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Flow Accelerates Interfacial Coupling Reactions

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ABSTRACT: Reactive coupling of functional polymer chains has been reported to be 3 orders of magnitude slower at static interfaces than under mixing conditions, and the reaction rates under mixing are close to the rates measured in homogeneous melts [Jeon et al. *Prog. Polym. Sci.* **2005**, *30*, 939]. However, due to the complexity of interfacial area generation during mixing, it was difficult to isolate the effects of flow on reaction kinetics. In this paper, a reactive multilayer system was created to explore this issue. A 640-layer polystyrene (PS)/poly(methyl methacrylate) (PMMA) sample was fabricated with a multilayer coextruder. Each component contained 10 wt % functional polymer, an amine-terminal PS (PS-NH_2), and an anthracence-labeled anhydride-terminal PMMA (PMMA-anh-anth), respectively. Coupling reactions between PS-NH_2/PMMA-anh-anth occurred during extrusion. The reaction conversion was measured with size exclusion chromatography, and interfacial morphology was monitored with both scanning and transmission electron microscopy. It was found that a significant amount of PS-*b*-PMMA copolymer formed during coextrusion, such that the interfaces of the extrudate were almost completely saturated with the block copolymers formed *in situ*. The coupling reaction of PS-NH_2/PMMA-anh-anth under coextrusion was as rapid as that under mixing and was up to 1000 times faster than that under quiescent annealing. Subsequent steady shear of the multilayer samples further increased the reaction conversion significantly but destroyed the layer structure. Micelles and swollen micelles were formed under shear. Dynamic shear did not promote any further reaction due to the already high interfacial coverage for the extrudate. In contrast, for a simple laminated bilayer sample with nearly zero interfacial coverage, reactive coupling was promoted significantly by dynamic shear as evidenced by interfacial roughening. We speculate that the high surface energy of the functional chain ends causes them to be depleted near the interface, leading to very slow coupling under quiescent conditions. Moreover, the diffusion of polymer chains very close to the surface has been reported to be much slower than in bulk. Under coextrusion or mixing, external flow increased the functional group concentration in the interfaces, restoring reaction rates to the level expected under homogeneous conditions. The uniformity of block copolymer formation across the coextruded sample argues that extensional deformation is more important than shear in accelerating coupling.

Introduction

Reactive blending is a successful strategy to compatibilize immiscible polymer blends.[1] The graft or block copolymers formed *in situ* by coupling of functional polymers stabilize the blend morphology and improve mechanical properties. During the past two decades, many aspects of reactive blending have been investigated,[2−24] for example, reactivity,[13] architecture,[3] molecular weight,[18,22] and concentration of functional polymers[23] as well as molecular weight and thermodynamics of matrix polymers.[5] For most of those studies, a bilayer sample geometry with a flat interface was annealed quiescently in order to separate reaction kinetics from interfacial area generation caused by the complex flows during melt blending. However, it was found that mixing did have profound effects on reaction kinetics.[3,25] For example, assuming second-order reaction kinetics, the rate constant for the coupling reaction of amine-terminal polystyrene (PS-NH_2)/anhydride-terminal poly(methyl methacrylate) (PMMA-anh) was about 1000 times faster in melt blending than that at a static interface, 64 kg/(mol min) vs 0.063 kg/(mol min).[3] For a heterogeneous system, coupling reactions can only occur at interfaces. Considering that a significant amount of interface was generated during mixing, the large difference observed in rate constant seemed reasonable. However, after normalizing by interfacial area, the rate constant under mixing was still ~300 times higher than that at static interfaces, 4200 kg/(mol min) vs 12 kg/(mol min).[3] Clearly, besides interfacial area generation, the complex flow under mixing also changed reaction kinetics significantly. When the same functional groups were attached to PS chains and brought together in a homogeneous polymer melt, the reaction rate is ~1000 kg/(mol min). Thus, it appears that static interfaces greatly retard the reaction between functional groups.

To explore mixing flow effects on coupling reactions, it is desirable to use simple flows like shear or extension on a flat interface. However, in order to subject a bilayer to these flows, the required sample thickness is on the order of millimeter. At such a layer thickness, it is very challenging to quantify the conversion of the coupling reaction. To increase the concentration of copolymer produced by coupling, the layer thickness needs to be decreased. This can be achieved either by decreasing sample thickness or by increasing layer number. In this work, a 640-layer PS-NH_2/anthracene-labeled PMMA-anh (PMMA-anh-anth) was fabricated via a multilayer coextrusion process. This large layer number gave enough interfacial area to enable copolymer quantification using a fluorescence detector with size exclusion

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Table 1. Characterization of Polymers Used in This Study

polymer	sources	M_n (kg/mol)	M_w/M_n	functionality
PS-NH_2-1	synthesized	37	1.21	0.72
PS-NH_2-2	synthesized	78	1.26	0.50
PMMA-anh-anth	synthesized	21	1.24	0.84
PMMA-anh	synthesized	40	1.30	1.00
PS	Styron 685D	140	2.0	
PMMA	Plexiglas V825-NA	52	2.0	

chromatography (SEC). The multilayer samples were used to investigate the effects of flow on polymer−polymer coupling reactions, i.e., reaction conversion and interfacial morphology development.

Experimental Section

Materials. The characteristics of the functional polymers used in this work are summarized in Table 1. They were synthesized by atom transfer radical polymerization (ATRP). Detailed procedures for synthesis and characterization of these polymers were described by Moon et al.[26] and by Zhang et al.[23] The molecular weight and its distribution were measured by SEC. The functionality of PS-NH_2 was measured by a fluorine NMR technique described by Ji et al.[27] and by coupling with excess PMMA-anh followed by conversion measurement using SEC. The functionality of PMMA-anh or PMMA-anh-anth was measured by coupling with excess PS-NH_2 followed by conversion measurement.

