Diffusion-Controlled Polymer−Polymer Reactions in Bulk: Novel Strategy for Model Experiments and Reactive Compatibilization Using Polymers Synthesized via Controlled Radical Polymerization

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Introduction. Theory by Doi,[1,2] de Gennes,[3,4] and others[5−16] has focused on diffusion-controlled interpolymer reactions in melts and blends.[5−16] There are many reasons for this interest. de Gennes said that diffusion-controlled binary reactions in nonentangled melts offered “probably the simplest touchstone for studies on Rouse dynamics.”[3] There is also interest in understanding the impacts of entanglements and flow on interpolymer reactions lacking an activation barrier. de Gennes[3] noted that a practical example of such reactions is polymer radical/polymer radical reactions in melt or solution, e.g., termination in free radical polymerization,[17,18] but for model studies he suggested the use of photophysical interactions, e.g., fluorescence/phosphorescence quenching[19,20] and excimer formation.[21] Photophysical interactions have the advantage of not modifying molecular weight (MW). However, while such interactions allow for studies of diffusion-limited interpolymer interactions in solution,[19−21] the short lifetime of the luminescence excited state (∼1−100 ns for fluorescence; ∼1−100 μs for phosphorescence) disallows their use for model studies of certain diffusion-controlled reaction regimes in melts and makes practical measurement in any reaction regime in melts difficult. Thus, photophysics has not yielded useful tests of theories of diffusion-controlled interpolymer reactions in bulk. Difficulty in obtaining polymer radicals of low polydispersity long prevented the use of interpolymer radical reactions in model studies. Recently, a strategy[14] was described involving photochemical cleavage at the center of a chain that yields two polymeric radicals, allowing the study of radical−radical reactions with highly correlated initial conditions, an interesting but limited case.

Diffusion-controlled interpolymer reactions may be useful in reactive processing and compatibilization of immiscible blends in which interpolymer reactions yield block or graft copolymers. There are many model and limited commercial examples of compatibilization using reaction of condensation-type functional groups.[22−29] While reaction of such groups on low-MW species has long been known to be chemically controlled, i.e., the reaction has an activation barrier and a rate parameter orders of magnitude smaller than that of a diffusion-controlled reaction, such interfacial reactions were only recently shown to be chemically controlled in polymer blends.[30,31] The much lower reactivity of condensation-type units located on different polymers as compared with interpolymer radical reactions suggests that advantage in reactive compatibilization may be achieved using interpolymer reactions lacking an activation barrier.

Employing polymers made by nitroxide-mediated controlled radical polymerization (NM-CRP), we demonstrate the potential utility of a novel strategy involving interpolymer radical reactions in model studies and in reactive processing/compatibilization. Recently, CRP has been useful in producing materials previously made only by anionic polymerization[32−38] as well as in developing new classes of materials, e.g., gradient copolymers.[39,40] Using polymers made by NM-CRP, we show that significant interpolymer coupling occurs during high-temperature melt processing. This is due to high “active” radical concentrations associated with the reversible capping reaction (in which polymer radicals become dormant by combination with a nitroxyl radical) being pushed to a state in which the capping is negligible. Melt processing which results in coupling of polymers made via NM-CRP is shown in polystyrene−polystyrene (PS−PS), PS−poly(4-methylstyrene) (PMS), and PS−poly(*n*-butyl methacrylate) (PnBMA) systems. Radical−radical coupling during melt processing is confirmed by gel permeation chromatography (GPC) with fluorescence detection of pyrene labels originally on one polymer species, similar to the work of Moon et al.,[41] who confirmed coupling of polymers containing comparatively slow-reacting condensation-type functional groups.

