Measuring Copolymer Formation from End-Functionalized Chains at a PS/PMMA Interface Using FRES and SEC

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ABSTRACT: Two experimental techniques, forward recoil spectrometry (FRES) and size exclusion chromatography with fluorescence detection (SEC/fluorescence), have been used to monitor independently the extent of reaction between model end-functional polymers at a PS/PMMA interface. Bilayer samples comprising a polystyrene layer containing ca. 8.4 wt % of amino-terminal deuterated polystyrene (dPS-NH_2, $M = 22\,000$ g/mol) on an anhydride-terminal fluorescent poly(methyl methacrylate) (*PMMA-anh, $M = 31\,200$ g/mol) layer were annealed at 174 °C for various periods. An interfacial excess observed in the FRES concentration profiles of the dPS-NH_2 in the PS layer was used to determine an interfacial coverage of diblock copolymer and a conversion of dPS-NH_2 to diblock copolymer. Similarly, the conversion of the fluorescent *PMMA-anh to diblock copolymer was measured using SEC coupled with a fluorescence detector. Both techniques indicate similar reaction kinetics: the formation of copolymer in the interfacial region continued over several hours and approached a steady-state value after 24 h. Interfacial coverages determined from both methods typically agreed to within 15−20%. This validation of the fluorescence approach is important for further investigation of polymer−polymer reaction kinetics and interfacial segregation during in situ reactive polymer compatibilization.

I. Introduction

The in situ formation of block or graft copolymer by the reactive coupling of functionalized chains at a polymer−polymer interface has applications to many polymer processing operations, particularly blend compatibilization. In general, rather little reaction is necessary during reactive compatibilization to create substantial changes in morphology or physical properties. For example, copolymer formation representing as little as 2% of the blend can stabilize the blend morphology and enhance interfacial adhesion.[1−3] Model studies of these interfacial reactions frequently rely on samples comprising polymer films of submicron thickness. Monitoring the extent of interfacial reaction in such thin film samples is often difficult, since the amount of copolymer formed is typically small: a 1 cm^2 sample with a thickness of 500 nm may contain only 1 μg of copolymer. In the past, depth profiling techniques such as neutron reflectivity,[4−6] forward recoil spectrometry (FRES),[7−10] and secondary ion mass spectrometry (SIMS)[11,12] have been employed to measure the amount of copolymer that resides at an interface between two immiscible polymers. Although these techniques provide quantitative descriptions of the interfacial region, deuterium labeling is usually necessary for contrast, limiting the types of model polymers available for testing. Sample preparation, as well as the experiments themselves, can sometimes be difficult or inconvenient to perform. Most importantly, thin film geometries do not permit the investigation of reaction kinetics under typical polymer processing conditions, and the accumulated evidence so far implies that intensive mixing plays a crucial role in reactive compatibilization. In a previous FRES study of a polystyrene (PS)−poly(methyl methacrylate) (PMMA) reaction at a single quiescent interface, it was conclusively demonstrated that bulk diffusion did not limit the reaction kinetics; i.e., the reaction reached a steady state on a time scale of tens of hours.[10] On the other hand, this reaction achieved a steady state in several minutes in a small cup-and-rotor mixer at a shear rate of ca. 80 s^{-1}.[13]

Size exclusion chromatography (SEC) has been used to measure the amount of copolymer formed at an interface in such processing situations.[1,13−15] Although SEC does not provide a concentration profile of the interfacial region, it can measure the extent of reaction that occurs between model reactive polymers by separating the higher molecular weight coupled product from the reactants. Unfortunately, the limited sensitivity of typical SEC refractive index detectors prevents detection of the small quantities of copolymer that form at an interface between polymer films of submicron thickness. In contrast to refractive index detectors, ultraviolet detectors can be selective for different polymer structures but also suffer from relatively poor sensitivity to small concentrations of polymer. Moon et al. have synthesized fluorescently labeled poly(methyl methacrylate) with a terminal anhydride group (*PMMA-anh) so that SEC with fluorescence detection can be applied to model thin film reaction experiments.[16] SEC/fluorescence was used to measure the amount of diblock copolymer formed at an interface between *PMMA-anh and amino-terminal polystyrene (PS-NH_2). The fluorescence labeling improved the sensitivity of the SEC analysis by a factor of 100 and was also selective for the *PMMA-anh. Because this labeling technique incorporates the fluorescent group into the initiator before polymerization, many different reactive polymers could be anionically synthesized for reaction kinetics studies. However, SEC/fluorescence requires that the PS/PMMA thin films be dissolved in solution to gauge the extent

