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Interpolymer radical coupling reactions during sonication of polymer solutions

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Abstract

Interpolymer radical coupling was investigated in polymer solutions exposed to high-intensity ultrasound. Fluorescence-detection gel permeation chromatography was used to characterize the sonication product from solutions of blends of high-molecular weight polystyrene (PS)/pyrene-labeled PS and poly(*n*-butyl methacrylate)/pyrene-labeled PS, showing that, along with chain scission leading to macroradical formation, sonochemically induced reactions can lead to interpolymer radical coupling and measurable block copolymer on timescales of 2–4 min. This investigation provides evidence of rapid in situ block copolymer formation that has previously been inferred without proof in sonication studies of polymer blends and their solutions. It is also consistent with recent studies of melt and solid-state processing of blends indicating that in situ interpolymer radical coupling is useful in reactive compatibilization.

Keywords: Sonication; Interpolymer radical coupling; Block copolymer formation

1. Introduction

Compatibilization of immiscible polymer blends is an area of research that presents significant academic and technological challenges [1–3]. Two approaches have dominated attempts to achieve blend compatibilization: the addition of premade block/graft copolymers [4–7] which may reduce interfacial tension at the interface [8] and/or provide steric hindrance to dispersed-phase coalescence [4,9], or reactions between functionalized polymers yielding interfacial block/graft copolymers [10–13]. Nonetheless, both methods suffer from significant drawbacks. The former method has severe kinetic and thermodynamic limitations, which have prevented commercial application [1], while the generally low reaction rates and necessity to modify addition-type polymers with functional groups has yielded only a limited number of commercial, compatibilized blends made by the latter method [2].

Recently, two studies [14,15] have suggested that compatibilization may be achieved via sonication of polymer blends in solution or in the melt. These studies attributed, without proof, such compatibilization to the coupling of macroradicals created from the cleavage of polymer chains. Specifically, Price and West [14] compared the morphologies realized pre- and post-sonication of a polystyrene (PS)/poly(methyl phenyl silane) system, hypothesizing that the finer morphology apparent in the sonicated system was due to the in situ formation of block copolymer. Recently, Kim and Lee [15] compared the morphologies of 70/30 wt% PS/polypropylene (PP) blends in the melt state pre-and post-sonication, finding that the sonicated blend possessed a finer morphology. Without explicit evidence, they ascribed such effects to the in situ copolymer formation between PP and PS macroradicals during sonication. However, interpolymer radical coupling reactions leading to block copolymer formation in immiscible blends have recently been quantified in two different studies, one related to the use of polymers made via nitroxide-mediated controlled-radical-polymerization (NM-CRP) to achieve coupling during melt-state processing [16,17], and the second related to the use of solid-state shear pulverization (SSSP) to achieve coupling during solid-state processing [18,19]. In the former case, melt processing leading to coupling of polymers made via NM-CRP was

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shown in PS/PS, PS/poly(4-methylstyrene), and PS/poly(*n*-butyl methacrylate) (PnBMA) blends. (For further information on NM-CRP, which can yield polymers that 'uncap' at high temperatures resulting in macroradical formation, see Refs. [16,20,21]). In the latter case, macroradical coupling during pulverization in the solid state was proven using high molecular weight (MW) PS/pyrene-labeled PS and high-MW poly(methyl methacrylate)/pyrene-labeled PS blends. (For further information on SSSP, see Refs. [22–25]). Proof of macroradical coupling was achieved by fluorescence-detection gel permeation chromatography (GPC) in which the signal associated with the pyrene label in the melt-mixed (NM-CRP study) or pulverized (SSSP study) blends was observed at elution times less than those of the unprocessed blends. The use of fluorescence-detection GPC to prove block copolymer formation during processing of immiscible blends was pioneered by Macosko and co-workers [26,27] who quantified interpolymer coupling via condensation reactions of functional groups covalently attached to the polymers.

