D}\gamma/T$, where \mathcal{D} is the molecular diffusion coefficient of the dispersed-phase polymer through the matrix polymer and γ is the interfacial energy between the two phases. As shown in Fig. 5, the 80/20 wt% PS/PCL blend without added copolymer follows Eq. (1), with $K = 0.22 \mu\text{m}^3/\text{min}$.

In contrast, as shown in Fig. 4c and d, addition of S/HS random copolymer to the PS/PCL blend yields many highly non-spherical dispersed-phase domains that coarsen during static, high-temperature annealing. (It is also interesting to note that the value of $D_n(0)$ for the blend with added SranHS is larger than that of the neat blend. This is due to the existence of a significant fraction of dispersed domains that have non-spherical, dumbbell shapes as shown in Fig. 4c. See Section 2 for a description of how effective diameters are determined

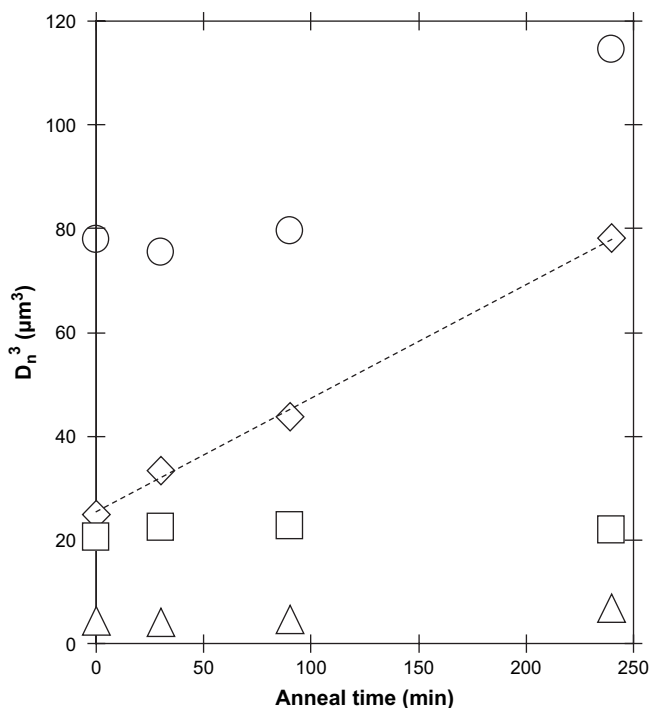


Fig. 5. Effect of annealing time on D_n^3 for 80/20 wt% PS/PCL blend sets shown in Fig. 4: blend without copolymer (diamonds), blend with SranHS (circles), blend with SgradHS1 (triangles), and blend with SgradHS2 (squares). Note: the straight line represents the best fit to Eq. (1) for the blend without copolymer.

for non-spherical, dispersed domains.) Furthermore, as shown in Fig. 5, the coarsening process for the blend with added S/HS random copolymer does not follow Eq. (1). We have previously reported similar effects, upon the addition of S/methyl methacrylate random copolymers to PS/poly(methyl methacrylate) (PMMA) blends [43], as have Lee et al. [61], who added S/methyl methacrylate random copolymers to poly(phenylene oxide)/PMMA blends. The latter case studied by Lee et al. [61] bears closer relationship to the PS/PCL blend system with added S/HS copolymer, because the styrene repeat units have attractive thermodynamic interactions with poly(phenylene oxide). Thus, although random copolymer addition to an immiscible blend can lead to the random copolymer forming an encapsulating layer at the blend interfacial regions [61], thereby impacting interfacial tension, this neither provides repulsive interactions of the dispersed-phase domains nor does it prevent coalescence or compatibilize the blends. As the current results indicate, this conclusion holds even in the case where relatively strong attractive interactions, e.g., hydrogen bonds, can be formed between one type of co-monomer unit in the random copolymer and the repeat unit of one of the homopolymers making up the blend. A recent study by Kuo and Chang [62] indicates that hydrogen bonds form readily in blends of S/HS random copolymers with PCL and in significant preference to self-association hydrogen bonds between hydroxyl groups on different HS units within the copolymer. For example, a 50/50 wt% blend of PCL with 87/13 mol% S/HS random copolymer results in a miscible blend with 13% of carbonyl units in PCL undergoing hydrogen bonding with hydroxyl units [62].

