Macromolecules **2002,** *35,* 9716−9722

In Situ Block Copolymer Formation during Solid-State Shear Pulverization: An Explanation for Blend Compatibilization via Interpolymer Radical Reactions

Andrew H. Lebovitz,[†] **Klementina Khait,**[†] **and John M. Torkelson**[*,†,‡]

Department of Chemical Engineering and Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208-3120

Received August 1, 2002

ABSTRACT: Interpolymer radical coupling reaction leading to block copolymer formation has been demonstrated for the first time in the solid state and in the absence of diffusion using solid-state shear pulverization. Radical coupling is often referred to as a diffusion-controlled reaction as it lacks an activation barrier to reaction. However, pulverization can lead both to intimate mixing, creating large interfacial area between blend components, and to chain scission, yielding polymer radicals and accommodating interpolymer coupling in the solid state. Fluorescence-detection gel permeation chromatography (GPC) was used to detect interpolymer reaction in high-molecular-weight (MW) polystyrene (PS)/pyrene-labeled PS and high-MW poly(methyl methacrylate) (PMMA)/pyrene-labeled PS blends. The latter system was chosen as PMMA/PS blend compatibilization was recently achieved via pulverization; this compatibilization was hypothesized to originate from in situ block copolymer formation via interpolymer radical coupling. Proof of coupling was obtained in this study from pyrene fluorescence in pulverized blends at GPC elution times less than those of the original pyrene-labeled PS. With the high-MW PS/pyrene-labeled PS mixture, comparison of label on coupled chains to label on chains that underwent scission indicates that ~5% of the pyrene-labeled chains undergoing scission were able to couple to radicals originating from the high-MW PS. The effect of MW, blend composition, and screw design on chain scission during pulverization was also studied.

Introduction

Compatibilization of immiscible polymer blends is a topic rich in scientific and technological challenges.[1−20] Interest in compatibilization arises from the ability to produce new materials by blending currently available homopolymers. Synergistic properties may result in a fraction of immiscible blends by maintaining dispersed-phase particle sizes within a certain size range, often on the order of 1 μm. Thus, polymer blend compatibilization has been defined by some as the achievement of a dispersed-phase domain size that is stable to static coarsening, i.e., stable to coarsening upon high-temperature annealing.[6,7]

Two main approaches have been investigated for achieving blend compatibilization: addition of premade block/graft copolymers to a blend which is then melt mixed[1,2,6−12] and reactive blending or compatibilization in which reactions between functionalized polymers yield interfacial block/graft copolymers during melt processing.[3−5,13−20] The former approach has led to many important scientific studies, but its application suffers from severe stumbling blocks associated with thermodynamics (low critical micelle concentrations in homopolymer),[2,21,22] kinetics (low diffusion rate of copolymer to the interface), and availability of appropriate block copolymers for use in compatibilization, with one block miscible in one blend component and a second block miscible in a second blend component. As a result, Koning et al.[3] have indicated that "no polymer blend compatibilized by addition of low levels of premade block/graft copolymers has been commercialized." In contrast, the second approach has led to some commercial application.[4,13] However, this method also suffers from limitations. For example, the condensation-type functional-group reactions employed in current reactive compatibilization efforts are chemically controlled rather than diffusion controlled; i.e., they have a high activation barrier to reaction leading to low reaction rate parameters[23] and relatively low reaction rates at melt processing temperatures. (While reactions of condensation-type functional groups on low-molecular-weight species have long been understood to be chemically controlled, interfacial reactions in blends between functional groups covalently attached to different polymer species were shown only recently to be chemically controlled.[24,25]) The necessity to modify addition-type polymers with functional groups has also limited the use of this method.

An alternative process, solid-state shear pulverization (SSSP), has recently been used to address limitations associated with melt-state processing of polymer blends.[26−33] SSSP is a continuous process employing an apparatus that roughly resembles a twin-screw extruder. However, the device is cooled in order to maintain the polymer in the solid state while it is exposed to high levels of shear and pressure, and the output is typically a powder or a particulate. The principles of SSSP are related to those of batch mechanical alloying processes[34] that have been of recent interest in polymer blend applications.[35−41] The pulverization process results in multiple fragmentation and fusion steps leading to a solid output which, in the case of blends, can yield number-average dispersed-phase domain sizes (D_n) ranging from microns to as small as several hundred nanometers.[26,31−33] Pulverization is also

---

[†] Department of Chemical Engineering.

[‡] Department of Materials Science and Engineering.

[*] To whom correspondence should be addressed: e-mail j-torkelson@northwestern.edu.

10.1021/ma021239y CCC: $22.00

useful in achieving efficient and intimate mixing of miscible or immiscible blends of polymers that have significantly dissimilar viscosities at melt processing conditions,[27,31] which as a result cannot be effectively melt mixed.