The as-made PMMA-anh-anth had a broad polydispersity of about 1.45. A narrower distribution is required to enable copolymer quantification, and thus fractionation with benzene/hexane was performed by dissolving about 41 g of PMMA-anh-anth in 4 L of benzene at room temperature under extensive stirring. Hexane (~2 L) was slowly added into the solution until it turned slightly cloudy, and the solution was left stationary in an ice bath overnight. The low molecular weight fraction was collected and concentrated, followed by precipitating the polymer in hexane. The yield was around 56%, and the PDI was 1.24 as reported in Table 1.

The commercial PS and PMMA used here were supplied by Dow Chemical and Arkema, respectively. The molecular weight and distribution listed in Table 1 were measured by SEC using PS standards. The viscosities were measured at 235 °C in a rotational shear rheometer (ARES, TA Instruments), using 25 mm parallel plates. The zero shear rate viscosities were achieved by applying the Cox−Merz rule to the dynamic frequency sweep data and fitting them with the Ellis model.[28] These parameters are reported in Table 2.

$$\eta(\tau) = \frac{\eta_0}{1+\left(\dfrac{\tau}{k}\right)^{s-1}} \qquad (1)$$

where η_0 is the zero shear rate viscosity, τ is the shear stress, and s and k are the Ellis parameters.

Multilayer Coextrusion. All the materials were dried under vacuum for 48 h before use (at 70 °C for commercial polymer pellets and at 25 °C for functional polymers). PS-NH_2-1 and PMMA-anh-anth were dispersed in the corresponding commercial polymer matrix (PS and PMMA, respectively) at a concentration of 10 wt % with a 16 mm corotating, intermeshing twin-screw extruder (Prism, 16TSC, $L/D = 25$) at 200 °C and 50 rpm. The blends were pelletized and dried in a vacuum oven at room temperature.

Coextrusion of the PS-NH_2/PMMA-anh-anth materials was performed with a multilayer coextruder at 235 °C. Details about the coextruder setup are provided by Zhao et al.[29] and Lee et al.[30] Initially, two polymers were brought together in a feed block and were arranged into a 20-alternating-layer arrangement. The thickness ratio (and thus the composition) of layers was controlled by the feed rate of each polymer melt, which was determined by gear pumps (Zenith PEPII) interfacing between a single-screw extruder and the feed block. Immediately after the feed block, the melt was formed into a square shape by a tapered die, followed by a series of multiplication dies. In these multiplication dies, the layers are first split into two parts at the middle in the vertical direction, and each part subsequently is compressed, rotated, stretched back to the original width, and finally restacked together with the number of layers being doubled. The final number of layers was determined as $N_0 \cdot 2^m$, where the initial number of layers is N_0 and the number of multiplication dies is m. The melt flow in the multiplication dies was kept in a square shape. Following the multiplication dies, a fishtail sheeting die was attached to convert the 10 × 10 mm square cross-section flow into a 51 mm wide by 2 mm thick rectangular shape. This flow into the sheeting die increased the area of each interface between the alternating layers by a factor of 5. After a die land, the multilayer flow was picked up by a water-cooled double chill roll and was stretched down to less than 1 mm thick, while being quenched to room temperature. The flow rate of each polymer was equal, and the total extrusion rate was 30 g/min.

Table 2. Ellis Model Parameters for the Commercial PS and PMMA at 235 °C

	PS	PMMA
η_0 (Pa s)	3900	6800
S	2.25	2.10
$k \times 10^{-3}$ (Pa)	19.0	56.0

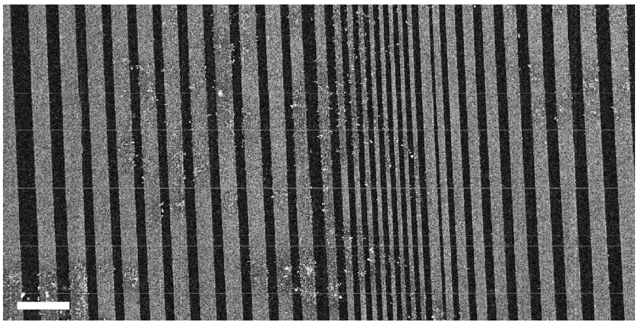


Figure 1. Part of the layer structure of SM640 observed with SEM in the backscatter mode. The PS layers were stained with RuO_4. The bright layer is PS, and the dark layer is PMMA. The scale bar represents 10 μm.

Starting with a 20-layer feed block, five multiplication dies created 640 layers. The average thickness of each layer was on the order of a micrometer. The layer structure of SM640 was observed by electron microscopy. A small piece of SM640 was microtomed at room temperature perpendicular to the flow direction with a glass knife to achieve a smooth flat surface. It was then immersed in RuO_4 (0.5% aqueous solution) for 45 min to selectively stain the PS layers for better contrast. After coated with 5 nm carbon, the sample was observed with a scanning electron microscope (S4700, Hitachi) in backscatter mode and an acceleration voltage of 5 kV. Figure 1 shows part of the layer structure of SM640. The bright layer is PS, and the dark layer is PMMA. As shown, the layer structure was clear and the interfaces were flat. However, as evident in Figure 1, the layer thickness was not uniform. There were periodic thin and thick layers across the whole sample. This nonuniformity was caused by the uneven flow path distribution in the multiplication dies, which was associated with the particular dies design used.[31,32] Since the focus of this work is on interfacial area, thickness uniformity is not critical.