As shown in Fig. 4e and f, when SgradHS1 is added to the 80/20 wt% PS/PCL blend, the resulting blend exhibits both a greatly reduced value of $D_n(0)$ when compared to either the blend without added copolymer or the blend with added SranHS and a lack of any significant coarsening in the average dispersed-phase domain size with long-term high-temperature annealing (see Fig. 5). The sharp reductions in $D_n(0)$, by a factor of 1.8 relative to the blend without copolymer, and K , to a value equivalent to zero within error ($0.01 \mu\text{m}^3/\text{min}$, to be exact), are only possible if the added copolymer imparts, though preferential location at the blend interfaces, a greatly reduced interfacial tension and the steric hindrance to prevent coalescence.

It is interesting to note that many of the dispersed-phase PCL domains in the blend with added SgradHS1 are non-spherical and maintain a non-spherical shape after long-term, high-temperature annealing. (See Fig. 6 for higher magnification SEM images.) This effect, in combination with major reduction in $D_n(0)$ values and the significant blend compatibilization achieved upon addition of SgradHS1 to the PS/PCL blend, strongly indicates that the addition of a small amount of SgradHS1 gradient copolymer to the blend results in a reduction of interfacial tension to very low levels as well as steric effects resisting coalescence. In contrast, addition of S/HS random copolymer to the blend yields non-spherical dispersed-phase domains but without a significant reduction in $D_n(0)$ or compatibilization. We note that

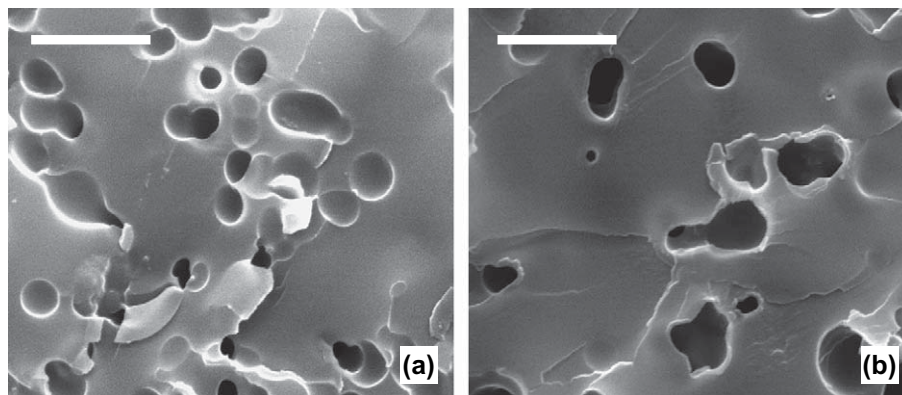


Fig. 6. Scanning electron micrographs of irregular, non-spherical PCL domains in the 80/20 wt% PS/PCL blend with SgradHS1 before (a) and after (b) annealing. Size bars represent 5 μm .

Dadmun et al. [63,64] have studied the importance of sequence distributions of ‘random-like’ copolymers on compatibilization efficiency using Monte-Carlo simulation. They concluded that in case of an equivalent overall copolymer composition, a ‘blocky’ sequence distribution with a polydispersity in copolymer composition leads to the most effective compatibilization. Our experimental results are in qualitative agreement with that conclusion.

Two other studies have recently noted the presence of highly non-spherical dispersed-phase domains in polymer blends compatibilized under conditions where hydrogen-bond formation could be present. Kobori et al. [65] found irregularly shaped, dispersed-phase domains in melt-processed blends of 80/20 wt% linear low density polyethylene/poly(4-hydroxystyrene) (PHS) with 20 parts per hundred polyethylene (PE)–PMMA *block* copolymer. In this case, hydrogen bonding occurs between the PHS dispersed phase and the ester units with the PMMA *block* of the PE–PMMA *block* copolymer. Interestingly, the dispersed-phase domains observed by Kobori et al. [65] in blends containing 5 parts per hundred PE–PMMA *block* copolymer were regular in shape. We have also recently observed the presence of highly non-spherical dispersed-phase domains in 80/20 wt% PS/PCL blends compatibilized with 5 wt% S/HS *block* copolymer [66]. In that system, we found that it was possible to achieve extremely small dispersed-phase domain sizes, ~ 100 nm in diameter, thereby yielding a nanostructured blend, also called a nanoblend [67], under the same processing conditions used in the present study involving S/HS gradient copolymers.