Most recently, quantitative proof of compatibilization of 90/10 and 80/20 wt % polystyrene (PS)/high-density polyethylene and 70/30 wt % PS/poly(methyl methacrylate) (PMMA) blends has been provided by demonstrating the invariance of D_n of the SSSP output to high-temperature annealing.[32] Pulverization can lead to chain scission, with number-average molecular weight (M_n) reduced by a few percent to as much as factors of 2−4, depending on polymer species and process conditions.[26,32] It has been hypothesized that chain scission, resulting in polymeric radicals, may be followed by some amount of in situ radical−radical coupling reactions forming block copolymer at interfacial regions in blends.[26,32] (In contrast to interpolymer coupling reactions between condensation-type functional groups, interpolymer radical−radical reactions do not have an activation barrier and thus proceed with high reaction rate parameters.[23] Such radical−radical reactions are referred to as diffusion-controlled reactions and have been of theoretical interest in reactive compatibilization[42−44] and are known to lead to efficient interpolymer coupling via termination in free radical polymerization.[45,46]) The recent study[32] demonstrating immiscible blend compatibilization via SSSP also showed that there was chain scission accompanying pulverization. However, the blends used in that study were not well designed to provide proof of in situ block copolymer formation.

With careful design of polymers used in the present study, we demonstrate quantitatively for the first time the in situ coupling of polymer radicals produced via chain scission during pulverization. While such reactions are "diffusion-controlled", the intense mixing achieved via pulverization, resulting in repeated creation of interfacial area, can allow for interfacial coupling reactions leading to block copolymer formation in the solid state in the absence of diffusion. This is shown with homogeneous coupling reactions involving PS/PS systems as well as with heterogeneous coupling reactions leading to block copolymer formation in PS/PMMA blends. Proof of coupling derives from a fluorescence-detection gel permeation chromatography method. This method has been used by Moon et al.,[47] who studied coupling with chemically controlled reactions of functionalized polymers, by Gray et al.[48,49] in their novel study of interpolymer radical coupling reactions leading to block copolymer formation during reactive blending of polymers made by nitroxide-mediated controlled radical polymerization, and by Lebovitz and Torkelson,[50] who demonstrated interpolymer radical coupling in sonicated polymer solutions.

Experimental Section

Synthesis of Pyrene-Labeled Monomer. 1-(1-Pyrene)-methyl methacrylate (MAPyrene) was synthesized in multiple batches by esterification of methacryloyl chloride and 1-pyrenemethanol.[51,52] 1-Pyrenemethanol (5.10 g per batch, Aldrich), triethylamine (10 mL, Aldrich), and anhydrous tetrahydrofuran (THF) (200 mL, Aldrich) were added to a 500 mL round-bottom flask cooled in an ice/water bath to 0 °C. A solution of methacryloyl chloride (6.84 mL, Aldrich) mixed with anhydrous THF (40 mL) was added dropwise to the 1-pyrenemethanol mixture over ∼2 h. The mixture was allowed to come to room temperature as it was stirred under continuous dry N_2 flow for a total reaction time of ∼24 h. The mixture was then contacted with an aqueous, saturated sodium bicarbonate solution in a separatory funnel. Solvent was removed from the resultant organic layer under reduced pressure to give a yellowish solid. The solid was dissolved in boiling ethanol and recrystallized in an ice/water bath. The resulting pale yellow solid (2.6 g average yield per batch) had a melting point of 94−100 °C and a molar extinction coefficient of 38 700 M^{-1} cm^{-1} (UV−vis absorbance at 345 nm). Identity of the MAPyrene product was confirmed using ^1H NMR and mass spectrometry, and the MAPyrene UV−vis absorbance spectrum closely resembled that of pyrene (shifted to longer wavelength by ∼8 nm).

Synthesis of Fluorescence Chromophore-Labeled PS. Pyrene-labeled PS (referred to as poly(styrene-*co*-MAPyrene) or poly(S-*co*-MAP)) was made in multiple batches by free radical polymerization using 2,2′-azobis(isobutyronitrile) (AIBN, Kodak) as initiator. 10 mL styrene (Aldrich, deinhibited prior to use) solutions containing 0.066 M MAPyrene and 0.0856 M AIBN were stoppered and purged with dry N_2 for 10 min prior to insertion in a 70 °C oil bath. Reactions were terminated after ∼9 h (∼50% styrene conversion) by quenching in an ice/water bath, followed by dissolution in methylene chloride and precipitation in methanol prior to drying overnight in a vacuum oven at 110 °C. The dissolution/precipitation was repeated five times in order to remove unreacted monomer, including MAPyrene, which was confirmed by fluorescence-detection gel permeation chromatography (GPC). GPC of the labeled PS yielded M_n = 107 000 g/mol and M_w = 202 000 g/mol. The pyrene chromophore content of the poly(S-*co*-MAP) was found via UV−vis absorbance to be 1 MAPyrene unit per 114 styrene repeat units.[53]

Synthesis of 11kPS. Low-molecular-weight (MW) PS was made in multiple batches by free radical polymerization using 25 mL of toluene (ACS grade, Fisher), 25 mL of styrene, and 0.117 M AIBN. Solutions were stoppered and purged with dry N_2 for 10 min prior to insertion in a 60 °C oil bath for ∼16 h (∼50% conversion). The PS was precipitated in methanol and dissolved in methylene chloride three times prior to drying overnight in a vacuum oven at 110 °C. GPC analysis yielded M_n = 11 000 g/mol (11kPS) and M_w = 20 000 g/mol.

Other PS and PMMA Homopolymers. Studies of interpolymer coupling via pulverization used either high-MW PS (M_n = 1 100 000 g/mol, M_w = 1 680 000 g/mol, determined by GPC) or high-MW PMMA (M_n = 1 350 000 g/mol, M_w = 1 740 000 g/mol, reported by the supplier) that were synthesized by Scientific Polymer Products and supplied as powder (high-MW PS) or a powder/particulate mix (high-MW PMMA). Examination of the chain scission capabilities of SSSP was done using a moderate-MW PS (M_n = 110 000 g/mol, M_w = 260 000 g/mol, determined by GPC, BASF) supplied as pellets.