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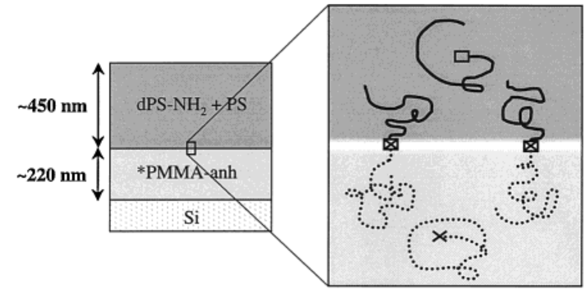

Figure 1. Bilayer samples were prepared by spin-coating a solution containing dPS-NH$_2$-22 (8.4 wt %) and PS onto *PMMA-anh layers previously spun from a toluene solution onto Si substrates. Samples for both FRES and SEC analysis were annealed simultaneously under vacuum at 174 °C.

Table 1. Materials Used

polymer	$M_n \times 10^{-3}$	M_w/M_n	functionality
PS	49	1.06	
dPS-NH$_2$-22	22	1.04	0.89
*PMMA-anh	31.2	1.03	0.95[a]

[a] NMR performed after coupling with amino-terminal poly(ethylene oxide) in solution to form diblock copolymer.

of interfacial reaction. Hence, it is desirable to compare the results from SEC/fluorescence to those obtained from an in situ experiment such as FRES, in which copolymer coverage is measured without disrupting the interfacial structure.

We have compared two different techniques that measure the amount of diblock copolymer formed at the interface between thin films containing deuterated PS-NH$_2$ and fluorescent *PMMA-anh. Forward recoil spectrometry (FRES) was used to obtain the concentration profile of dPS-NH$_2$ in the thin film samples depicted in Figure 1. The interfacial coverage Σ (chains/nm^2) was determined directly from these concentration profiles. Additional thin film samples were simultaneously subjected to SEC/fluorescence analysis, and the interfacial coverage Σ was determined from the conversion of the *PMMA-anh to diblock copolymer, as observed in the SEC trace.

II. Experimental Section

Polymer Synthesis and Characterization. The characteristics of the polymers used in this study are listed in Table 1. A polystyrene standard, PS-49 ($M = 4.9 \times 10^4$ g/mol), purchased from Pressure Chemical was used as a matrix in these experiments. Perdeuterated polystyrene end-functionalized with an aliphatic amine group (dPS-NH$_2$) was synthesized by J. Cernohous and A. Hirao at the Tokyo Institute of Technology.[10,17] The molecular weight of the dPS-NH$_2$-22 was confirmed via size exclusion chromatography (SEC) combined with low-angle laser light scattering. At the time of synthesis, thin layer chromatography/flame ionization detection (TLC/FID) showed 93% functionality on the dPS-NH$_2$-22 polymer. The dPS-NH$_2$-22 was also titrated with HClO$_4$ to a blue end point in a 1:1 v/v solution of benzene and glacial acetic acid using crystal violet as an indicator.[18] This titration indicated 84% functionality for the dPS-NH$_2$ polymer. The average functionality from these two experiments is given in Table 1.