Shear Experiments. Before shear, SM640 was annealed at 150 °C for 5 min to remove any residual stress from coextrusion.

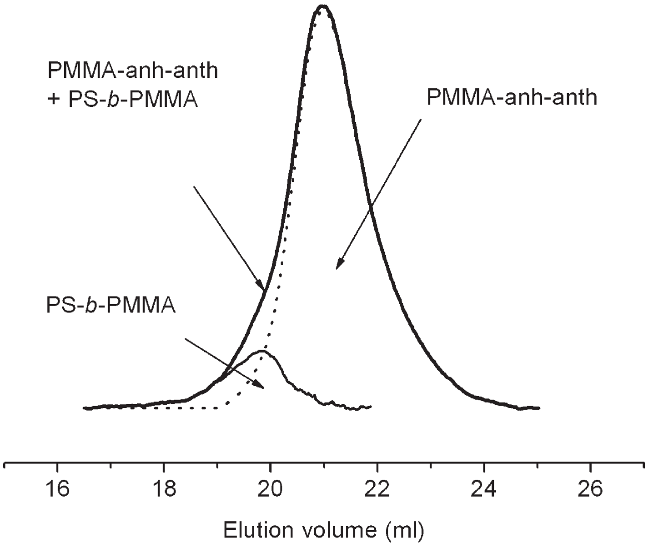


Figure 2. Curve subtraction for PMMA-anh-anth conversion determination. The thick solid line is the SEC trace of the SM640 extrudate (using a fluorescence detector). The pure PMMA-anh-anth trace (shown by the dotted line) was subtracted from the SM640 trace to obtain the PS-*b*-PMMA trace (thin solid line). The area under the PS-*b*-PMMA indicates that 7.5% of the PMMA-anh-anth has coupled with PS-NH_2-1. Unreacted PS-NH_2-1 and PS are both invisible to the fluorescence detector.

Shims were used to maintain the thickness. The multilayer was then cut into round disks with a homemade hot wire cutter, and the fused edge was removed with a razor blade. The disks were dried in a vacuum oven at room temperature overnight.

All shear experiments were accomplished using 25 mm parallel plates in an ARES rheometer. A multilayer disk was loaded between the two plates at 200 °C under a nitrogen environment. After waiting for 10 min to reach thermal equilibrium, different shear flows were applied. For dynamic shear, the frequency (ω) ranged from 0.05 to 10 rad/s, and the strain amplitude (γ) ranged from 0.05% to 15%. For steady shear, the shear rate used was 1 s^{-1}. After shear, the samples were quenched in liquid nitrogen. As a control, a SM640 disk was also annealed without shear in the rheometer at the same temperature, followed by quenching in liquid nitrogen.

PS/PMMA bilayers were also sheared between parallel plates. Homopolymer disks, PS (or PS-NH_2) and PMMA (or PMMA-anh), were molded with a hot press at 200 °C. They were loaded between the parallel plates and were slightly pressed (with an axial force of ~50 g). The bilayer samples were then annealed or sheared similarly to SM640. For consistency, the PMMA disk was always loaded on the bottom plate.

Size Exclusion Chromatography (SEC). SEC was used for molecular weight characterization as well as reaction conversion measurement. A Waters 590 SEC equipped with three Phenomenex Phenogel columns (5 μm bead size), an internal refractive index detector (Water 410), an external UV detector (Spectroflow 757, Kratos Analytical Instruments), and an external fluorescence detector (F-1050, Hitachi) was used. Ten PS standards ranging in molecular weight from 540 to 370 000 g/mol were used to calibrate the columns. Molecular weights of PMMA were calculated using universal calibration.[33]

The PMMA-anh-anth conversion was measured with the fluorescence detector. After shearing (or annealing), a small piece of sample was cut from the edge of the disk with a hot wire cutter and was dissolved in THF with two drops of phenyl isocyanate to quench the unreacted PS-NH_2. The excitation and emission wavelengths were set at 358 and 402 nm, respectively. Figure 2 shows a typical SEC trace for SM640 from the fluorescence detector. PS and PS-NH_2 homopolymers are invisible to the fluorescence detector. The conversion of PMMA-anh-anth was achieved through peak subtraction, as described by Jeon et al.[3] As shown in the figure, the thick solid line was from SM640 and the dotted line was from the starting material, PMMA-anh-anth. By subtracting the PMMA-anh-anth trace from the SM640 trace, the peak for the copolymer product PS-*b*-PMMA was obtained, as shown by the thin solid line. The PMMA-anh-anth trace was multiplied by a constant to adjust the peak subtraction to give a Gaussian curve for PS-*b*-PMMA. The PMMA-anh-anth conversion was calculated from the ratio of the area under the PS-*b*-PMMA trace to the area under the PMMA-anh-anth + PS-*b*-PMMA trace.