Pulverization. Mixtures of 95/5 wt % high-MW PS/poly(S-*co*-MAP) or 95/5 wt % high-MW PMMA/poly(S-*co*-MAP) were dry blended and then processed using a Berstorff pulverizer at a screw speed of 420 rpm (PS blend) or 200 rpm (PMMA blend). 11kPS and moderate-MW PS were pulverized at 200 rpm. Feed rates were ∼0.11 kg/h, the temperature was maintained below the polymer glass transitions, and the screw configuration was designed to provide substantial shear.[54] Other information regarding SSSP, including equipment description, is in refs 26−30.

Confirmation of Interpolymer Radical Coupling Reactions. Changes in MW distribution were quantified using a Waters Breeze GPC, calibrated with monodisperse PS and equipped with UV−vis absorbance, refractive index (RI), and fluorescence detectors, using THF (HPLC grade, Aldrich) flowing at 1 mL/min. Interpolymer radical coupling was studied using GPC fluorescence detection set to pyrene (336 nm excitation, 368 nm emission) by comparing the elution or retention times for pre-SSSP poly(S-*co*-MAP) with those of the post-SSSP high-MW PS/poly(S-*co*-MAP) and high-MW PMMA/poly(S-*co*-MAP) blends. Fluorescence spectra were obtained using a SPEX Fluorolog spectrophotometer (328 nm excitation).

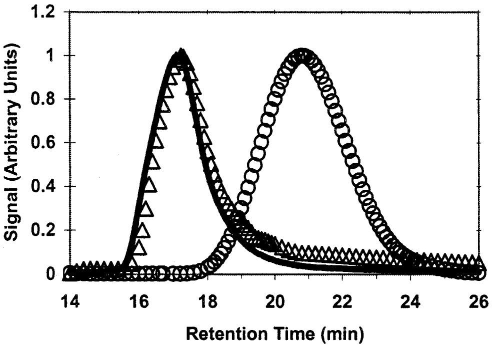

Figure 1. Fluorescence-detector GPC chromatograms for (○) poly(S-*co*-MAP) with sensitivity to pyrene label, (—) high-MW PS with sensitivity to phenyl rings, and (△) high-MW PMMA. All data are normalized to a value of 1.0 with respect to the peak of the GPC signal. (Note: to plot PMMA results with the fluorescence-detector chromatograms, PMMA data from the RI detector were corrected to account for detector delay time between the RI and fluorescence detectors.)

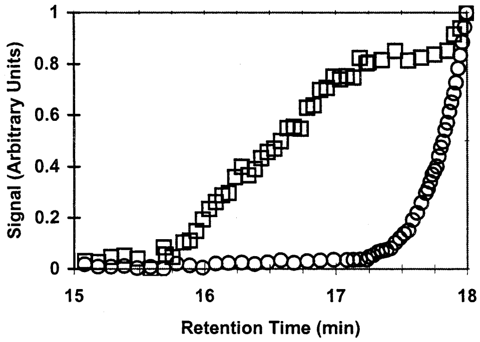

Figure 2. Fluorescence-detector GPC chromatograms with sensitivity to pyrene label for (○) poly(S-*co*-MAP) (unprocessed) and (□) 95/5 wt % high-MW PS/poly(S-*co*-MAP) pulverized blend.

Results and Discussion

A. In Situ Interpolymer Radical Coupling via Pulverization. To perform proof-of-principle studies of interpolymer radical coupling via SSSP, mixtures must be carefully designed so that unequivocal evidence is obtained from analysis of the SSSP product. Figure 1 shows that the original poly(S-*co*-MAP) yields essentially no signal at GPC elution times less than 17.25 min. By mixing this polymer with high-MW PS or high-MW PMMA which exhibits substantial signal at GPC elution times less than 17.25 min (see Figure 1), it is possible to verify or disprove the presence of in situ interpolymer coupling reactions via pulverization. The fluorescence-detector signal in the post-SSSP mixture at elution times below 17.25 min should occur only if some of the pyrene labels are attached to chains resulting from the coupling of polymer radicals made by in situ scission of poly(S-*co*-MAP) and high-MW PS or high-MW PMMA.

Figure 2 compares the fluorescence-detector GPC data in the region pertinent for proving the presence of interpolymer radical coupling in a 95/5 wt % high-MW PS/poly(S-*co*-MAP) pulverized blend. A small shoulder is exhibited by the pulverized blend at elution times between 15.7 and 17.25 min, where the pre-SSSP high-MW PS elutes but the pre-SSSP poly(S-*co*-MAP) does not. This shoulder at elution times less than 17.25 min represents ~0.7% of the total area under the fluorescence-detector GPC chromatogram for the pulverized blend, meaning that during pulverization a minimum of 0.7% of the original poly(S-*co*-MAP) underwent scission followed by coupling with polymer radicals originating from the high-MW PS.[55] Thus, SSSP yields not only chain scission but also substantial interfacial area accommodating interpolymer radical coupling during the many repeated fragmentation and fusion cycles accompanying pulverization. (The interpolymer radical coupling reaction requires a several angstrom reaction radius, which can only be achieved via pulverization if the process results in intimate mixing via production of substantial interfacial area between the original polymers undergoing coupling.)