While NM-CRP and pulverization yield thermochemical and mechanochemical bases, respectively, for interpolymer radical coupling leading to block copolymer formation, the hypotheses expressed in prior sonication studies point toward a sonochemical basis for interpolymer radical coupling reactions either in solution or the melt state. In sonochemical processes, high-intensity ultrasonic waves are produced, bringing about cavitation in which macroscopic vapor bubbles are formed and eventually collapse [28]. The implosion of such bubbles results in powerful shock waves radiating throughout the polymeric sample, inducing shear and leading to homolytic cleavage of polymer chains. Many studies, e.g. Refs. [29–33], have quantitatively investigated via GPC the relative reductions in MW and polydispersity associated with the sonochemically-induced chain scission of homopolymer solutions. However, only Fujiwara and co-workers have investigated the ability of high-intensity ultrasound to lead to interpolymer coupling reactions, finding via selective solvent extraction combined with Fourier transform infrared spectroscopy that interpolymer coupling can occur at long sonication times (up to 6 h) with solutions of poly(vinyl chloride) (PVC)/poly(vinyl alcohol) (PVA) blends [34].

In this communication, the fluorescence-detection GPC technique previously utilized to confirm interpolymer radical coupling and block copolymer formation in NM-CRP and SSSP studies of blends is used to provide conclusive evidence of interpolymer radical coupling at short sonication times (2–4 min) in solutions of high-MW PS/pyrene-labeled PS and of PnBMA/pyrene-labeled PS. These results support the assertions of Price and West [14] and Kim and Lee [15] and indicate that the macroradical coupling needed for blend compatibilization may be achieved at sonochemical processing times considerably shorter than previously suggested.

2. Experimental

2.1. Materials

Sonication studies used blends of high-MW PS (Pressure Chemical, $M_n = 1{,}520{,}000$ g/mol, $M_w = 1{,}920{,}000$ g/mol, reported by the supplier) with pyrene-labeled PS ($M_n = 91{,}000$ g/mol, $M_w = 169{,}000$ g/mol, GPC data analyzed relative to PS standards) and PnBMA ($M_n = 239{,}000$ g/mol, $M_w = 388{,}000$ g/mol, GPC data analyzed using a universal calibration method with Mark-Houwink parameters from the literature) with pyrene-labeled PS ($M_n = 100{,}000$ g/mol, $M_w = 181{,}000$ g/mol, GPC data analyzed relative to PS standards). The two pyrene-labeled PS samples were synthesized by bulk free radical polymerization of styrene in the presence of a small amount of 1-(1-pyrene)methyl methacrylate, the latter made via esterification of methacryloyl chloride and 1-pyrene methanol [35]. The pyrene label content of both pyrene-labeled PS samples was determined via UV–vis absorbance to be 1 pyrene label per 114 styrene repeat units. The PnBMA was also synthesized by bulk free radical polymerization using 2,2′-azobisisobutyronitrile as the initiator. GPC chromatograms of the polymers used in each blend are given in Fig. 1.

2.2. Sonication

A 1 wt% solution of an 80/20 wt% high-MW PS/pyrene-labeled PS blend was prepared in 20 ml toluene and then deoxygenated by bubbling dry N_2 for ~10 min. The solution was sonicated for 10 min while maintaining a constant flow of dry N_2, using a Misonix Inc. model XL-2020 Ultrasonic Liquid Processor sonicator set at a reading of 5. (According to Misonex, the sonicator has a displacement amplitude of ~60 μm at a dial reading of 5). 0.5 ml aliquots were removed from the reaction mixture at 1 min intervals and allowed to evaporate, after which they were placed in a vacuum oven at 110 °C overnight. A similar procedure was used for sonication of a 4 wt% solution of a 70/30 wt% PnBMA/pyrene-labeled PS blend prepared in 40 ml toluene. In this instance, 2 ml aliquots of the sonication product were evaporated followed by extraction with 2 ml of a selective solvent, 2-propanol, which is a theta solvent for PnBMA and a nonsolvent for PS [16]. The sonication product was allowed to dissolve overnight in 2-propanol and filtered to separate the solution from undissolved remnants.