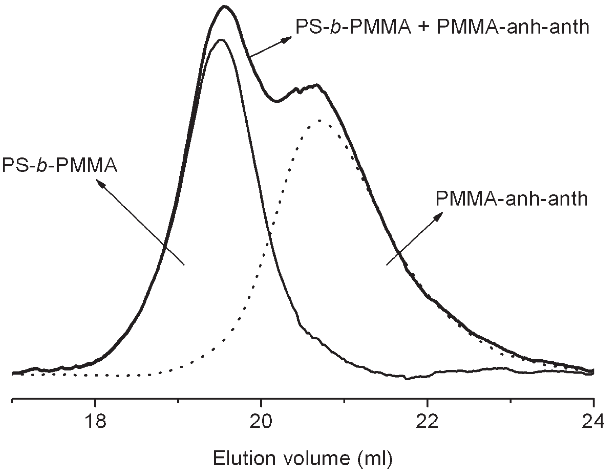


Figure 3. SEC traces for SM640 after solution reaction at room temperature for 48 h. The thick solid line is the solution reaction mixture, and the dotted line is the PMMA-anh-anth. The thin solid line is for the PS-*b*-PMMA product achieved by curve subtraction.

Transmission Electron Microscopy (TEM). SM640 and the bilayer samples were microtomed perpendicular to the layers (Reichert UltraCut S ultramicrotome) at room temperature with a diamond knife to give ca. 70 nm thick specimens. The PS phase was selectively stained with RuO_4 vapor (0.5% aqueous solution) for ~30 min to increase contrast. The morphology was observed with TEM (JEOL 1210) at 120 keV.

Results

Coupling Reaction during Coextrusion. The maximum coupling of PS-NH_2-1 and PMMA-anh-anth in SM640 was measured by reaction in solution. A small piece of SM640 was dissolved in THF and was stirred at room temperature for 48 h. SEC analysis (Figure 3) showed that the PMMA-anh-anth conversion was ~47.5%. The weight composition of SM640 was 50/50, and the functional polymer concentration in each component was 10 wt %. On the basis of molecular weight and functionality, the anhydride/amine stoichiometric ratio for SM640 was 2.1:1, which should give 48% PMMA-anh-anth conversion upon complete reaction. Thus, we can conclude that the twin-screw compounding and the multilayer extrusion did not affect the reactivity of the functional polymers.

During multilayer coextrusion, the two melt streams, PS and PMMA, were brought together in the feed block, and a large amount of interfacial area was generated in the multiplication and the sheeting dies. During this process, PS-NH_2-1 and PMMA-anh-anth coupled with each other. The amount of reaction was quantified after quenching the unreacted PS-NH_2-1 in SM640 with phenyl isocyanate. The PMMA-anh-anth conversion was measured to be ~7.5% (see Figure 2).

To better understand the extent of the coupling reaction during coextrusion, the block copolymer interfacial coverage (Σ), defined as the number of block copolymer chains per unit interfacial area, was evaluated. As shown in Figure 1, the interfaces of SM640 were flat and well-defined. Thus, Σ for SM640 can be calculated from the PMMA-anh-anth conversion (α) with eq 2.

$$\Sigma = \frac{\rho_{\mathrm{PMMA}} l \varphi_{\mathrm{PMMA}} c_{\text{PMMA-anh-anth}} \alpha N_{\mathrm{AV}}}{n M_{\mathrm{n,\,PMMA\text{-}anh\text{-}anth}}} \qquad (2)$$

Here, ρ_{PMMA} is the density of PMMA (1.19 g/cm^3), l the total thickness of SM640 (0.68 mm), ϕ_{PMMA} the PMMA volume fraction in SM640 (0.5), $c_{\text{PMMA-anh-anth}}$ the weight concentration of PMMA-anh-anth in the PMMA layer (0.1), α the conversion of PMMA-anh-anth (0.075 from Figure 2), N_{AV} Avogadro's number, n the number of interfaces (n = 639 for SM640), and $M_{\mathrm{n,PMMA\text{-}anh\text{-}anth}}$ the number-average molecular weight of PMMA-anh-anth. From eq 2, Σ for the SM640 extrudate is about 0.13 chains/nm^2. Note that Σ as calculated is an average over all the interfaces.

The maximum amount of block copolymer that can reside in a flat interface (called the saturation or maximum block copolymer interfacial coverage, Σ*) can be calculated from the thickness of a monolayer and the polymer chain volume. For a symmetric block copolymer, the thickness of such a monolayer is half the *d*-spacing (*d*) in the ordered lamellar structure. Anastasiadis et al. measured *d* for a series of symmetric PS-*b*-PMMA diblocks using small-angle neutron scattering and reported the correlation of *d* with copolymer molecular weight.[34] On the basis of their empirical correlation, Σ* for a symmetric block copolymer with the same molecular weight as the PS-*b*-PMMA formed here was estimated to be ~0.17 chains/nm^2. Considering that our PS-*b*-PMMA was not symmetric (the PS block was significantly longer than the PMMA block), the real Σ* might be smaller than this calculated value.

Based on the above calculation, the interfaces of SM640 were almost saturated with block copolymers. This indicated significant coupling reaction during coextrusion. Since 80% of the interface between PS and PMMA was created in the sheeting die and it is at the end of the extruder, the sheeting die is where most of the reaction must occur. At a total flow rate of 30 g/min, the average linear velocity of the polymer melt in the die was about 5 mm/s. Thus, the residence time in the sheeting die was less than 10 s. This suggests that the coupling reaction of PS-NH$_2$/PMMA-anh-anth is very fast during coextrusion. Our previous studies on this[23] and similar PS-NH$_2$/PMMA-anh systems[18] showed that under static conditions it took more than 24 h to reach interfacial saturation. Clearly, coextrusion significantly accelerated the PS-NH$_2$/PMMA-anh coupling reaction and reduced the reaction time by more than 3 orders of magnitude.