Experimental Section. Styrene, 4-methylstyrene, and butyl methacrylate (Aldrich, 99%) were deinhibited with inhibitor remover and CaH_2. 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) and benzoyl peroxide (BPO) were used as received (Aldrich). 1-(1-Pyrene)methyl methacrylate (MAPyrene) was synthesized as described elsewhere.[42,43] Alkoxyamine 29 was synthesized as described by Benoit et al.[44] Polymerizations were done at 125 °C following a 30 min N_2 purge. Unlabeled PS (PS−TEMPO) and PMS (PMS−TEMPO) were made via two-step chain extension. 50 mL of styrene and a 1.3:1 ratio of TEMPO:BPO (0.2194 g of BPO) were combined and polymerized for 24 h. 20 mL of 4-methylstyrene and a 1.3:1 molar ratio of TEMPO:BPO (0.0720 g of BPO) were combined and polymerized for 8 h. Then 3.7×10^{-3} mol/L of macroinitiator and monomer (300 mL of styrene or 90 mL of 4-methylstyrene) were combined and polymerized for 15 and 35 min for PS and PMS, respectively. Polymer was precipitated and dried under vacuum for several hours. $M_n = 37\,800$ and $M_w/M_n = 1.3$ for PS−TEMPO, while $M_n = 49\,600$ and $M_w/M_n = 1.4$ for PMS−TEMPO.[45] Unlabeled PnBMA (PnBMA-29) was made by combining 25 mL of butyl methacrylate and 3.7×10^{-3} mol/L alkoxyamine 29 and reacting for 30 min, resulting in $M_n = 107\,000$ and $M_w/M_n = 1.7$.[46,47] Pyrene-labeled PS (*PS−TEMPO) was made via chain extension. 10 mL of styrene and a 1.3:1 molar ratio of TEMPO:BPO (0.2283 g of BPO) were combined and reacted for 4 h. 10 mL of styrene was combined with 3.7×10^{-2} mol/L of the resulting macroinitiator and 0.04 mol % MAPyrene; samples *PS−TEMPOa and *PS−TEMPOb were polymerized for 15 and 30 min, respectively. $M_n = 11\,300$ and $M_w/M_n = 1.15$ for *PS−

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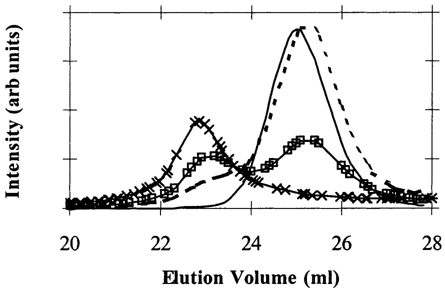

Figure 1. GPC fluorescence-detector chromatograms (sensing pyrene label) of codissolved, precipitated, and dried mixtures of PS–TEMPO and *PS–TEMPOa after melt processing at 200 °C for (- - -) 3 min and (□) 10 min. Also shown are chromatograms of the original PS–TEMPO (×) and *PS–TEMPOa (—). (Note: To plot PS–TEMPO results with the fluorescence-detector chromatograms, PS–TEMPO data from the refractive index detector were corrected to account for detector delay volume between the refractive index and fluorescence detectors.[48] Also, to help guide the eye, solid curves have been added going through the "□" and "×" symbols.)

TEMPOa; $M_n = 12\,300$ and $M_w/M_n = 1.17$ for *PS–TEMPOb. From UV–vis absorbance, both pyrene-labeled PS samples had one pyrene label per 1300 styrene units, meaning that less than 10% of the chains were labeled.

Before and after melt processing, labeled polymer was characterized by GPC (tetrahydrofuran as eluent) using a fluorescence detector (336 nm excitation and 368 nm emission for pyrene label).[48] Samples were processed as follows. Mixtures of 95/5 wt % unlabeled/labeled polymer were either codissolved, precipitated, and dried under vacuum for several hours, yielding intimate mixtures, or were made by hand-mixing dry powder. Mixtures were melt-processed for 3–10 min in a small cup-and-rotor mixer (Atlas Electric Devices Mini-MAX Molder) at 150–200 °C.[49,50]

Results and Discussion. Figure 1 shows chromatograms for PS–TEMPO and *PS–TEMPOa before and after melt processing. The unreacted PS–TEMPO has a peak intensity at an elution of ~22.8 mL. In contrast, the unreacted, lower MW labeled *PS–TEMPOa exhibits signal between 23.5 and 27.5 mL, with a peak at ~24.8 mL. Radical–radical coupling of *PS–TEMPOa to PS–TEMPO is evident after codissolution and precipitation followed by melt processing at 200 °C. After melt processing for 3 min, an intensity shoulder develops between 22.0 and 24.0 mL elution, while melt processing for 10 min results in a second peak between 22.0 and 24.0 mL. Thus, the after-melt-processing chromatograms show the presence of pyrene labels on significantly higher MW chains, associated with the lower elution volume peaks or shoulders, than in the before-melt-processing chromatogram. Crude deconvolution of the two peaks for the mix processed for 10 min suggests that as much as 40% of the pyrene label is attached to coupled polymer. This occurs only if melt processing is accompanied by radical–radical coupling. Based on the preponderance of unlabeled PS in the blend, the majority of the coupling experienced by the *PS–TEMPOa is heterocoupling, with the lower MW *PS–TEMPOa reacting with the higher MW PS–TEMPO.[51,52] Hence, in situ radical–radical coupling at common melt-processing conditions using PS synthesized via NM-CRP is proven.