Fluorescent poly(methyl methacrylate) end-functionalized with an anhydride group (*PMMA-anh) was also synthesized.[16] As described in ref 16, 1-(2-anthryl)-1-phenylethylene containing a fluorescent anthracene group was used to initiate the polymerization of methyl methacrylate monomer. Di-*tert*-butyl maleate was used to terminate the polymerization. The polymer was then pyrolyzed under vacuum at 210 °C for 1 h to convert the maleate to an anhydride functionality. The *PMMA-anh molecular weight was determined by SEC. The functionality was determined by first coupling the *PMMA-anh with an excess of amino-terminal poly(ethylene oxide) (M = 5000 g/mol) in THF to form a diblock copolymer.[19] The reaction was brought to completion by heating the solution for at least 24 h at 70 °C. The copolymer product and any nonfunctional *PMMA were then separated from the excess poly(ethylene oxide) using SEC. The ratio of the integrated *PMMA ester proton peak and the PEO backbone proton peak observed in ^{1}H NMR was then compared to the theoretical ratio for a *PMMA−PEO diblock copolymer of appropriate molecular weight. This procedure indicated the *PMMA-anh to be ca. 95% functional. The error in this analysis is estimated to be ±10%.

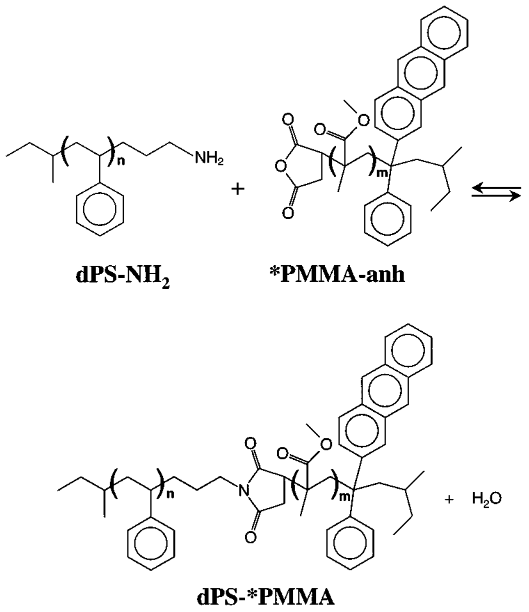

Figure 2. Perdeuterated polystyrene with an amine end group reacts with fluorescent poly(methyl methacrylate) with an anhydride end group to form a dPS-*PMMA diblock copolymer. (The formation of the amic acid intermediate is not shown.)

Sample Preparation. *PMMA-anh was dissolved in toluene (~4.3 wt % *PMMA-anh) and spun at 1000 rpm onto silicon wafers. Ellipsometry indicated these films to be approximately 220 nm thick. The bilayer samples depicted in Figure 1 were then prepared by dissolving a mixture of dPS-NH$_2$ (8.4 wt %) and PS-49 in a solution of 87:13 v/v cyclohexane and toluene to form a ~4.5 wt % polymer solution. This mixture of cyclohexane and toluene does not dissolve the PMMA layer, as determined by ellipsometry and atomic force microscopy (AFM). This polymer solution was then spun directly onto the *PMMA-anh layer at 1000 rpm to form the bilayer shown in Figure 1. This sample preparation was performed rather than the film-floating procedure described elsewhere, because the PS molecular weight was not sufficient to form a stable film on a water bath.[10] Other sets of reactive samples, constructed using both sample preparation techniques, exhibited equivalent extents of conversion.[20] Ellipsometry indicated the PS layer to be approximately 450 nm thick. Samples for both FRES and SEC/fluorescence analysis were constructed and annealed simultaneously at 174 °C under vacuum (<20 mTorr) for various periods. The reaction of dPS-NH$_2$ with *PMMA-anh to form dPS-*PMMA diblock copolymer is shown in Figure 2.

Forward Recoil Spectrometry. FRES was performed at the Ion Beam Analysis Facility at the University of Minnesota. A 3.0 MeV He$^+$ ion beam was incident on each sample at an angle of 15°, and an energy-sensitive detector with a 12 μm Mylar stopping foil was placed at an angle of 30° to the beam direction. This geometry allowed a depth of ~700 nm to be profiled with a depth resolution of ca. 90 nm. The beam current was set between 10 and 15 nA, and 20 μC of charge was