Interfacial Morphology Development during Coextrusion. It has been reported that for a PS-NH$_2$/PMMA-anh bilayer there was significant roughening as the interface was filled with block copolymers during annealing.[23,35] Figure 4 shows micrographs of the interfaces of SM640; no significant macroscopic roughening is observed. We speculate that the higher molecular weight (both functional and nonfunctional polymers) and lower functional polymer concentration may be the reasons for this. Indeed, Yin et al. and Zhang et al. reported that these factors could retard or reduce roughening.[22,23] For SM640, occasional evidence of interfacial emulsification was observed, as shown in Figure 4b. This is also consistent with the high block copolymer coverage measured.

Effect of Steady Shear Flow. SM640 samples were sheared at $\dot{\gamma}$ = 1 s^{-1} and 200 °C after extrusion, followed by quenching in liquid nitrogen. The PMMA-anh-anth conversion was again measured by SEC. As shown in Figure 5, the conversion increased from 7.5% to a plateau (~14%) within 10 min. Thus, the conversion almost doubled compared to the sample without shearing. As also shown in Figure 5, no significant changes in conversion were observed after quiescent annealing at 200 °C for 2 h. This confirms that flow in the die led to the enhanced reaction and also indicates that the interface was near saturation after coextrusion. The layer structure of the sheared SM640 was assessed by SEM. As shown in Figure 6, the well-defined layer structure of SM640 was destroyed by the large deformation. Previously, Levitt reported that for a nonreactive PS/amorphous polyamide (aPA) multilayer (layer thickness on the order of 20 μm) the layer structure broke up at strains above 1000.[36] One expects that this transition strain should decrease with layer thickness. For SM640, the layer thickness was on the order of 1 μm and the layer structure broke at a much lower strain (~100), before eventually converting to the particle/matrix morphology shown in Figure 6.

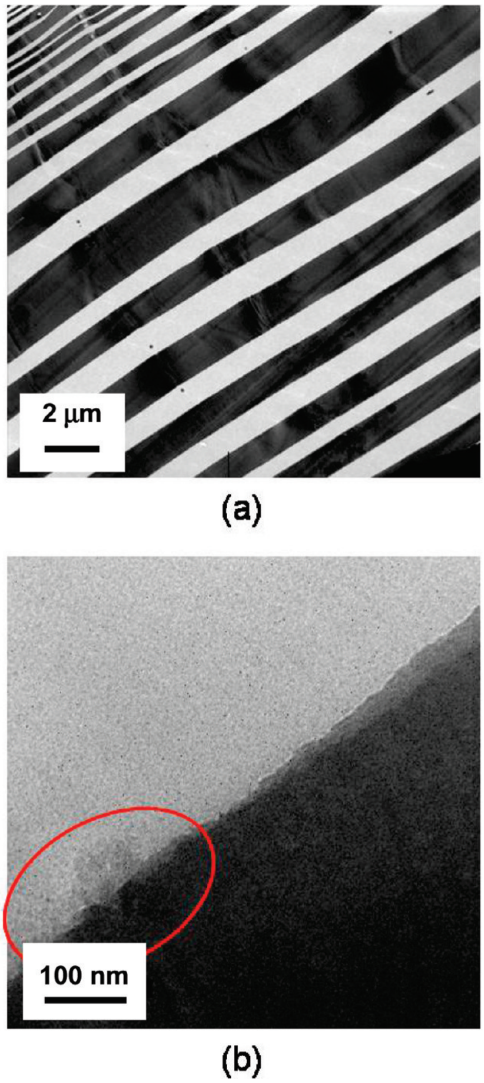


Figure 4. Interfacial morphology of SM640 as observed with TEM under (a) low and (b) high magnifications. The dark PS layers were stained with RuO$_4$. Emulsification (as indicated by the red circle) was occasionally observed in the interfacial region.

As the layers of SM640 broke up under shear, fresh interfacial area was generated. This led to more coupling between PS-NH$_2$-1 and PMMA-anh-anth, resulting in higher PMMA-anh-anth conversion. The copolymers formed *in situ*