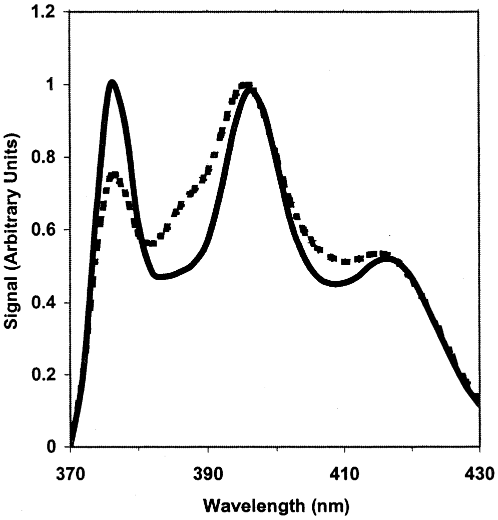

Figure 3. Fluorescence emission spectra for (– –) poly(S-*co*-MAP) (unprocessed) and (—) 95/5 wt % high-MW PS/poly(S-*co*-MAP) pulverized blend (fraction between 16.25 and 17.25 min elution time, according to Figure 2). All data are normalized to a value of 1.0 with respect to the peak of fluorescence intensity.

To ensure that the fluorescence signal present at elution times less than 17.25 min, taken to be indicative of interpolymer radical coupling, was not anomalous but instead was characteristic of the MAPyrene label, a GPC fractionation was performed. Specifically, 1 mL fractions of GPC eluent from the 95/5 wt % high-MW PS/poly(S-*co*-MAP) pulverized blend were collected between 16.25 and 17.25 min, the fluorescence detector interval in which the presence of pyrene originates from coupled chains; each fraction was collected three times. The collected eluent was dried, and a solution was made in toluene. The fluorescence spectrum of the resulting solution was compared with that of the original unpulverized poly(S-*co*-MAP). As shown in Figure 3, the pulverized blend yields an emission spectrum similar to that of the unprocessed poly(S-*co*-MAP), indicating that the fluorescence present in the pulverized blend at 16.25–17.25 min elution time is due to the presence of pyrene label in the polymer originating from interpolymer radical coupling during SSSP. As a further check of this point, an attempt to measure a similar emission spectrum from a poly(S-*co*-MAP) sample collected at 16.25–17.25 min elution time, which yielded no signal with the GPC fluorescence detector, also yielded no signal outside of noise with the spectrofluorimeter at wavelengths characteristic of pyrene.

The reaction of poly(S-*co*-MAP) and high-MW PS macroradicals provides proof-of-principle that interpolymer radical coupling can occur via pulverization. Extending this to the study of in situ block copolymer

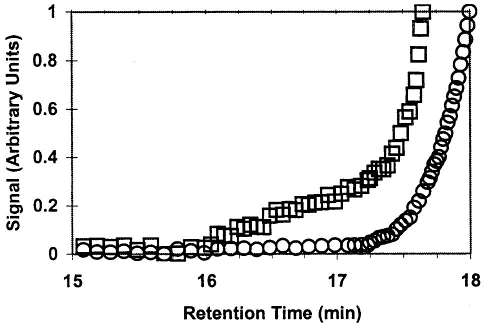

Figure 4. Fluorescence-detector GPC chromatograms with sensitivity to pyrene label for (○) poly(S-*co*-MAP) (unprocessed) and (□) 95/5 wt % high-MW PMMA/poly(S-*co*-MAP) pulverized blend.

formation during pulverization, relevant for reactive blending leading to compatibilization, a 95/5 wt % high-MW PMMA/poly(S-*co*-MAP) blend was studied. Figure 4 compares the fluorescence-detector GPC data for original poly(S-*co*-MAP) and the 95/5 wt % high-MW PMMA/poly(S-*co*-MAP) pulverized blend. It is evident that the fluorescence signal is present in the pulverized blend at elution times in the range of 16.1−17.25 min, where there is no signal from the neat poly(S-*co*-MAP). On the basis of arguments made previously, this signal at low elution times signifies the presence of block copolymer made by coupling of polymer radicals resulting from scission of high-MW PMMA and poly(S-*co*-MAP) during pulverization. Thus, the hypothesis for the origin of the recently achieved compatibilization of a pulverized PS/PMMA blend,[32] i.e., in situ block copolymer formation resulting from coupling of polymer radicals formed via chain scission, is quantitatively supported by the present study. Analysis of the shoulder in Figure 4 at elution times less than 17.25 min indicates that, at a minimum, 0.1% of the pyrene label is attached to block copolymer after pulverization.