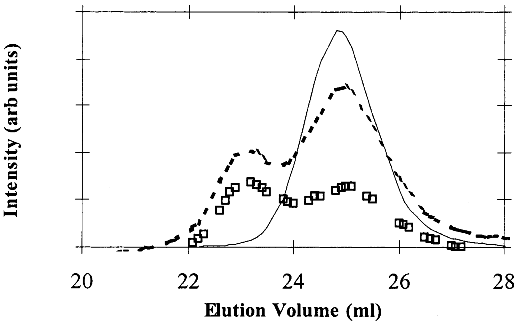

Figure 2. GPC fluorescence-detector chromatograms (sensing pyrene label) comparing impact of method of mixing PS–TEMPO and *PS–TEMPOb *before* melt processing on radical–radical coupling achieved *during* melt processing: (□) codissolved, precipitated, and dried mix and then melt processed at 180 °C for 10 min; (- - -) sample made by hand-mixing dry powder and then melt processed at 180 °C for 10 min. Also shown is the original *PS–TEMPOb (—) chromatogram.

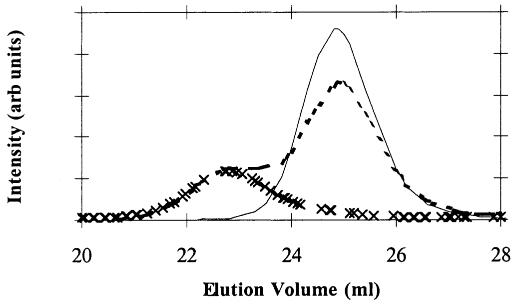

Figure 3. GPC fluorescence-detector chromatogram (sensing pyrene label) of codissolved, precipitated, and dried mixture of PMS–TEMPO and *PS–TEMPOb after melt processing at 160 °C for 5 min: (- - -). Also shown are chromatograms of the original PMS–TEMPO (×) and *PS–TEMPOb (—). (Note: To plot PMS–TEMPO results with the fluorescence-detector chromatograms, PMS–TEMPO data from the refractive index detector were corrected to account for detector delay volume between the refractive index and fluorescence detectors.[48])

While codissolution/precipitatation yields intimate physical mixing prior to melt processing, this is a poor model for processing applications. Figure 2 compares chromatograms for a 95/5 wt % PS–TEMPO/*PS–TEMPOb sample mixed by codissolution and precipitation followed by melt processing at 180 °C for 10 min with a sample that was hand-mixed (dry powder) prior to melt processing at 180 °C for 10 min. Based on the double peaks, both samples show substantial radical–radical coupling upon melt processing. Crude peak deconvolution suggests that nearly one-half of the pyrene labels in the sample that was first codissolved are on coupled chains while nearly one-third of the labels in the initially hand-mixed sample are on coupled chains. Thus, an initially segregated state of the sample prior to melt processing does not preclude significant coupling during melt mixing of polymers made by NM-CRP.

To demonstrate relevance for reactive compatibilization, this approach has been generalized for coupling between PS and different polymers. Figure 3 shows chromatograms for a sample of PMS–TEMPO and *PS–TEMPOb before and after melt processing at 160 °C for 5 min. After processing, pyrene label is significantly present on chains consistent with the elution volumes of the higher MW PMS–TEMPO, indicating that in situ radical–radical reaction has occurred between the higher MW PMS–TEMPO and the lower MW *PS–TEMPOb. Figure 4 shows chromatograms

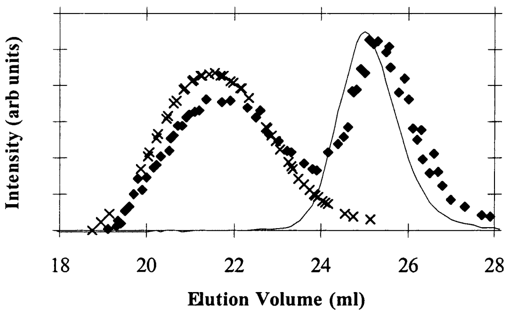

Figure 4. GPC fluorescence-detector chromatogram (sensing pyrene label) of hand mixture (dry powder) of PnBMA-29 and *PS−TEMPOa after melt processing at 180 °C for 5 min (◆). Also shown are GPC chromatograms of the original PnBMA-29 (×) and *PS−TEMPOb (—) before mixing and melt processing. (Note: To plot PnBMA-29 results with the fluorescence-detector chromatograms, PnBMA-29 data from the refractive index detector were corrected to account for detector delay volume between the refractive index and fluorescence detectors.[48])

before and after processing of PnBMA-29 and *PS-TEMPOa at 180 °C for 5 min. After melt mixing there is a double peak, with the new peak at elution volumes consistent with the higher MW PnBMA-29. Crude peak deconvolution indicates that after melt mixing at least one-half of the label is located on coupled chains, much of it on block copolymer, even though the polymers were simply hand-mixed as dry powder before melt mixing.[53,54]