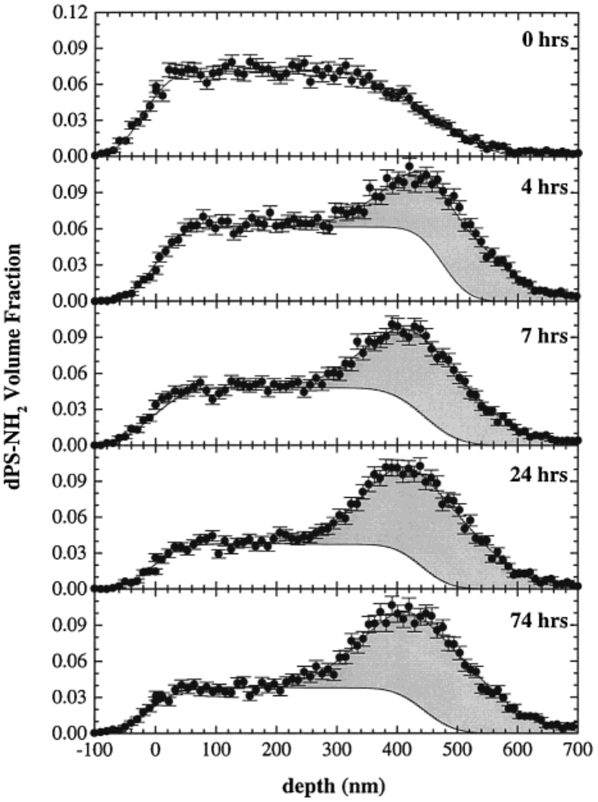

Figure 3. FRES concentration profiles showing the evolution of interfacial excess (shaded area) with annealing time of dPS-NH_2-22/*PMMA-anh-32 bilayer samples at 174 °C.

collected for each spectrum, over 20−25 min. In general, one spot on each sample was tested. On one sample annealed for 7 h, spectra were collected in four different spots for 5 μC each and added together. The spectrum from this summation resulted in a concentration profile that was indistinguishable from a profile obtained from a 20 μC test of the same sample. The spectra were converted from yield vs energy data to volume fraction vs depth using standard FRES analysis procedures.[20,21] The volume fraction of the reactive samples was scaled from the ratio of deuteron to proton yields from spectra of samples containing known volume fractions of nonfunctional dPS and PS.

SEC with Fluorescence Detection. After annealing, each sample for SEC/fluorescence analysis was dissolved in approximately 2 mL of THF for 24 h. Two drops of phenyl isocyanate were added to each THF solution to prevent any further reaction between dPS-NH_2 and *PMMA-anh in solution after the annealing procedure. A 100 μL aliquot of each solution was then injected into a Waters 150C ALC/GPC equipped with three Phenomenex Phenogel columns (5 μm bead size), an internal refractive index detector, and a Hitachi F1050 external fluorescence detector. The fluorescence detector excitation and emission wavelengths were 358 and 405 nm, respectively. The bandwidth of the fluorescence detector was fixed at 15 nm. The dimension of the flow cell was 1.3 mm × 1.3 mm × 12 mm. SEC traces were collected at ambient temperature using THF as the eluent.

III. Results and Discussion

Figure 3 shows FRES concentration profiles for the bilayer samples after 0, 4, 7, 24, and 74 h of annealing at 174 °C. The appearance of a relatively broad interfacial region (ca. 150 nm) in the unannealed sample is an artifact of the spin-coating procedure used to construct the samples. Optical microscopy of the PS layer indicates that such a profile results from roughness of the PS free surface, rather than a nonuniform PS/PMMA interface. As noted above, AFM and ellipsometry measurements indicate that the PS/PMMA interface is smooth prior to reaction and that spin-coating the PS layer does not cause an intermixing or broadening of the PS/PMMA interface. Because the PS free surface becomes more uniform as the samples are annealed, a resolution of ca. 90 nm is used to describe both the surface and interface in the fitting procedures discussed below. A peak near the PS/PMMA interface emerges within 4 h of annealing. This interfacial excess, shown as the shaded area in the other concentration profiles in Figure 3, is evidence of copolymer formation from the reaction of the dPS-NH_2 with the *PMMA-anh chains. The peak at the interface increases in amplitude with time, while the free surface volume fraction correspondingly decreases.