The lesser coupling (observed at elution times less than 17.25 min) in Figure 4 as compared with Figure 2 may be due to the fact that PS radical−PS radical reactions proceed mostly by combination rather than disproportionation.[56] It is unknown whether PS radical−PMMA radical coupling undergoes combination to the same extent. As this is the first quantitative demonstration of block copolymer formation during solid-state processing of polymer blends, greater study will be needed to understand the relative roles of combination and disproportionation in interpolymer radical reactions during such processing as well as the impact of polymer composition on the efficiency of intimate mixing and chain scission. (See section B.) Reactions between polymer radicals and oxygen that lead to radical stabilization and reduce the potential for interpolymer radical coupling during pulverization also merit further study.[28,57,58]

It is noteworthy that the role of efficient mixing, vital to interpolymer radical coupling leading to block copolymer formation at polymer−polymer interfaces via pulverization, has also been shown to be important in achieving block copolymer formation via reactive melt processing of polymers containing condensation-type functional groups.[19,20,24,25] These chemically controlled reactions between functional groups typically have high activation barriers, leading to relatively low reaction rate parameters. In contrast, interpolymer radical reactions do not have an activation barrier and possess reaction rate parameters that may be orders of magnitude greater than those of chemically controlled reactions.[23] Just as intense melt mixing results in greater frequency of contact between functional groups and thereby leads to enhanced interpolymer coupling via chemically controlled reactions,[19] intense mixing during pulverization can result in contact between radicals on different polymers and thereby leads to rapid interpolymer coupling via “diffusion-controlled reactions” in the solid state where there is no diffusion.

B. Quantification of in Situ Chain Scission via SSSP. A necessary condition for achieving interpolymer coupling via pulverization is the in situ production of macroradicals, created from the cleavage of polymer chains. By focusing on elution times above 17.25 min, fluorescence-detector GPC data yield M_n values of the poly(S-*co*-MAP) pre- and postpulverization in the blend of 107 000 and 94 600 g/mol, respectively. Assuming that each poly(S-*co*-MAP) chain underwent at most one scission event, 14% of the original poly(S-*co*-MAP) chains experienced scission during SSSP.[59] (A figure of 13.1% of the chains undergoing scission is obtained by assuming that none of the poly(S-*co*-MAP) in the pulverized blend observed at elution times exceeding 17.25 min underwent scission followed by coupling. The 13.1% figure does not count the 0.7% of poly(S-*co*-MAP) that is found at elution times less than 17.25 min in the pulverized blend and must be on coupled chains.) This suggests that, under the conditions employed in pulverizing the 95/5 wt % high-MW PS/poly(S-*co*-MAP) blend, ∼5% of the poly(S-*co*-MAP) radicals produced in situ via SSSP underwent coupling with radicals originating from the high-MW PS in the blend. (This value of ∼5% is obtained by taking the ratio of 0.7% of pyrene that is in coupled chains to the 14% of pyrene in original chains that led to polymer radicals due to chain scission.) While this level of interpolymer coupling may seem modest, Macosko et al.[6] have shown that interfacial regions in an immiscible blend with copolymer levels far from saturation are effective in preventing static coalescence, and compatibilizing the blend, via steric effects.

It is more difficult to estimate the fraction of poly(S-*co*-MAP) radicals produced in situ that couple to macroradicals originating from the high-MW PMMA during SSSP of the high-MW PMMA/poly(S-*co*-MAP) blend. While the PMMA blend was pulverized using conditions similar to the PS blend, there was a much higher level of chain scission of the poly(S-*co*-MAP) in the PMMA blend. The fluorescence-detector GPC chromatogram yielded M_n of 30 000 g/mol for the poly(S-*co*-MAP) after SSSP processing, indicating that there were 3 times as many poly(S-*co*-MAP) chains in the pulverized high-MW PMMA blend than in the pulverized high-MW PS blend. The high level of scission of the poly(S-*co*-MAP) due to SSSP and the bimodal structure of its resulting GPC chromatogram, the latter indicating substantial amounts of polymer that did not cleave as well as polymer that underwent scission multiple times, makes it difficult to estimate the fraction of pyrene label in the PMMA blend that was on chains undergoing scission leading to macroradical formation. Additionally, the fact that a greater fraction of the high-MW PMMA relative to the high-MW PS elutes at times overlapping the elution times for the original poly(S-*co*-MAP) suggests that more of the interpolymer coupling in the PMMA blend should result in pyrene fluorescence signal at elution

Table 1. GPC Comparison of Chain Scission via SSSP for (a) Moderate-MW PS and (b) 11kPS via SSSP Using Four Different Screw Designs

screw	M_n (g/mol)	M_w (g/mol)
	(a) Moderate-MW PS	
unprocessed	1.1E+05[a]	2.6E+05
A	5.5E+04	1.1E+05
B	6.3E+04	1.7E+05
C	9.3E+04	2.1E+05
D	8.7E+04	2.2E+05
	(b) 11kPS	
unprocessed	1.1E+04	2.0E+04
A	1.0E+04	2.0E+04
B	1.1E+04	2.1E+04
C	1.1E+04	2.0E+04
D	1.1E+04	2.0E+04

[a] Read as 1.1 × 10^5.

times exceeding 17.25 min, making it difficult to account for much of the coupling occurring in that blend. Despite the problems in quantifying chain scission, the presence of signal at elution times between 16.1 and 17.25 min in Figure 4 is proof that in situ block copolymer formation occurred in the high-MW PMMA/poly(S-*co*-MAP) blend via interpolymer coupling reaction during pulverization.

Comparison to the level of chain scission in the 70/30 wt % PS/PMMA blend that was recently shown[32,60] to be compatibilized via SSSP is revealing. The PS in that blend, which did not contain pyrene label, experienced a reduction in M_n from 101 000 g/mol pre-SSSP to 73 000 g/mol post-SSSP. Thus, the level of PS chain scission occurring with pulverization of that blend was significantly less than that observed in the 95/5 wt % high-MW PMMA/poly(S-*co*-MAP) blend under investigation here. Nevertheless, that lower level of chain scission and associated macroradical production in the PS/PMMA blend studied in ref 32 was sufficient to achieve compatibilization via block copolymer formation resulting from interpolymer coupling.