2.3. Confirmation of interpolymer coupling reactions

Changes in MW distribution due to sonication were quantified using a Waters Breeze GPC apparatus, calibrated with monodisperse PS standards and equipped with UV–vis absorbance, refractive index (RI), and fluorescence detectors, using tetrahydrofuran (HPLC grade, Aldrich) flowing at 1.0 ml/min as the eluent. Interpolymer radical coupling in

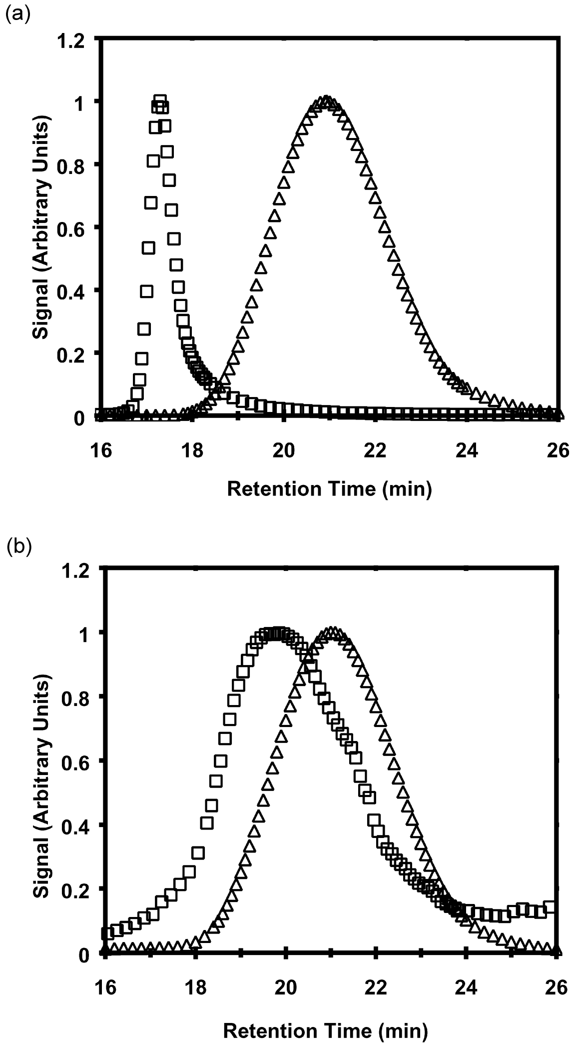

Fig. 1. Fluorescence-detector GPC chromatograms for blends of a) high-MW PS (□) and pyrene-labeled PS (△) and b) PnBMA (□) and pyrene-labeled PS (△). Note: to plot PnBMA results with the fluorescence-detector chromatograms, PnBMA data from the RI detector were corrected to account for detector delay time between the RI and fluorescence detectors. In the case of high-MW PS, the fluorescence detector was set to phenyl ring fluorescence; in the case of pyrene-labeled PS, the fluorescence detector was set to pyrene label fluorescence.

the high-MW PS/pyrene-labeled PS blend was characterized using the GPC fluorescence detector set to pyrene fluorescence (excitation at 336 nm, emission at 368 nm) by comparing the pre-sonication elution or retention times for pyrene-labeled PS with those of the post-sonication blends. (For further description of methodology, see Refs. [16,18]). In the case of the PnBMA/pyrene-labeled PS blend, interpolymer radical coupling leading to block copolymer formation was confirmed simply by the presence of pyrene fluorescence in the extracted, post-sonicated samples. A control study in which the pre-sonication PnBMA/pyrene-labeled PS blend was extracted using the procedure described in Section 2.2 above yielded no pyrene signal in the fluorescence-detection GPC chromatogram, indicating that it is not possible to extract PS homopolymers along with PnBMA.