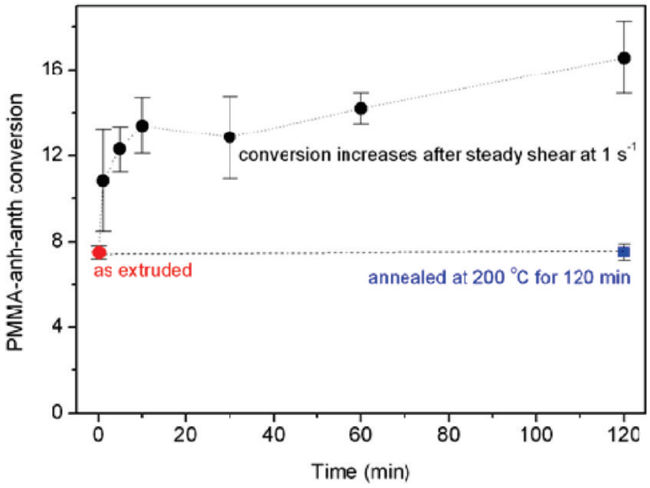
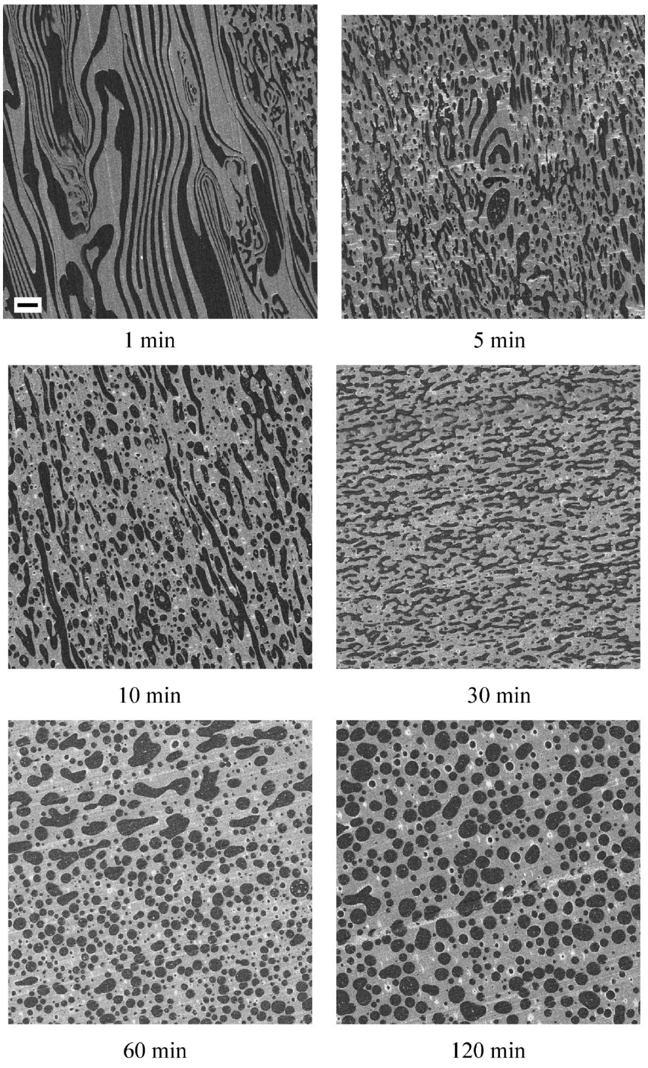


Figure 5. PMMA-anh-anth conversion of SM640 after shearing at 1 s^{-1} and 200 °C for different times. Each data point is the average of three samples, and the error bar represents the standard deviation. The initial point is for the extrudate.


1 min 5 min

10 min 30 min

60 min 120 min

Figure 6. SEM images show the morphology evolution of SM640 under steady shear at 1 s^{-1} and 200 °C. In the images, the bright phases are PS, and the dark phases are PMMA. The scale bar represents 10 μm.

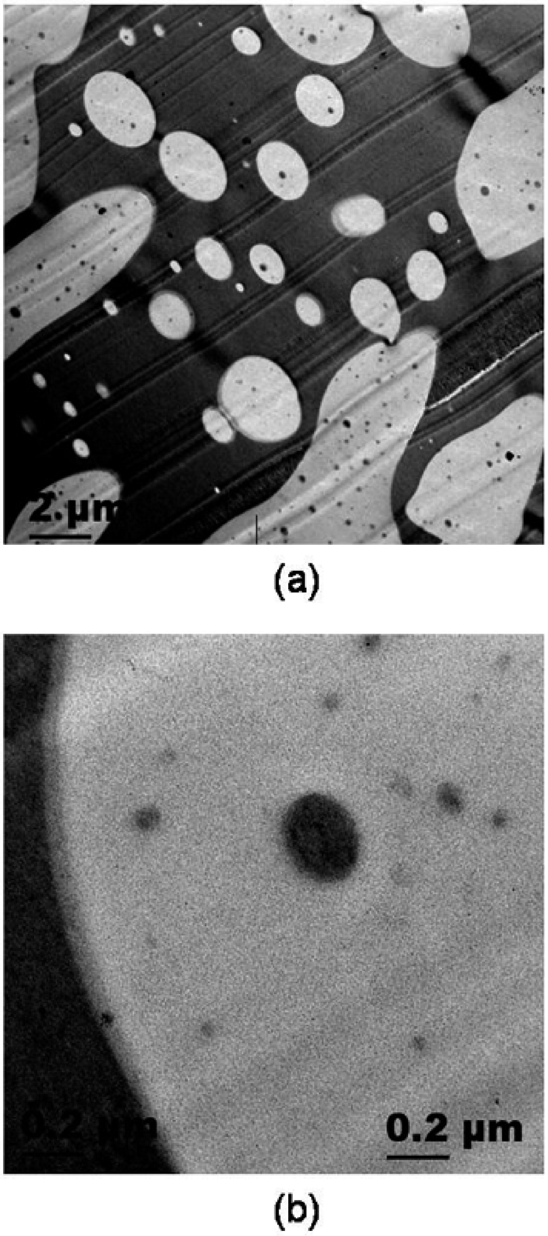


Figure 7. TEM images of SM640 after shearing at 1 s^{-1} and 200 °C for 2 h. Here, the dark phases are PS, and the white phases are PMMA. The dark inclusions in the PMMA phases are presumed to be micelles and swollen micelles.

not only stayed at the interfaces but also formed micelles and swollen micelles in both the PS and PMMA phases, as shown in Figure 7. These micelles probably account for most of the increase in conversion shown in Figure 5.

Effect of Sinusoidal Shear. SM640 was also sheared dynamically under various conditions, with frequencies ranging from 0.05 to 10 rad/s and strain amplitudes from 0.05 to 15%. The reaction conversion did not change significantly.[37,44] Kim et al. and Xie et al. reported that dynamic shear could have significant effects on coupling reactions.[9−11,19−21] However, the samples used in their studies were laminated rather than extruded, and little reaction happened during the lamination process. Therefore, we speculate that the minimal reaction observed with SM640 under dynamic shear was due to the interface already being highly covered with block copolymer. To confirm this hypothesis, fresh PS/PMMA interface was created by laminating PS-NH$_2$-2 and PMMA-anh disks in the parallel plate rheometer. The resulting bilayer was sheared dynamically in a similar manner as SM640.