While the data indicate that greater levels of PMMA in a PS/PMMA blend lead to greater PS chain scission during SSSP, results in ref 32 indicate that greater levels of polyethylene in a PS/polyethylene blend lead to lesser PS chain scission during SSSP. This complex dependence of pulverization-induced scission on blend composition deserves further study.

Although the SSSP studies with the two poly(S-*co*-MAP) blends were designed to prove in situ interpolymer coupling via pulverization, the high-MW components are atypical of PS or PMMA used in blends for technological application or scientific investigation. Thus, a limited study was undertaken using low-MW and moderate-MW PS in order to examine the effects of screw design and polymer MW on the degree of chain scission resulting from SSSP. As Table 1 illustrates, MW plays a key role in the degree of scission occurring during pulverization. The 11kPS, with its M_n and M_w values invariant with pulverization, does not undergo scission when any of four screw designs is employed. This may be understood to result from the fact that when polymer samples undergo fracture, chains that are of MW comparable to or less than the MW between entanglements, 18 000 g/mol for PS,[61] will experience chain pullout rather than scission.[62,63] However, under identical pulverization conditions, the entangled chains of the moderate-MW PS sample (original $M_n = 110\,000$ g/mol) undergo chain scission. When the pulverizer screw was designed to yield higher shear conditions (designs "A" and "B"), greater chain scission occurred than when the screw was designed with elements imposing lower shear (designs "C" and "D"). Previous work has also shown that pulverization of polymer above the entanglement MW can be achieved without measurable chain scission.[27,28]

Table 1 indicates that the level of scission achieved by SSSP of the moderate-MW PS sample can be "tuned"[64] over a broad range, with reductions of 50% and 58% in M_n and M_w, respectively, with screw design "A", meaning that on average each chain undergoes scission once, to smaller reductions of 15% and 19% in M_n and M_w, respectively, with screw design "C". The ability to control the degree of chain scission achieved during SSSP underscores its utility in producing materials that are tailored to meet specific applications. (It should be noted that no cross-linking was evident in pulverized polymers from this study; on the contrary, pulverized samples from this and previous studies[26,27,30−33] dissolved in appropriate solvents. At most, small levels of pulverization-induced branching of polyolefins have been inferred from rheological properties.[28] In contrast, Smith et al.[35] reported significant cross-linking during batch, cryogenic mechanical milling of polyisoprene/PMMA blends. As pulverized polyisoprene blends have not yet been studied, it is uncertain whether SSSP can yield cross-linking of polymers originally without cross-links.) A screw design resulting in little or no chain scission could be used when intimate mixing is desired without reduction in polymer MW, as in the efficient mixing of polymers of substantially different melt viscosity.[27,30] Conversely, screw designs yielding moderate chain scission may be appropriate for blend compatibilization in which both intimate mixing and chain scission followed by in situ block copolymer formation are desired.

Conclusions

The hypothesis that solid-state shear pulverization of blends can result in cleavage of polymer chains leading to in situ block copolymer formation via interpolymer radical coupling has been proven; this hypothesis has been offered as an explanation of the recent compatibilization[32] obtained during pulverization of PS/polyethylene and PS/PMMA blends. Interpolymer radical coupling reactions occurred during pulverization of homogeneous blends of high-MW PS/poly(S-*co*-MAP) and immiscible blends of high-MW PMMA/poly(S-*co*-MAP). Evidence of interpolymer coupling was obtained via fluorescence-detection GPC used to sense the attachment of pyrene labels, originally on poly(S-*co*-MAP), to coupled chains of higher MW than the poly(S-*co*-MAP). In the high-MW PS/poly(S-*co*-MAP) system, a minimum of 0.7% of pyrene units originally on poly(S-*co*-MAP) was on coupled chains after pulverization, and ~5% of all macroradicals resulting from poly(S-*co*-MAP) scission underwent coupling to macroradicals resulting from high-MW PS scission. These results demonstrate that interpolymer coupling by diffusion-controlled reactions can occur in the absence of diffusion as long as there is intense mixing in the solid state resulting in polymer radical−polymer radical contact.

The "tunability"[64] of in situ polymer radical formation was shown by alteration of SSSP screw design; designs imposing greater shear yielded greater chain scission. Scission levels were also shown to be sensitive to blend composition and MW. In the latter case, scission does not occur during SSSP if the MW is comparable to or less than the MW between entanglements.

Acknowledgment. This work was supported by Material Sciences Corp. and the NSF-MRSEC program (Grant DMR-0076097) at the Materials Research Center of Northwestern University.