3. Results and discussion

In order to perform proof-of principle studies of interpolymer radical coupling via sonication, it is necessary to design the mixtures carefully so that unequivocal evidence is obtained from analysis of the sonication product. Fig. 1a shows that the original pyrene-labeled PS employed in the high-MW PS/pyrene-labeled PS study yields essentially no signal at GPC elution times less than 17.7 min. Given that the high-MW PS exhibits substantial signal at GPC elution times significantly less than 17.7 min (see Fig. 1a), it is possible to verify the presence of sonication-induced interpolymer coupling reactions based on the GPC elution times at which the pyrene signal is observed in the post-sonication solutions. The presence of fluorescence signal in the post-sonication mixture at elution times significantly less than 17.7 min should occur only if a fraction of the pyrene labels is attached to chains resulting from the coupling of polymer radicals made by in situ scission of pyrene-labeled PS and high-MW PS. Determination of interpolymer radical coupling in the PnBMA/pyrene-labeled PS system is accomplished using GPC in a slightly different manner and is independent of elution time of the sonicated product. As 2-propanol does not dissolve PS homopolymer (see Section 2.2 earlier), the presence of pyrene signal in the fluorescence-detection GPC data of the extracted solution resulting from the sonicated product is indicative of styrene blocks attached to PnBMA blocks in copolymer formed via interpolymer radical coupling. Thus, any level of pyrene signal in the post-sonication extracted product is proof of block copolymer formation.

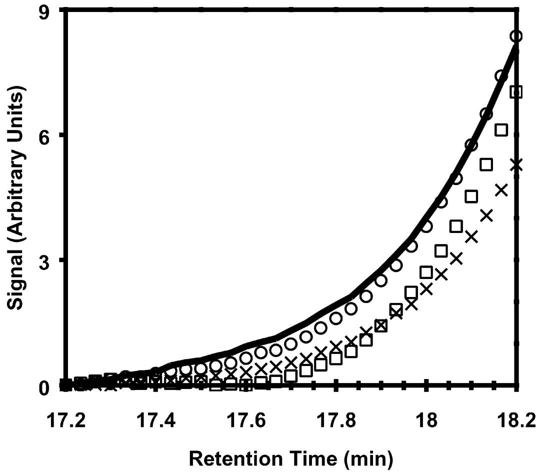

Fig. 2. Fluorescence-detector GPC chromatograms with sensitivity to pyrene label for 80/20 wt% PS ($M_n = 1{,}520{,}000$ g/mol)/pyrene-labeled PS ($M_n = 91{,}000$ g/mol) blend sonicated for 0 min (□), 2 min (○), 3 min (—), and 10 min (×).

Fig. 2 shows fluorescence-detector GPC data characteristic of the PS containing pyrene label in the region pertinent for proving the presence of interpolymer coupling in the 80/20 wt% high-MW PS/pyrene-labeled PS sonicated blend. Prior to sonication, there is no fluorescence signal at elution times less than 17.7 min. As shown in Fig. 2, after sonication for 2 min there is a small amount of GPC signal exhibited by the PS/PS blend at elution times as low as 17.3 min, indicating that some of the pyrene label is covalently attached to polymer made via interpolymer coupling reaction of polymeric radicals resulting from sonochemically induced chain scission. (Replicate GPC runs demonstrated good reproducibility of GPC signal, indicating that the 0.4 min difference in signal onset between the pre-sonicated sample and the sample sonicated for 2 min is related to interpolymer coupling during short-term sonication).