When SgradHS2, with a much lower S content than the SgradHS1, is added to the PS/PCL blend, the dispersed-phase PCL domains observed prior to annealing are similar in average size and shape (mostly spherical) to those observed in the blend without added copolymer (see Fig. 4g). However, close inspection reveals that the size distribution of PCL domains in the unannealed blend with added SgradHS2 is substantially broader than in the other blend sets and that in rare instances coalescence is possible during long-term, high-temperature annealing (see Fig. 4h). To assess quantitatively the distribution of the dispersed PCL domain sizes, we have calculated the ratio of D_{vs} (volume-weighted particle size/area-weighted particle size) to D_n for each blend sample (see Table 2). This ratio is akin to the polydispersity index for average molecular weights in quantifying dispersion. Among the four blend sets, the blend with added SgradHS2 exhibits the maximum D_{vs}/D_n values for all annealing conditions. Most notably, the initial value of $D_{vs}/D_n = 1.79$, before annealing, of the blend with SgradHS2 is much larger than those of other blends, which have initial D_{vs}/D_n values of 1.26–1.28.

This phenomenon may be explained by the fact that during melt processing SgradHS2 is less likely to be located as heavily at interfacial region as SgradHS1 due to its much higher HS content, which should lead to substantial ‘dissolution’ of SgradHS2 into interior of the PCL phase. This could result in an uneven interfacial coverage by the SgradHS2 copolymer that is insufficient to alter interfacial tension dramatically. Nonetheless, as shown in Fig. 5, the addition of SgradHS2 to the PS/PCL blends yields much better resistance

Table 2

Average dispersed-phase domain sizes obtained via image analysis of scanning electron micrographs in 80/20 wt% PS/PCL blends – effects of annealing times at 210 °C and 5 wt% copolymer addition

Added S/HS copolymer	0-min Anneal		30-min Anneal		90-min Anneal		240-min Anneal	
	D_n (μm)	D_{vs}^a/D_n	D_n (μm)	D_{vs}/D_n	D_n (μm)	D_{vs}/D_n	D_n (μm)	D_{vs}/D_n
No copolymer	2.92	1.27	3.22	1.49	3.52	1.73	4.27	2.03
SranHS	4.27	1.28	4.22	1.32	4.30	1.30	4.86	1.46
SgradHS1	1.62	1.26	1.61	1.32	1.66	1.30	1.90	1.38
SgradHS2	2.74	1.79	2.81	1.77	2.83	1.75	2.79	2.16

^a $D_{vs} = \text{Sum}(D_i^3)/\text{Sum}(D_i^2)$ and represents the ratio of the volume-weighted average diameter to area-weighted average diameter; thus, the ratio D_{vs}/D_n provides a quantitative indication of the polydispersity in dispersed-phase domain sizes.

to PCL domain coalescence than the addition of a random copolymer, even with a higher S content. This may be attributed to the gradient sequence distribution along the copolymer chain, which is much more likely than a random sequence distribution to yield interfacial conditions necessary to suppress dispersed-domain coalescence. This result is evidence of the fact that chain architecture is an important factor in the effectiveness of copolymers as compatibilizers of immiscible blends.