References and Notes

(1) Molau, G. E. *J. Polym. Sci., Part A* **1965**, *3*, 4235.
(2) Anastasiadis, S. H.; Gancarz, I.; Koberstein, J. T. *Macromolecules* **1989**, *22*, 1449.
(3) Koning, C.; Van Duin, M.; Pagnoulle, C.; Jerome, R. *Prog. Polym. Sci.* **1998**, *23*, 707.
(4) Majumder, B.; Paul, D. R. In *Polymer Blends*; Paul, D. R., Bucknell, C. B., Eds.; Wiley: New York, 2000; Vol. 1, p 539.
(5) Litmanovich, A. D.; Plate, N. A.; Kudryavtsev, Y. V. *Prog. Polym. Sci.* **2002**, *27*, 915.
(6) Macosko, C. W.; Guegan, P.; Khandpur, A. K.; Nakayama, A.; Marechal, P.; Inoue, T. *Macromolecules* **1996**, *29*, 5590.
(7) Sundararaj, U.; Macosko, C. W. *Macromolecules* **1995**, *28*, 2647.
(8) Ramic, A. J.; Stehlin, J. C.; Hudson, S. D.; Jamieson, A. M.; Manas-Zloczower, I. *Macromolecules* **2000**, *33*, 371.
(9) Eastwood, E. A.; Dadmun, M. D. *Macromolecules* **2002**, *35*, 5069.
(10) Milner, S. T.; Xi, H. W. *J. Rheol.* **1996**, *40*, 663.
(11) Cigana, P.; Favis, B. D. *Polymer* **1998**, *39*, 3373.
(12) Brahimi, B.; Aitkadi, A.; Ajii, A.; Fayt, R. *J. Polym. Sci., Part B: Polym. Phys.* **1991**, *29*, 945.
(13) Weber, M. *Macromol. Symp.* **2002**, *181*, 189.
(14) Scott, C. E.; Macosko, C. W. *Polymer* **1994**, *35*, 5422.
(15) Triacca, V. J.; Ziaee, S.; Barlow, J. W.; Keskkula, H.; Paul, D. R. *Polymer* **1991**, *32*, 1401.
(16) Tan, N. C. B.; Tai, S. K.; Briber, R. M. *Polymer* **1996**, *37*, 3509.
(17) Xanthos, M.; Dagli, S. S. *Polym. Eng. Sci.* **1991**, *31*, 929.
(18) Liu, N. C.; Baker; W. E.; Russell, K. E. *J. Appl. Polym. Sci.* **1990**, *41*, 2285.
(19) Orr, C. A.; Adedeji, A.; Hirao, A.; Bates, F. S.; Macosko, C. W. *Macromolecules* **1997**, *30*, 1243.
(20) Orr, C. A.; Cernohaus, J. J.; Guegan, P.; Hirao, A.; Jeon, H. K.; Macosko, C. W. *Polymer* **2001**, *42*, 8171.
(21) Major, M. D.; Torkelson, J. M.; Brearley, A. M. *Macromolecules* **1990**, *23*, 1711.
(22) Shull, K. R.; Kramer, E. J.; Hadziioannou, G.; Tang, W. *Macromolecules* **1990**, *23*, 4780.
(23) Orr et al. provide data in ref 20 on activation barriers for typical chemically controlled interpolymer coupling reactions as well as comparative information on reaction rate parameters for chemically controlled vs diffusion-controlled interpolymer reactions. For example, acid−oxazoline interpolymer reactions are described as having a 65 kJ/mol activation energy. On the basis of discussion in ref 43, Orr et al. estimate expected values of diffusion-controlled interpolymer reactions during shear-flow melt mixing as being on the order of 10^7 kg/(mol min), which is about 4−8 orders of magnitude greater than observed with the various chemically controlled interpolymer coupling reactions they studied.
(24) Schulze, J. S.; Moon, B.; Lodge, T. P.; Macosko, C. W. *Macromolecules* **2001**, *34*, 200.
(25) Schulze, J. S.; Cernohous, J. J.; Hirao, A.; Lodge, T. P.; Macosko, C. W. *Macromolecules* **2000**, *33*, 1191.
(26) Furgiuele, N.; Lebovitz, A. H.; Khait, K.; Torkelson, J. M. *Macromolecules* **2000**, *33*, 225.
(27) Furgiuele, N.; Lebovitz, A. H.; Khait, K.; Torkelson, J. M. *Polym. Eng. Sci.* **2000**, *40*, 1447.
(28) Ganglani, M.; Torkelson, J. M.; Carr, S. H.; Khait, K. *J. Appl. Polym. Sci.* **2001**, *80*, 671.
(29) Khait, K.; Torkelson, J. M. *Polym.-Plast. Technol.* **1999**, *38*, 445.
(30) Khait, K.; Torkelson, J. M. *Int. Polym. Proc.* **2000**, *15*, 343.
(31) Lebovitz, A. H.; Torkelson, J. M. *Polym. Mater. Sci. Eng.* **2001**, *85*, 530.
(32) Lebovitz, A. H.; Khait, K.; Torkelson, J. M. *Macromolecules* **2002**, *35*, 8672.
(33) Lebovitz, A. H.; Khait, K.; Torkelson, J. M. *Polymer*, in press.
(34) Maurice, D. R.; Courtney, T. H. *Metall. Trans. A: Phys. Metal. Mater. Sci.* **1990**, *21*, 289.
(35) Smith, A. P.; Ade, H.; Balik, C. M.; Koch, C. C.; Smith, S. D.; Spontak, R. J. *Macromolecules* **2000**, *33*, 2595.
(36) Smith, A. P.; Bai, C.; Ade, H.; Spontak, R. J.; Balik, C. M.; Koch, C. C. *Macromol. Rapid Commun.* **1998**, *19*, 557.
(37) Smith, A. P.; Spontak, R. J.; Koch, C. C.; Smith, S. D.; Ade, H. *Macromol. Mater. Eng.* **2000**, *274*, 1.
(38) Smith, A. P.; Ade, H.; Koch, C. C.; Smith, S. D.; Spontak, R. J. *Macromolecules* **2000**, *33*, 1163.
(39) Chen, Z.; Wang, Q. *Polym. Int.* **2001**, *50*, 966.
(40) Font, J.; Muntasell, J.; Cesari, E. *Mater. Res. Bull.* **1999**, *34*, 2221.
(41) Cavalieri, F.; Padella, F. Bourbonneux, S. *Polymer* **2002**, *43*, 1155.
(42) O'Shaughnessy, B.; Sawhney, U. *Macromolecules* **1996**, *29*, 7230.
(43) Fredrickson, G. H.; Leibler, L. *Macromolecules* **1996**, *29*, 2674.