To determine the interfacial coverage from the FRES concentration profiles, the spectra were fit first with a profile that is the sum of a Guassian function, representing the interfacial excess, and a rectangular block.[10] The peak position of the Gaussian function coincides with the edge of the rectangular block near the PS/PMMA interface. The width (2σ) of the Gaussian function used to model the interfacial excess ranges from 150 to 160 nm. This profile was then convoluted with another Gaussian representing the instrumental response function (resolution 90 nm) and fit to the spectra by minimizing the χ^2 statistical parameter. Typical values of the normalized χ^2 parameter ranged from 0.8 to 1.2. After the data were fit, a quantity $\bar{\phi}_{\mathrm{dPS}}$ that represents the volume fraction of unreacted dPS-NH_2 chains far from the PS/PMMA interface was then calculated.[7] $\bar{\phi}_{\mathrm{dPS}}$ has the same magnitude as the height of the rectangular block used to fit the data. The width of the rectangle of height $\bar{\phi}_{\mathrm{dPS}}$ is determined by the concentration profile of an unannealed sample, a rule of mass conservation from unannealed to annealed samples, and the peak position, as previously described.[10] The interfacial excess z_i* was then calculated using the following integral:

$$z_i^* = \int_{-\infty}^{+\infty} (\phi(x) - \bar{\phi}_{\mathrm{dPS}})\, \mathrm{d}x \qquad (1)$$

where $\phi(x)$ is the volume fraction from the fit to the data at depth x. Values of the interfacial excess z_i* were then averaged across the three methods and were found to agree to within 8%. The interfacial excess z_i* is directly proportional to the interfacial coverage Σ (chains/nm^2):

$$\Sigma = \frac{z_i^* \rho_0}{N} \qquad (2)$$

where ρ_0 is the dPS segment density and N is the dPS-NH_2 degree of polymerization. These values of the interfacial coverage are plotted as squares in Figure 4. The error bars represent one standard deviation of the average z_i* values, propagated through eq 2.

Figure 5 shows the SEC traces obtained from samples constructed and annealed simultaneously with those samples used in the FRES analysis. Analysis of the SEC traces was performed using the commercially available Microcal Origin software. The SEC traces were first corrected for baseline drift. The peak located near the elution volume of 19.9 mL results from the coupling of the dPS-NH_2 with the *PMMA-anh and increases in amplitude with time. A small peak is observed at this position in the unannealed sample, as well as in SEC

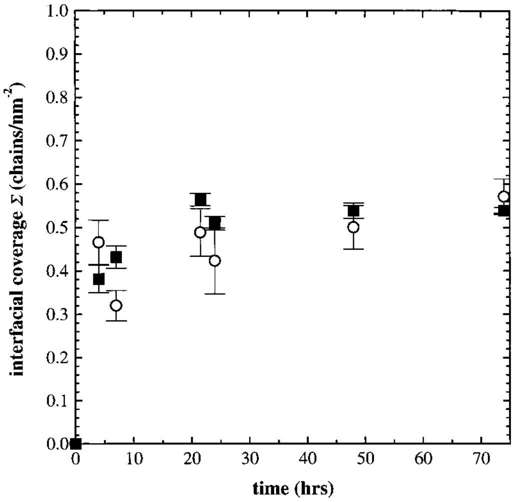

Figure 4. Interfacial coverage Σ in chains/nm^2 as a function of time at 174 °C from FRES (■) and from SEC/fluorescence analysis (○).