We note that the elevated T_g values of the S/HS copolymers led us to pre-mix the copolymers with the PS/PCL blend prior to mixing in the melt state using a mini-max mixer (with three steel spheres added to provide for enhanced mixing [5,43,66]). The method of pre-mixing employed here involved co-dissolving PS, PCL, and copolymer followed by precipitating and drying. The same approach was used to pre-mix the blend without added copolymer, thus providing a fair comparison of the impact of S/HS copolymer on blend morphology. To determine the impact of our mixing method on morphology, we did two comparative studies: one involved a solution-mixed, precipitated, and dried neat PS/PCL blend that did not experience any melt processing, and a second involved pre-mixing of PS and SgradHS2 by co-dissolution, casting, and drying and then melt mixing the dried PS/SgradHS2 blend with PCL pellets. Scanning electron microscopy of the neat blend without copolymer and without melt mixing (not shown here) revealed a much finer dispersion of PCL domains than those shown in Fig. 4a; this indicates that melt processing at higher temperature causes significant net coalescence of the as-precipitated solution blends. Scanning electron microscopy of the blend resulting from the second comparative study (not shown here) revealed that the complex mixing protocol results in a coarser morphology than that shown in Fig. 4g, where the blend was made using our regular protocol of co-dissolution of PS, PCL and SgradHS2, followed by precipitation, drying, and melt processing. This result may be due to a low dispersion efficiency of the mini-max mixer when processing blends of unmixed polymers with significantly different viscosity.

We note that our method of mixing by co-dissolution and precipitation of all blend components followed by drying and melt processing, which was also employed in Refs. [8] and [24] for compatibilization studies of other blend/copolymer systems, does not lend itself to commercial-scale production of polymer blends. However, in other studies related to dispersion in and compatibilization of polymer blends, we have shown that well-dispersed, and, in some cases, compatibilized blends can be achieved by solid-state shear pulverization [18,22,23,67–69]. In particular, SSSP has yielded compatibilized PS/polyethylene blends by addition of S/ethylene-butylene/S triblock copolymer [18] and compatibilized PS/poly(methyl methacrylate) nanoblends by addition of S/methyl methacrylate gradient copolymer [67]. We plan in the future to study a combination of SSSP, an industrially-scalable process, and the addition of gradient copolymers containing hydrogen-bonding moieties, e.g., S/HS gradient copolymers, as a means to yield compatibilized blends.

3.3. Effect of added copolymer and compatibilization on PCL crystallization/melting behavior

Since PCL is a semi-crystalline polymer, monitoring the crystallization and melting behaviors of the dispersed PCL phase can provide further information on the impact of the interfacial activity of S/HS copolymers in PS/PCL blends. The effect of S/HS copolymer addition on the non-isothermal crystallization (cooling rate of 20 °C/min) behavior of PCL as observed via DSC is given in Fig. 7. Upon addition of S/HS copolymers, there are reductions in the onset and peak crystallization temperature (T_c) of PCL, which reflect restricted crystallization of PCL in the presence of thermodynamically favorable intermolecular interaction [47–50]. (In one recently reported case [62], the hydrogen bonds formed between a 55/45 mol% S/HS copolymer and PCL in a 50/50 wt% miscible blend led to total suppression of PCL crystallization even when the PCL had been cooled to a temperature of -100 °C.) However, it is noteworthy that there are similar degrees of change in the PCL crystallization in the blends with SranHS and with SgradHS1 although the morphologies of the blends are significantly different. This result supports the argument that when gradient and random S/HS copolymers of similar styrene content are added to PS/PCL blends, there are similar degrees of contact of the copolymers with the interiors of the PCL domains. This is true even though the difference in sequence distribution can result in vastly different interfacial activities of gradient and random S/HS copolymers as evidenced by the blend morphology study.