(44) Fredrickson, G. H.; Milner, S. T. *Macromolecules* **1996**, *29*, 7386.
(45) O'Neil, G. A.; Torkelson, J. M. *Trends Polym. Sci.* **1997**, *5*, 349.
(46) O'Neil, G. A.; Torkelson, J. M. *Macromolecules* **1999**, *32*, 411.
(47) Moon, B.; Hoye, T. R.; Macosko, C. W. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2177.
(48) Gray, M. K.; Kinsinger, M. I.; Torkelson, J. M. *Polym. Prepr.* **2002**, *43* (2), 112.
(49) Gray, M. K.; Kinsinger, M. I.; Torkelson, J. M. *Macromolecules* **2002**, *35*, 8261.
(50) Lebovitz, A. H.; Torkelson, J. M., manuscript in preparation.
(51) Robello, D. R. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 1.
(52) Deppe, D. D.; Dhinojwala, A.; Torkelson, J. M. *Macromolecules* **1996**, *29*, 3898.
(53) UV absorbance characterization of MAPyrene label content in poly(S-*co*-MAP) accounted for the several nanometers shift in the absorbance spectrum of MAPyrene monomer relative to the MAPyrene covalently attached to the copolymer.
(54) It is not currently possible to estimate values of shear experienced by the polymer during solid-state shear pulverization. However, it is possible to adjust the screw design in a number of ways to increase or decrease the extent of shear, e.g., by altering the gap between screw elements and the barrel, adding elements to alter residence time in the pulverizer, or selecting screw elements imparting different levels of shear to the polymer.
(55) Some of the signal at elution times exceeding 17.25 min is likely due to chains resulting from interpolymer coupling, but we are not able to distinguish those coupled chains from chains that did not undergo scission or from polymer radicals that did not couple. Hence, we indicate that *at a minimum* 0.7% of the original poly(S-*co*-MAP) in the pulverized blend ended up in coupled chains.
(56) Berger, K. C.; Meyerhoff, G. *Makromol. Chem.* **1975**, *176*, 1983.
(57) Sohma, J. *Pure Appl. Chem.* **1983**, *55*, 1595.
(58) Sakaguchi, M.; Yamaguchi, T.; Shimada, S.; Hori, Y. *Macromolecules* **1993**, *26*, 2612.
(59) Analysis of GPC data using RI detection, which yields sensitivity to all of the polymer in the 95/5 wt % high-MW PS/poly(S-*co*-MAP) and high-MW PMMA/poly(S-*co*-MAP) blends, allows for an approximate indication of the level of chain scission of the high-MW blend components. For both high-MW PS and high-MW PMMA, it appears that several percent of the chains underwent scission during blend pulverization. After accounting for the much higher MW and wt % in the blends of the high-MW polymer as compared with the poly(S-*co*-MAP), this means that roughly comparable levels of polymer radicals originating from high-MW polymer and from poly(S-*co*-MAP) were formed in situ during blend pulverization.
(60) For the 70/30 wt % PS/PMMA blend studied in ref 32, there was no coarsening within error of dispersed-phase particle size of the pulverized blend over a period of 4 h of static annealing at 190 °C. The number-average dispersed phase particle size was 1.8 ± 0.1 μm prior to annealing and 2.0 ± 0.1 μm after 4 h of annealing. In contrast, an identical blend that was not pulverized but instead was melt-mixed via twin-screw extrusion yielded a factor of 4 increase in number-average dispersed phase particle size after only 2 h of static annealing at 190 °C.
(61) Majeste, J.-C.; Montfort, J.-P.; Allal, A.; Marin, G. *Rheol. Acta* **1998**, *37*, 486.
(62) Washiyama, J.; Kramer, E. J.; Creton, C. F.; Hi, C.-Y. *Macromolecules* **1994**, *27*, 2019.

(63) A study using a custom-built "Dental Burr Grinding Instrument" (Sambasivam, M.; Klein, A.; Sperling, L. H. *J. Appl. Polym. Sci.* **1995**, *58*, 357) has shown that 32 000 g/mol monodisperse PS undergoes 100% chain pullout during fracture while under identical fracture conditions chain scission becomes increasingly important as molecular weight increases.

(64) While it is possible to object to the description of "tuning" or "tunability" of the level of chain scission achieved by alteration of pulverizer screw design, we believe that this is an appropriate description of the current state of the art. Like a musical instrument being tuned because it is too sharp or too flat, the approach involved with adjustment of pulverizer screw design to "tune" chain scission is one in which it is currently possible to predict whether certain designs will provide for greater or lesser chain scission. However, it is not possible to know a priori the exact level of chain scission that can be achieved via a new screw design (or via the application of a new polymer or new blend to an old screw design).

MA021239Y