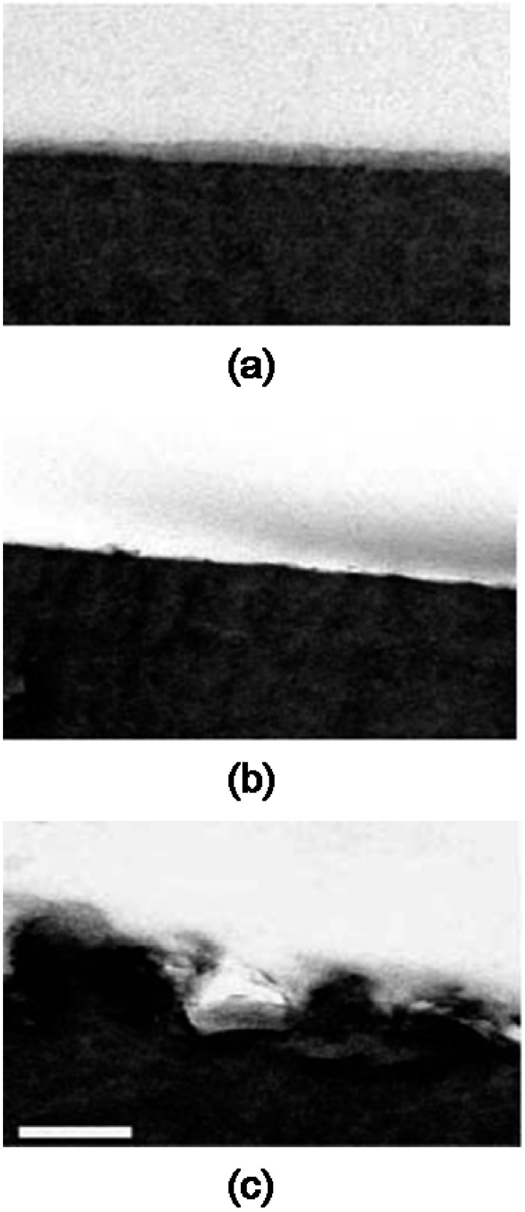


Figure 8. Interfacial morphology after 1 h at 200 °C for various bilayers: (a) quiescent PS-NH_2-2/PMMA-anh bilayers, (b) nonreactive PS/PMMA-anh bilayers, dynamically sheared (γ = 1%, ω = 1 rad/s), and (c) PS-NH_2-2/PMMA-anh bilayers dynamically sheared (γ = 1%, ω = 1 rad/s). The scale bar represents 100 nm.

However, the reaction conversion for this sample could not be measured directly due to the single interface and thus small amounts of copolymer. For such a bilayer system, it has been reported that interfacial roughening could be closely correlated with Σ.[23,36] Therefore, the interfacial morphology was measured via TEM. As shown in Figure 8b, for a nonreactive bilayer (PS/PMMA-anh), no roughening was observed. This showed that the dynamic shear itself does not cause any interfacial roughening. For a reactive bilayer, PS-NH_2-2/PMMA-anh, however, the interfaces showed different behaviors with and without dynamic shear, as shown in Figures 8a and 8c, respectively. Significant roughening happened to the sample under dynamic shear, indicating more coupling reaction compared to that without shear. This suggests that dynamic shear can promote the coupling reaction when the initial interface has only a low coverage of block copolymer. However, the dramatic viscosity increase reported by Kim et al. and Xie et al. was not observed for the PS/PMMA bilayer, as discussed in the Appendix.[9−11,19−21]

Discussion

Origin of Reaction Acceleration. The reaction between cyclic anhydride/amine first creates an amic acid intermediate and then proceeds to imide formation. The imidization step is rapid and irreversible at high temperature. The amic acid formation is slow, reversible, and the rate-limiting step.[24] Thus, second-order reaction kinetics describes the cyclic anhydride/amine reaction well. For SM640, only one flow rate was used for the coextrusion. From this one data point, using the reactant concentration and the residence time, the rate constant was estimated to be ca. 70 kg/(mol min). To normalize the rate constant by interfacial volume following Jeon et al.,[3] the ratio of interfacial thickness to layer thickness for SM640 was used for those flat interfaces. The rate constant is thus about 7000 kg/(mol min). This is comparable to that achieved for a melt blending system as well as for homogeneous melt reaction and is much higher than that for a quiescent bilayer.[3,25]

The coextrusion temperature for SM640 was 235 °C, significantly higher than the annealing temperature of 175 °C for the bilayers reported in the literature.[3−5,7,18,23] One possibility is that the higher temperature caused the higher reaction rate observed during extrusion. However, for the coupling reaction of PS-NH_2/PMMA-anh, no significant change in reaction rate was found as temperature increased from 175 to 200 °C.[23,38] Therefore, we conclude that temperature is not the main cause here.

Rather, we speculate that the high shear and extensional deformation in the sheeting die caused the reaction to accelerate. Chain ends with functional groups like amine or anhydrides have high surface energy. Under molten conditions, these functional chain ends tend to be depleted near the surfaces or interfaces, as demonstrated by Elman et al. using neutron reflectometry.[39] Thus, under quiescent conditions, the functional group concentration in the interfacial layer is low, resulting in a slow coupling reaction. During coextrusion or mixing, convection could possibly overcome the high surface energy of the functional groups. Also, Zheng et al. have shown that diffusion rates of polymer chains are up to an order of magnitude slower near interfaces.[40] Flow could help to overcome this slow diffusion.