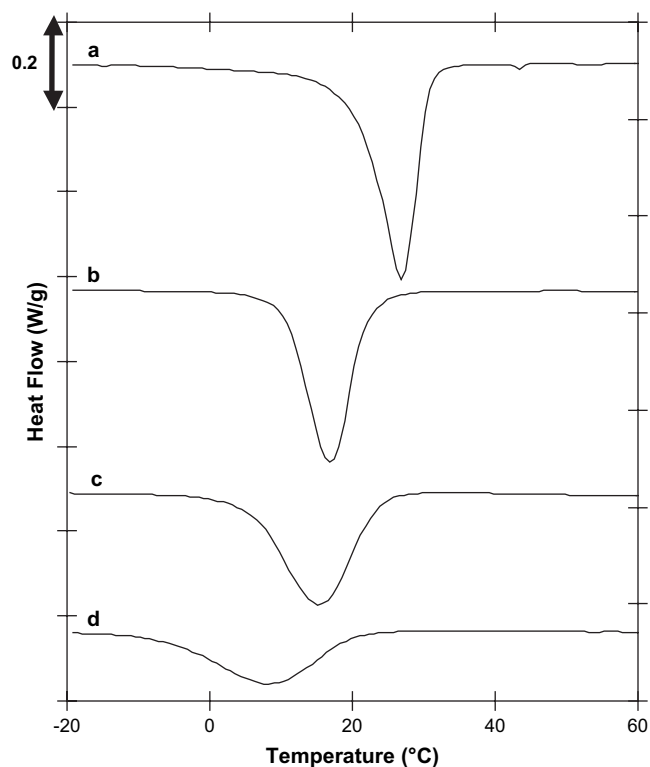


Fig. 7. Non-isothermal crystallization curves (via DSC) of PCL domains in 80/20 wt% PS/PCL blend sets: (a) without copolymer, (b) with SranHS, (c) with SgradHS1, and (d) with SgradHS2.

In contrast to relatively modest effects of SranHS or SgradHS1 addition to the blends on PCL crystallization, adding SgradHS2 (with its high HS content) to the blend has a very large effect on the non-isothermal crystallization of PCL. As compared with the blend without added copolymer, the blend with added SgradHS2 exhibits reductions in the onset T_c of 10 °C and the peak T_c of 19 °C as well as a 46% reduction in enthalpy of crystallization. The fact that the morphology of the blend with SgradHS2 is not as fine as that of the blend with SgradHS1 rules out the possibility that the dispersed PCL phase is being impacted by fractional (or confined) crystallization effects [69–74]. Instead, it reinforces the argument that there is a significant portion of the added SgradHS2 present in the interior of PCL domains, which could result in not only an impediment to PCL crystallization but also a lesser amount of interfacial SgradHS2 as compared to SgradHS1. Previous studies [46–50] regarding the miscibility of binary blends of PCL and S/HS random copolymers and the effect of S/HS copolymers on the suppression of PCL crystallization and melting support the favorable presence of SgradHS2 in PCL domains. In particular, Ahn et al. [46] have indicated that, based on the presence of a single T_g , S/HS random copolymers with as little as 10 mol% HS content can yield apparent miscibility in binary blends with PCL. Consequently, a reduced level of interfacial coverage by SgradHS2 in the PS/PCL blend may provide an explanation for the broader distribution and larger average domain size of PCL as compared to the blend with SgradHS1.

The melting curves of the 80/20 wt% PS/PCL blends are provided in Fig. 8. These heating curves were obtained

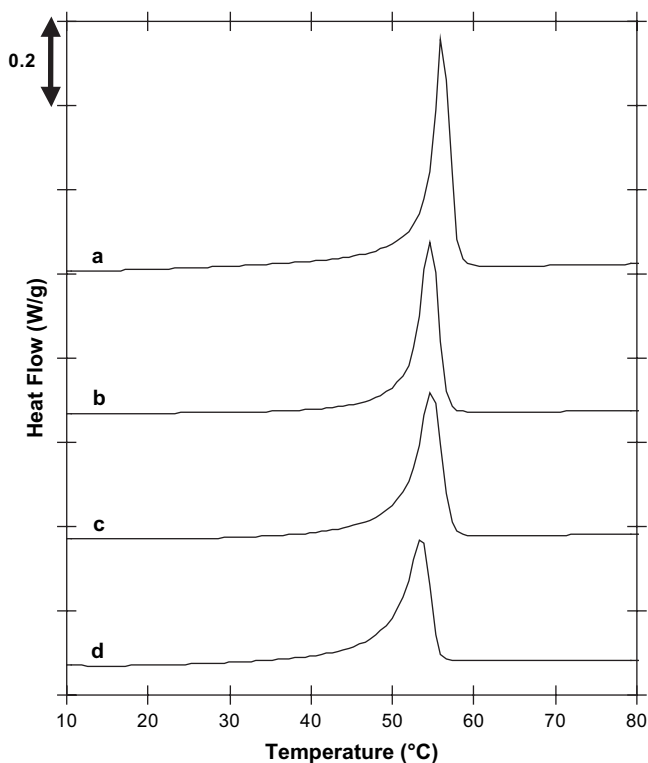


Fig. 8. Melting curves (via DSC) of PCL domains in 80/20 wt% PS/PCL blend sets: (a) without copolymer, (b) with SranHS, (c) with SgradHS1, and (d) with SgradHS2.