This signal at elution times less than 17.7 min represents ~0.07% of the total area under the fluorescence-detector GPC chromatogram, meaning that during sonication a minimum of 0.07% of the original pyrene-labeled PS underwent scission followed by coupling with polymer radicals originating from the high-MW PS. (Some of the signal at elution times exceeding 17.7 min is also due to chains resulting from interpolymer radical coupling, but the fluorescence GPC detector is unable to distinguish between those coupled chains and chains that did not undergo scission or from polymer radicals that did not couple. Hence, we indicate that at a minimum 0.07% of the original pyrene-labeled PS in the sonicated blend is present in coupled chains.) The intensity of the GPC signal representing coupled chains increases between 2 and 3 min of sonication time (see Fig. 2), at which time at least ~0.08% of the original pyrene-labeled PS participated in interpolymer radical coupling reactions. At sonication times exceeding 3 min, the fluorescence-detection GPC results indicate a reduction in signal at elution times less than 17.7 min. For example, the curve in Fig. 2 representing the high-MW PS/pyrene-labeled PS blend after sonication for 10 min indicates that many of the chains resulting from interpolymer coupling at 2–3 min sonication have undergone substantial chain scission upon further exposure to high-intensity ultrasound.

A necessary condition for achieving interpolymer radical coupling via sonication is the in situ production of macroradicals, created from the cleavage of polymer chains. Fig. 3 illustrates the evolution in MW distribution of the sonicated bimodal PS mixture in the high-MW PS/pyrene-labeled PS blend. Prior to sonication, two peaks are present in the UV–vis absorbance-detector GPC chromatogram, with the absorbance detector set at 254 nm for phenyl ring absorbance (indicative of PS, not of pyrene label). The peak intensities of the high-MW PS and pyrene-labeled PS occur at elution times of ~17.3 min and ~21 min, respectively. After 5 min exposure of the solution blend to high-intensity ultrasound, the chromatogram peak representing the high-MW PS has shifted by more than 1 min to longer elution times, and there is little chromatogram signal at 17.3 min or earlier, meaning that sonication resulted in efficient chain scission of the high-MW PS. Furthermore, the disparity between the two elution peaks present in the blend prior to sonication has become much less pronounced after sonication for 5 min. Upon 10 min of sonication, the high-MW PS peak has shifted by ~1 min to longer elution times relative to the 5 min sonication trial, signifying the ongoing destruction of high-MW PS chains. In addition, the GPC chromatogram appears as a broad peak, with the long-elution-time signal being little affected by an increase in sonication time from 5 to 10 min. These results are in accord with other sonication studies [29–31] that have reported that the rate of chain degradation or scission increases with increasing MW, with a limiting MW below which no further degradation occurs.

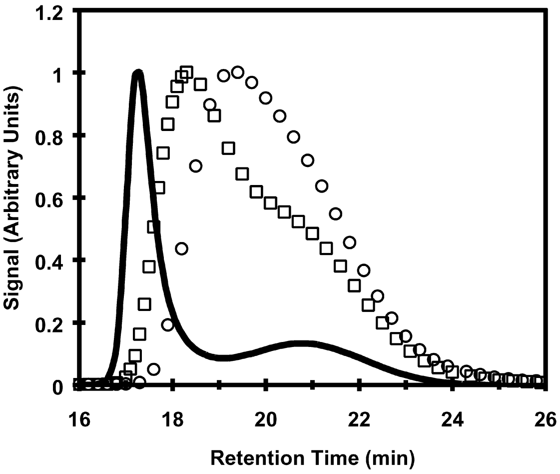

Fig. 3. UV–vis absorbance-detector GPC chromatograms with sensitivity to phenyl rings for 80/20 wt% PS (M_n = 1,520,000 g/mol)/pyrene-labeled PS (M_n = 91,000 g/mol) blend exposed to high-intensity ultrasound for 0 min (—), 5 min (□), and 10 min (○).

Thus, Fig. 3 demonstrates that chain scission, a prerequisite for interpolymer radical reactions, is easily achieved provided that the chains are not of very low MW. Furthermore, it is evident from Fig. 3 that only a small degree of chain scission is necessary for interpolymer radical coupling reactions to take place. Comparing the MW of the pyrene-labeled PS before and after 3 min of sonication reaction, fluorescence-detector GPC data yield M_n values of 91,000 and 88,000 g/mol, respectively. Nonetheless, this reduction in M_n of only 3.3% may result in a measurable degree of interpolymer radical coupling as shown in Fig. 2. While this level of interpolymer coupling may seem modest, in the context of blend compatibilization Macosko et al. [4] have shown that copolymer levels far from saturation at interfacial regions in an immiscible blend are effective in preventing static coalescence, and compatibilizing the blend, via steric effects.