As discussed above, both extensional and shear deformation were experienced by SM640. All the layers will experience the same extensional stress as they pass through the die. However, layers near the wall will see much higher shear stress than those near the center. If we assume that effects on reaction are proportional to the magnitude of the stress, then if extension is dominant, we would expect uniform reaction conversion or block copolymer interfacial coverage for all the interfaces. However, if shear stress controls this process, we would expect block copolymer interfacial coverage to increase from the center interfaces to the surface interfaces. Previously, we reported that the interfacial strength for a 20-layer PS-NH_2/PMMA-anh was uniform across the layers,[41] which argues for extension playing the major role in increasing reaction rate. However, Creton et al. reported that when the molecular weight of block copolymers was low (lower than twice of the entanglement molecular weight), the interfacial adhesion reached a plateau after Σ was higher than a critical value.[42] This critical interfacial coverage was typically quite small, for example, 0.04 chains/nm^2 for polystyrene-*b*-poly(vinylpyridine). Therefore, for the PS-NH_2/PMMA-anh system, we cannot conclude that Σ is independent of layer position based solely on interfacial strength. The above-reported Σ of 0.13 chains/nm^2 is an average value over all 639 interfaces; thus, it is possible that Σ varies with distance from the wall. To measure the block copolymer interfacial coverage on the center layers versus coverage on the layers near the die walls, we divided the 639 interfaces into three groups by separating a piece of SM640 into three equal-thickness sheets (two surface sheets and one central sheet). The PMMA-anh-anth conversion for each sheet was measured by SEC, and no significant difference in reaction conversion was observed. This suggests that, in fact, Σ did not vary with interface location and therefore supports that extensional deformation is the main driving force for the reaction acceleration during coextrusion.

Summary

Coupling reaction occurred during the coextrusion of a 640-layer PS-NH$_2$/PMMA-anh-anth multilayer (SM640). The copolymers formed *in situ* almost completely filled the interfaces. Considering the short residence time in the extruder, the coupling reaction was as fast as that under mixing as well as under homogeneous conditions, and was as much as 1000 times faster than that under static annealing. The interfaces of the extrudate were still well-defined and flat, although occasionally emulsification was observed at the interfaces. Subsequent steady shear of SM640 destroyed the well-defined layer structure, and micelles and swollen micelles were formed. In contrast, dynamic shear showed no significant effect on the reaction conversion due to the high copolymer coverage for the extrudate. However, when a fresh-made bilayer sample was dynamically sheared, the coupling reaction was promoted significantly as indicated by interfacial roughening.

We speculate the large difference in interfacial reaction rate between that observed during extrusion or mixing and that under quiescent conditions is the result of flow overcoming the combined effects of high surface energy of the functional groups and slow diffusion near a static interface. The high surface energy of the functional chain ends tend to deplete them from the interface, and low diffusion near the interface slows their approach, leading to very slow coupling under quiescent conditions. Under coextrusion or mixing, convection increases the functional group concentration in the interfaces, restoring reaction rates to values expected under homogeneous conditions. The uniformity of block copolymer formation across the sample argues that extensional deformation is more important than shear in accelerating coupling.

Appendix. Rheological Response during Dynamic Shear

For a freshly made PS-NH$_2$/PMMA-anh bilayer, the interface roughened significantly under dynamic shear as shown in Figure 8. However, its rheological responses (G', G'', or η^*) did not change much over time. This result contradicts that reported by Kim and co-workers for a PS-COOH and PMMA-GMA (glycidyl methacrylate) bilayer, where dramatic increase in viscosity was observed when the bilayer was subjected to a small-amplitude dynamic shear.[9-11] They argued that the increase was caused by the rough interface induced by the coupling reaction. Obviously, that was not the case for PS-NH$_2$/PMMA-anh.

The viscosity of a layered sample (for example a bilayer) can be calculated from the viscosity and thickness of each layer with eq 3.[43]

$$\frac{h}{\eta} = \frac{h_1}{\eta_1} + \frac{h_2}{\eta_2} \tag{3}$$

where η_i and h_i are the viscosity and thickness of the layers, respectively. Indeed, this correlation described the viscosity of a PS/PMMA bilayer well, 2500 Pa s (measured) vs 2660 Pa s (calculated). A reactive bilayer could be treated as a trilayer, with the copolymers at the interface as a individual layer. Its viscosity can be calculated from eq 4:

$$\frac{h}{\eta} = \frac{h_1}{\eta_1} + \frac{h_2}{\eta_2} + \frac{h_{\text{int}}}{\eta_{\text{int}}} \tag{4}$$

η_{int} and h_{int} are the viscosity and thickness of the interfacial layer, copolymers. For a reactive bilayer with layer thickness on the order of millimeter, the thickness of the interfacial copolymer layer is normally less than 50 nm. From eq 4, its effect on the apparent viscosity will be minimal, even if the copolymer viscosity is much higher than its parent functional polymers.

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(44) In a previous study, the PMMA layer of a reactive PS/PMMA multilayer contained impact modifier (rubbery particles with size about 200 nm). For those multilayer samples, little coupling of PS-NH_2/PMMA-anh was detected for the extrudate. However, after subjection to dynamic shear, a significant amount of coupling reaction was observed. The mechanism to explain why no reaction happened during coextrusion and how it was promoted by sinusoidal oscillation remains unclear. Details can be found in refs 25, 37.