Table 3

Summary of crystallization (data taken upon cooling from melt state) and melting (data taken upon heating from crystallized state) behaviors of dispersed PCL domains in 80/20 wt% PS/PCL blends

Added S/HS copolymer	Crystallization			Melting		
	Onset T_c (°C)	Peak T_c (°C)	ΔH_c (J/g PCL)	Onset T_m (°C)	Peak T_m (°C)	ΔH_m (J/g PCL)
No copolymer	31	27	58	31	56	66
5 wt% SranHS	24	17	48	32	55	48
5 wt% SgradHS1	24	15	41	32	55	51
5 wt% SgradHS2	21	8	31	31	53	49

immediately after the cooling curves showing non-isothermal crystallization in Fig. 7. A summary of the thermal analysis data associated with Figs. 7 and 8 is given in Table 3. The PCL melting behavior follows trends similar to those described above for non-isothermal crystallization. Compared to the neat PS/PCL blend, all PS/PCL blends with added S/HS copolymer yield small melting point depressions, as observed by peak melting temperature, with the largest reduction observed in the blend with added SgradHS2. Relative to the PS/PCL blend without copolymer, the blends with S/HS copolymer also exhibit reductions in the enthalpy of melting. Further study of this behavior will be needed to determine detailed mechanisms associated with modification of crystallization/melting behaviors in blends containing crystallizable dispersed-phase domains and compatibilized via copolymers with hydrogen-bonding moieties.

4. Summary

Two S/AS gradient copolymers were synthesized by NM-CRP, and one S/AS random copolymer was made by ConvFRP; these copolymers were hydrolyzed to obtain S/HS copolymers. The S/HS random copolymer and the S/HS gradient copolymer of nearly identical overall composition, 57 mol% S and 59 mol% S, respectively, yield one T_g and two T_g s, respectively, after high-temperature annealing. Thus, the gradient copolymer is ordered (microphase separated) while the random copolymer is disordered. A S/HS gradient copolymer with a much lower S content, 25 mol%, yields a broad T_g .

Each of these S/HS copolymers was added (at 5 wt%) to immiscible 80/20 wt% PS/PCL blends in order to test their effectiveness as blend compatibilizers. This blend system is special because of the ability of the hydroxyl functionalities on the HS units to form hydrogen bonds with the ester functionalities in the PCL. After melt processing each blend, compatibilization was evaluated by the evolution of the number-average dispersed-phase PCL domain size as a function of static, high-temperature annealing time. While addition of the 57/43 mol% S/HS random copolymer did not yield compatibilization, addition of the 59/41 mol% S/HS gradient copolymer led to a major reduction in the size of the dispersed-phase domains, which were often irregular in shape, as well as stabilization of the dispersed phase against static coarsening, i.e., blend compatibilization. When a gradient copolymer with a lower styrene content (25/75 mol% S/HS)

was added to the blend, it yielded compatibilization but without a significant reduction in domain size. These results indicate that gradient copolymers can be very effective compatibilizers of immiscible blends, especially in the presence of hydrogen-bonding interactions. Thermal analyses of the blend samples also revealed that the hydrogen-bonding interaction between S/HS copolymers and the dispersed PCL phase can alter the crystallization and melting behavior of the semi-crystalline PCL domains.

Acknowledgments

The support of the NSF-MRSEC program (grants DMR-0076097 and DMR-0520513), Northwestern University and a 3M Fellowship (to JK) are gratefully acknowledged. We also acknowledge the use of the scanning electron microscope in a shared user facility of the Northwestern University Materials Research Center.