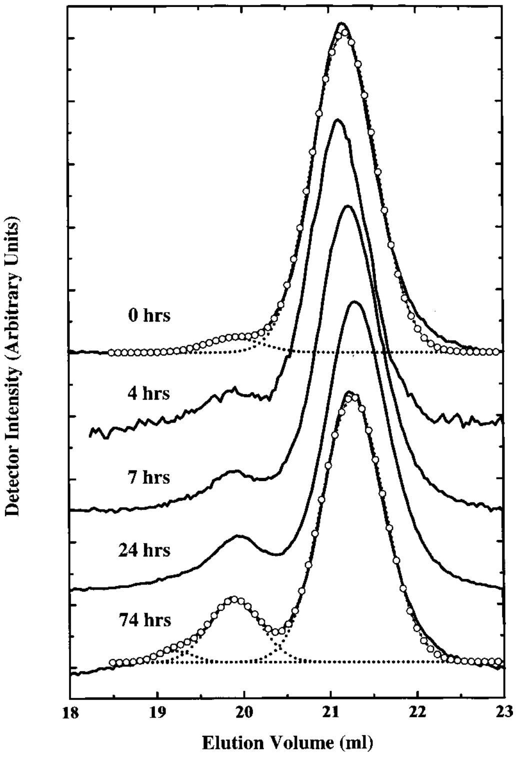

Figure 5. SEC chromatograms showing the conversion of *PMMA-anh as a function of time at 174 °C. The sum of two Gaussian peaks (○) is shown fit to the SEC trace (solid line) for the unannealed sample. For annealing times longer than 20 h, a sum of three Gaussian peaks was fit to the SEC trace. An example is given for the sample annealed for 74 h. The individual Gaussian peaks are also indicated (dashed lines).

traces of pure *PMMA-anh. However, this peak is not present in the maleate-terminal *PMMA precursor that is pyrolyzed to generate the anhydride functionality.[16,19] Thus, during the pyrolysis step in the *PMMA-anh synthesis, a small amount (3.69%) of the *PMMA-anh couples with itself. The area of this small peak in the unannealed sample relative to the total area beneath the trace is subtracted from the area of the coupled peak in the SEC traces from the other annealing periods. We believe it is unlikely that the peak observed at an elution volume of 19.9 mL is solely due to the *PMMA-anh coupling, in light of the reaction of the dPS-NH$_2$ observed in the FRES profiles. The larger peak at an elution volume of 21.2 mL represents unreacted *PMMA-anh in the system.

The SEC traces were then fit with a series of Gaussian peaks. For samples annealed for less than 20 h, two peaks were fit to the trace, centered at elution volumes of 19.9 and 21.2 mL. For samples annealed for longer times, a small shoulder became apparent at an elution volume of 19.2 mL. This third peak presumably represents a species with a molecular weight greater than that expected for a dPS-*PMMA diblock copolymer product and is discussed in more detail below. SEC traces with two peaks and a shoulder were fit with three Gaussian functions accordingly. The areas beneath these peaks were then used to calculate a conversion p of *PMMA-anh to dPS-*PMMA diblock copolymer for each sample using the following equation:

$$p = \frac{A - 0.0369A_{\mathrm{total}}}{A_{\mathrm{total}}} \tag{3}$$

where A is the area beneath the fit to the coupled peak occurring at elution volume 19.9 mL and A_{total} is the total area beneath the fit to all the peaks in the trace. The subtraction of the small peak at an elution volume of 19.9 mL observed in the unannealed sample is shown in the numerator of eq 3 and represents 3.69% of the total area beneath the SEC trace of the sample. Equation 3 also assumes the shoulder at 19.2 mL observed at long times does not represent copolymer formation from the amine–anhydride reaction. The conversion p is then used to estimate an interfacial coverage Σ in chains/nm^2, assuming the reaction occurs in the interfacial region:

$$\Sigma = \frac{ph\rho N_{\mathrm{Av}}}{M_{\mathrm{n}}} \tag{4}$$

where h is the thickness of the PMMA layer determined from ellipsometry, ρ is the density of PMMA, M_{n} is the *PMMA-anh number-average molecular weight, and N_{Av} is Avogadro's number. Equation 4 is analogous to eq 2, where the product ph corresponds to an interfacial excess of reacted PMMA chains. These values of the interfacial coverage are plotted as circles in Figure 4. The error bars are calculated using the errors given by Microcal Origin, propagated through eqs 3 and 4.

Figure 4 compares the interfacial coverages observed using FRES to those obtained from SEC/fluorescence. Both techniques indicate similar reaction kinetics: the formation of copolymer in the interfacial region continues over several hours and appears to approach a steady-state value after 24 h. In general, the interfacial coverages determined from both methods agree on average within 17%. Relative errors in the FRES measurements themselves range from 2 to 8%, whereas relative errors in the SEC measurement are slightly larger, ranging from 7 to 18%. The best agreement between the two data sets occurs at long times, when both the FRES concentration profile and the SEC trace are well developed in terms of signal-to-noise ratio.