Fluorescence-GPC data pertinent for illustrating interpolymer radical coupling reaction in the PnBMA/pyrene-labeled PS system are shown in Fig. 4. Fig. 4 indicates that

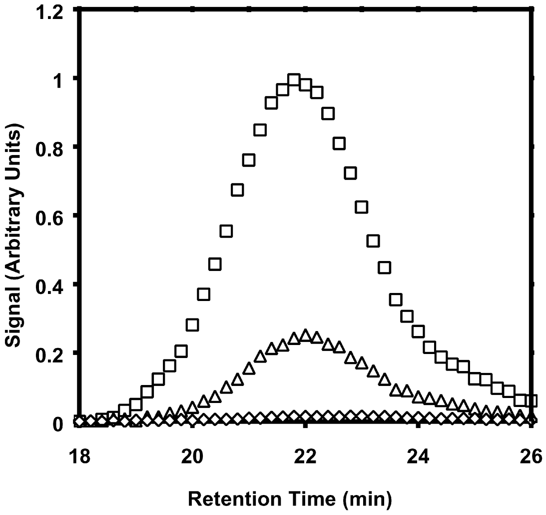

Fig. 4. Fluorescence-detector GPC chromatograms with sensitivity to pyrene label for 70/30 wt% PnBMA ($M_n = 239,000$ g/mol)/pyrene-labeled PS ($M_n = 100,000$ g/mol) blend sonicated for 0 min (◇), 2 min (□), and 4 min (△).

appreciable amounts of pyrene-labeled PS are sensed by the fluorescence detector from samples collected after 2 and 4 min of sonication time. As these samples were extracted prior to GPC analysis with a selective solvent, 2-propanol, that was unable to dissolve PS homopolymer, the fluorescence-GPC signals present in Fig. 4 must originate from the attachment of PS blocks to PnBMA blocks via interpolymer coupling reaction. In order to prove that the extraction process was effective in removing all PS from solution, an identical analysis was performed for the 0 min (pre-sonication) sample collected and extracted from the same solution used in the sonication experiment. The results of this control experiment indicate a complete lack of fluorescence-GPC signal, confirming that the data shown in Fig. 4 must represent PnBMA/PS block copolymer created during sonication.

The shape and position of the peaks shown in Fig. 4 may be used to provide information about the degree of chain scission and radical recombination occurring during sonication. By comparing the areas underneath the peaks of the sonicated samples to that of the pyrene-labeled PS, all of known concentrations, the wt% conversion from homopolymer to block copolymer after 2 and 4 min of sonication are estimated as 0.20 and 0.05%, respectively. The apparent decrease in conversion with increasing sonication time from 2 to 4 min illustrates the susceptibility of the copolymers to undergo further chain scission with continued exposure to high-intensity ultrasound. The continual degradation of block copolymer is manifested in the small shift in the fluorescence-GPC data shown in Fig. 4 to longer retention times with increasing sonication.

Finally, it is important to note the that the interpolymer coupling observed in these experiments occurs at a timescale as much as two orders of magnitude lower than those studied by Fujiwara et al. [34] using sonicated PVC/PVA blends. While their study indicated the occurrence of interpolymer coupling over a 6 h period, here the coupling of polymer radicals is measurable after only several minutes of sonication reaction. Therefore, the present study has shown that sonication may result in the cleavage of polymer chains and the subsequent recombination of macroradicals within short experimental times, confirming points inferred in two recent studies [14,15] of sonicated blends and providing another example of the ability of interpolymer radical coupling to result in block copolymer formation in processes that generate macroradicals.

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