References

- [1] Wu S. *Polymer* 1985;26:1855–63.
- [2] Bartczak Z, Argon AS, Cohen RE, Weinberg M. *Polymer* 1999;40:2331–46.
- [3] Koning C, van Duin M, Pagnoulle C, Jerome R. *Prog Polym Sci* 1998;23:707–57.
- [4] Corte L, Leibler L. *Polymer* 2005;46:6360–8.
- [5] Macosko CW, Guegan P, Khandpur AK, Nakayama A, Marechal P, Inoue T. *Macromolecules* 1996;29:5590–8.
- [6] Thomas S, Prud'homme RE. *Polymer* 1992;33:4260–8.
- [7] Kim HC, Nam KH, Jo WH. *Polymer* 1993;34:4043–51.
- [8] Auschra C, Stadler R, Voigtmartin IG. *Polymer* 1993;34:2094–110.
- [9] Edgecombe BD, Stein JA, Frechet JM, Xu Z, Kramer EJ. *Macromolecules* 1998;31:1292–304.
- [10] Sundararaj U, Macosko CW. *Macromolecules* 1995;28:2647–57.
- [11] Lyu S, Jones TD, Bates FS, Macosko CW. *Macromolecules* 2002;35:7845–55.
- [12] McKay ID. *J Appl Polym Sci* 1991;42:281–95.
- [13] Jeon HK, Zhang JB, Macosko CW. *Polymer* 2005;46:12422–9.
- [14] Fayt R, Jerome R, Teyssie P. *J Polym Sci Part B Polym Phys* 1982;20:2209–17.
- [15] Harrats C, Fayt R, Jerome R, Blacher S. *J Polym Sci Part B Polym Phys* 2003;41:202–16.
- [16] Jannasch P, Wessen B. *J Appl Polym Sci* 1995;58:753–70.
- [17] Gonzalez-Montiel A, Keskkula H, Paul DR. *J Polym Sci Part B Polym Phys* 1995;33:1751–67.
- [18] Tao Y, Lebovitz AH, Torkelson JM. *Polymer* 2005;46:4753–61.
- [19] Wildes G, Keskkula H, Paul DR. *J Polym Sci Part B Polym Phys* 1999;37:71–82.
- [20] Kim HY, Jeong U, Kim JK. *Macromolecules* 2003;36:1594–602.
- [21] Harrats C, Omonova T, Groeninckx G, Moldenaers P. *Polymer* 2004;45:8115–26.
- [22] Lebovitz AH, Khait K, Torkelson JM. *Macromolecules* 2002;35:9716–22.
- [23] Lebovitz AH, Khait K, Torkelson JM. *Macromolecules* 2002;35:8672–5.
- [24] Kobori Y, Akiba I, Akiyama S. *Polymer* 2000;41:5971–5.
- [25] Watanabe N, Akiba I, Akiyama S. *Eur Polym J* 2001;37:1837–42.
- [26] Huang JM, Cheng HJ, Wu JS, Chang FC. *J Appl Polym Sci* 2003;89:1471–7.
- [27] Xu Z, Kramer EJ, Edgecombe BD, Frechet JM. *Macromolecules* 1997;30:7958–63.
- [28] Anastasiadis SH, Gancarz I, Koberstein JT. *Macromolecules* 1989;22:1449–53.
- [29] Mekhilef N, Favis BD, Carreau PJ. *J Polym Sci Part B Polym Phys* 1997;35:293–308.
- [30] Georges MK, Veregin RPN, Kazmaier PM, Hamer GK. *Macromolecules* 1993;26:2987–8.
- [31] Hawker CJ. *Acc Chem Res* 1997;30:373–82.
- [32] Davis KA, Matyjaszewski K. *Adv Polym Sci* 2002;159:2–166.
- [33] Matyjaszewski K, Ziegler MJ, Arehart SV, Greszta D, Pakula T. *J Phys Org Chem* 2000;13:775–86.
- [34] Min K, Li M, Matyjaszewski K. *J Polym Sci Part A Polym Chem* 2005;43:3616–22.
- [35] Farcet C, Charleux B. *Macromol Symp* 2002;182:249–60.
- [36] Lefay C, Charleux B, Save M, Chassenieux C, Guerret O, Magnet S. *Polymer* 2006;47:1935–45.
- [37] Gray MK, Zhou H, Nguyen ST, Torkelson JM. *Polymer* 2004;45:4777–86.