The principal source of error in the SEC/fluorescence technique arises from the appearance of peaks that result from reactions other than the amine–anhydride interfacial reaction. In general, two types of side reactions are observed: a self-coupling of *PMMA during the pyrolysis step that end-functionalizes the polymer and formation of a species with a higher molecular weight during the annealing of the thin film samples. As described above, the area beneath the peak that represents the self-coupled *PMMA can be determined from an unannealed sample and subtracted from traces taken at longer annealing times. This introduces an additional error in the experiment on the order of 3−5%.

More importantly, the small shoulder that appears at an elution volume of 19.2 mL after 20 h of annealing may be evidence of a side reaction that results in a high molecular weight *PMMA species. This species has a molecular weight of at least 7.0×10^4 g/mol, which is greater than 5.3×10^4 g/mol expected for a dPS−*PMMA block copolymer. Given the propensity of anthracene to undergo photooxidation modifications,[22] we believe a relatively slow oxidative coupling at the anthracene site may join a few *PMMA polymer chains together to form this species. To investigate this further, we constructed thin film samples comprising a *PMMA-anh film covered with a nonreactive PS homopolymer layer. SEC/fluorescence indicated the *PMMA-anh indeed reacted to form a higher molecular weight species. When thin films of nonfluorescent PMMA-anh were annealed, no further self-coupling was observed beyond what was found following pyrolysis. The dimensions of these nonfluorescent thin film samples (5 cm × 5 cm × 220 nm) provided sufficient mass to be analyzed using an SEC with a refractive index detector. This result implies that the anthracenyl group is involved in the side reaction, rather than the anhydride functionality. Including the area beneath the peak at 19.2 mL as if it represented amine−anhydride reaction will result in a higher interfacial coverage than observed with FRES by as much as 25%. This side reaction is clearly the largest source of error in the SEC/fluorescence procedure. However, it may be possible to reduce the formation of the high molecular species by diluting the number of *PMMA-anh chains in the system. Such an approach is feasible without sacrificing too much signal due to the enhanced sensitivity of the SEC/fluorescence technique.

In contrast, a depth profiling method such as FRES does not suffer from the types of error as SEC. In these experiments, any coupled dPS-NH_2 or *PMMA-anh material will remain in the bulk rather than segregating to the interfacial region and thus will not be included in determination of the interfacial excess. The primary source of error in the FRES experiment lies in the determination of the width of the rectangle of height $\bar{\phi}_{dPS}$ in the fitting procedure described above. Furthermore, beam damage in FRES may result in the loss of protons and deuterons from the sample.[23] If the protons are lost from the sample much faster than the deuterons, the yield of the proton signal used to normalize the deuteron signal will be smaller than expected, resulting in a higher measured volume fraction of deuterated polymer in the concentration profile and an overestimation of the interfacial coverage. To minimize beam damage, the exposure of the sample to the beam was limited in these experiments. Most important, the FRES experiment is constrained to the investigation of planar geometries, whereas SEC/fluorescence is a viable technique for measuring the extent of interfacial reaction in blending situations.[24]

It should be noted that the interfacial coverages obtained from both methods indicate a much higher interfacial coverage than that expected from the data of Anastasiadis et al. for a pure diblock copolymer of the same molecular weight ($\Sigma_{diblock} = 0.171$ chains/nm^2).[25] This has been observed in previous work with similar molecular weight reactants and may be a sign of interfacial roughening.[9,10,26,27] AFM images of the FRES samples in this study indeed indicate interfacial roughening. When the PS layer is washed away using a mixture of 87:13 v/v cyclohexane/toluene, AFM of the now-revealed PS/PMMA interface yields root-mean-square roughnesses of approximately 20 nm.[28] Future work will examine this interfacial roughening phenomenon in greater detail.