Relevance to model studies was also shown using a solution-cast film of 95/5 wt % PS−TEMPO/*PS−TEMPOa. Heating at ∼170−180 °C for 10 min yielded about one-third of pyrene label on coupled chains. Thus, polymers made via NM-CRP can undergo efficient interpolymer radical−radical coupling at conditions amenable to model studies and reactive compatibilization. Application of this new strategy to such studies is underway as is comparison to another approach using solid-state shear pulverization with which in situ reactive compatibilization of immiscible blends has recently been achieved.[55−58] Effort is also focused on better understanding the NM-CRP process itself.[59,60]

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(47) The value of 1.7 for M_w/M_n of PnBMA-29 indicates that some of the chains may no longer be "living". This value of polydispersity index is consistent with other acrylate/methacrylate polymers made via NM-CRP; e.g., see ref 44 and Keoshkerian, B.; Szkurhan, A. R.; Georges, M. K. *Macromolecules* **2001**, *34*, 6531.

(48) GPC chromatograms for unlabeled polymers were obtained using a refractive index detector. To plot the chromatograms for unlabeled and labeled polymer samples in the same figure, the detector delay volume of 0.145 mL between the refractive index and fluorescence detectors was subtracted from all refractive index data.

(49) The rotor speed was set at either 56 or 73 rpm with load times between 30 and 55 s. The standard sample size of this MiniMAX molder is 4 cm^3, the loading volume used in the studies described here.

(50) The range of melt-mixing temperatures used in this study (150−200 °C) was chosen to determine whether this approach had a significant limitation at lower melt-processing temperatures due to reduced “active” radical populations. For the limited, proof-of-principal studies undertaken here, no significant limitation was observed for the selected melt-mixing temperatures.

(51) For the sample mixture in Figure 1 the molar ratio of *PS−TEMPOa to PS−TEMPO is 1 to 5.7.

(52) Given the 1 to 5.7 molar ratio of *PS−TEMPOa to PS−TEMPO in the mixture yielding the results shown in Figure 1, it is clear that the *PS−TEMPOa chains underwent coupling reactions primarily with PS−TEMPO chains (heterocoupling) while the PS−TEMPO chains would be expected to undergo coupling reactions more often with other PS−TEMPO chains (homocoupling).

(53) A control experiment was performed on a 95/5 wt % PnBMA/PS mixture to verify that thermal scission or melt-processing induced scission of the PS was not the cause of the observed effects in Figures 1−4. The PnBMA described in the Experimental Section was used. The PS used was synthesized via anionic polymerization and had a M_n = 7100 g/mol and a $M_w/M_n = 1.2$ according to the fluorescence detector of the GPC; as it was not made by NM-CRP, there is no ability of the PS to undergo interpolymer radical coupling in the absence of chain scission. The mixture was melt processed at 180 °C for 10 min. The sample was analyzed via GPC after melt processing, yielding M_n = 7400 g/mol and a $M_w/M_n = 1.2$ according to the fluorescence detector with fluorescence coming from the phenyl rings of the PS chains. Additionally, no “double” peak was found as shown in Figures 1−4. Thus, within experimental error, the before and after melt-processing GPC chromatograms are the same, ruling out thermally induced or melt-processing induced scission of PS as the cause for the interpolymer coupling effects observed in Figures 1−4.

(54) A second technique was employed to confirm block copolymer formation, that involving extraction with a selective solvent. According to ref 45, 2-propanol is a Θ solvent for PnBMA and a nonsolvent for PS. 0.0535 g of the melt-processed (180 °C, 5 min) 95/5 wt % PnBMA/PS blend from Figure 4 was dissolved in 25 mL of 2-propanol. The sample was allowed to dissolve overnight and filtered to separate the solution from undissolved sample remnants. The solution was analyzed for the presence of styrene repeat units and pyrene labels using a UV−vis spectrophotometer. Absorbance peaks were observed in the 240−270 nm range characteristic of styrene repeat units and at 336 nm characteristic of pyrene label. GPC was also used to characterize the solution. The fluorescence detector was set to the excitation and emission wavelengths of styrene repeat units (254 and 340 nm, respectively). Analysis showed that the polymer containing styrene repeat units in the extracted solution had a M_n = 66 400 g/mol, which can result only because the PS present before melt processing (with M_n = 11 300 g/mol) underwent substantial interpolymer coupling with PnBMA to yield block copolymer.

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