- [38] Gray MK, Zhou H, Nguyen ST, Torkelson JM. *Macromolecules* 2004;37:5586–95.
- [39] Gao B, Chen XY, Ivan B, Kops J, Batsberg W. *Macromol Rapid Commun* 1997;18:1095–100.
- [40] Woo DJ, Kim J, Zhou H, Nguyen ST, Torkelson JM. *Polymer* 2006;47:3287–91.
- [41] Shull KR. *Macromolecules* 2002;35:8631–9.
- [42] Lefebvre MD, Dettmer CM, McSwain RL, Xu C, Davila JR, Composto RJ, et al. *Macromolecules* 2005;38:10494–502.
- [43] Kim J, Gray MK, Zhou H, Nguyen ST, Torkelson JM. *Macromolecules* 2005;38:1037–40.
- [44] Coleman MM, Painter PC. *Prog Polym Sci* 1995;20:1–59.
- [45] He Y, Zhu B, Inoue Y. *Prog Polym Sci* 2004;29:1021–51.
- [46] Ahn TO, Eum HS, Jeong HM, Park JY. *Polym Bull* 1993;30:461–7.
- [47] Lezcano EG, Coll CS, Prolongo MG. *Polymer* 1996;37:3603–9.
- [48] Vaidya MM, Levon K, Pearce EM. *J Polym Sci Part B Polym Phys* 1995;33:2093–108.
- [49] Zhou H, Xiang ML, Chen WJ, Jiang M. *Macromol Chem Phys* 1997;198:809–17.
- [50] Chen HL, Wang SF, Lin TL. *Macromolecules* 1998;31:8924–30.
- [51] Gray MK, Zhou H, Nguyen ST, Torkelson JM. *Macromolecules* 2003;36:5792–7.
- [52] Ellison CJ, Torkelson JM. *Nat Mater* 2003;2:695–700.
- [53] Gray MK, Kinsinger MI, Torkelson JM. *Macromolecules* 2002;35:8261–4.
- [54] Chen XY, Jankova K, Kops J, Batsberg W. *J Polym Sci Part A Polym Chem* 1999;37:627–33.
- [55] Kruse TM, Souleimonova R, Cho A, Gray MK, Torkelson JM, Broadbelt LJ. *Macromolecules* 2003;36:7812–23.
- [56] O'Neil GA, Torkelson JM. *Trends Polym Sci* 1997;5:349–55.
- [57] O'Neil GA, Torkelson JM. *Macromolecules* 1999;32:411–22.
- [58] Crist B, Nesarikar AR. *Macromolecules* 1995;28:890–6.
- [59] Siggia ED. *Phys Rev A* 1979;20:595–605.
- [60] Song SW, Torkelson JM. *Macromolecules* 1994;27:6389–97.
- [61] Lee MS, Lodge TP, Macosko CW. *Macromol Chem Phys* 1998;199:1555–9.
- [62] Kuo SW, Chang FC. *Macromolecules* 2001;34:7737–43.
- [63] Dadmun MD. *Macromolecules* 2000;33:9122–5.
- [64] Eastwood E, Viswanathan S, O'Brien CP, Kumar D, Dadmun MD. *Polymer* 2005;46:3957–70.
- [65] Kobori Y, Yasumitsu R, Akiba I, Akiyama S, Sano H. *e-Polymers* 2004;4:1–6.
- [66] Kim J, Torkelson JM, in preparation.
- [67] Tao Y, Kim J, Torkelson JM, submitted for publication.
- [68] Furgieue N, Lebovitz AH, Khait K, Torkelson JM. *Macromolecules* 2000;33:225–8.
- [69] Lebovitz AH, Khait K, Torkelson JM. *Polymer* 2003;44:199–206.
- [70] Tol RT, Mathot VBF, Groeninckx G. *Polymer* 2005;46:383–96.
- [71] Shi D, Yin JH, Ke Z, Gao Y, Li RK. *J Appl Polym Sci* 2004;91:3742–55.
- [72] Zhu L, Cheng SZD, Calhoun BH, Ge Q, Quirk RP, Thomas EL, et al. *Polymer* 2001;42:5829–39.
- [73] Scaffaro R, La Mantia FP, Canfora L, Polacco G, Filippi S, Magagnini P. *Polymer* 2003;44:6951–7.
- [74] Wilkinson A, Clemens ML, Harding VM. *Polymer* 2004;45:5239–49.