Finally, several hours of annealing is required to observe significant reaction in this system. On the basis of an estimate of the diffusion coefficient for this molecular weight of dPS-NH_2 at 174 °C, a dPS-NH_2 chain should be able to diffuse through the PS bulk in less than 0.01 h.[29] This implies that the reaction is not controlled by the diffusion of the dPS-NH_2 chains in the PS bulk, in contrast to the assumptions of recent theories.[30−33] Similar conclusions have been reached from other experiments.[10,34]

IV. Conclusions

Forward recoil spectrometry (FRES) and size exclusion chromatography with fluorescence detection (SEC/fluorescence) have been used to monitor independently the extent of reaction between model end-functional polymers at a PS/PMMA interface. Bilayer samples comprising a polystyrene layer containing amino-terminal deuterated polystyrene (dPS-NH_2) on an anhydride-terminal fluorescent poly(methyl methacrylate) (*PMMA-anh) layer were annealed at 174 °C for various periods. An interfacial excess observed in the FRES concentration profiles of the dPS-NH_2 in the PS layer was used to determine an interfacial coverage of diblock copolymer, a measure of conversion of dPS-NH_2 to diblock copolymer. Similarly, the conversion of the fluorescent *PMMA-anh to diblock copolymer was measured using size exclusion chromatography coupled with a fluorescence detector. Interfacial coverages determined from both methods agreed on average to within 17%. Both methods also indicated that the formation of copolymer occurs over several hours and appears to approach a steady-state value after 24 h, confirming that the reaction rate is not bulk diffusion-controlled. These experiments demonstrate that the detection of fluorescent tracer molecules successfully characterizes the reaction kinetics of end-functionalized chains at polymer−polymer interfaces. The validation of the SEC/fluorescence technique is essential for the further investigation of interfacial reaction kinetics in systems experiencing typical polymer processing conditions.

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References and Notes

(1) Guégan, P.; Macosko, C. W.; Ishizone, T.; Hirao, A.; Nakahama, S. *Macromolecules* **1994**, *27*, 4993.

(2) Nakayama, A.; Inoue, T.; Guégan, P.; Macosko, C. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34*, 840.

(3) Beck Tan, N. C.; Tai, S.-K.; Briber, R. M. *Polymer* **1996**, *37*, 3509.
(4) Russell, T. P.; Anastasiadis, S. H.; Menelle, A.; Felcher, G. P.; Satija, S. K. *Macromolecules* **1991**, *24*, 1575.
(5) Russell, T. P.; Menelle, A.; Hamilton, W. A.; Smith, G. S.; Satija, S. K.; Majkrzak, C. F. *Macromolecules* **1991**, *24*, 5721.
(6) Dai, K. H.; Norton, L. J.; Kramer, E. J. *Macromolecules* **1994**, *27*, 1949.
(7) Shull, K. R.; Kramer, E. J.; Hadziioannou, G.; Tang, W. *Macromolecules* **1990**, *23*, 4780.
(8) Shull, K. R.; Kellock, A. J.; Deline, V. R.; MacDonald, S. A. *J. Chem. Phys.* **1992**, *97*, 2095.
(9) Jiao, J.; Kramer, E. J.; de Vos, S.; Möller, M.; Koning, C. *Macromolecules* **1999**, *32*, 6261.
(10) Schulze, J. S.; Cernohous, J. J.; Hirao, A.; Lodge, T. P.; Macosko, C. W. *Macromolecules* **2000**, *33*, 1191.
(11) Brown, H. R.; Char, K.; Deline, V. R.; Green, P. F. *Macromolecules* **1993**, *26*, 4155.
(12) Char, K.; Brown, H. R.; Deline, V. R. *Macromolecules* **1993**, *26*, 4164.
(13) Orr, C. A. Ph.D. Thesis, University of Minnesota, 1997.
(14) Okamoto, M.; Inoue, T. *Polym. Eng. Sci.* **1993**, *33*, 175.
(15) Orr, C. A.; Adedeji, A.; Hirao, A.; Bates, F. S.; Macosko, C. W. *Macromolecules* **1997**, *30*, 1243.
(16) Moon, B.; Hoye, T. R.; Macosko, C. W. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2177.
(17) Ueda, K.; Hirao, A.; Nakahama, S. *Macromolecules* **1990**, *23*, 939.
(18) Sela, M.; Berger, A. *J. Am. Chem. Soc.* **1955**, *77*, 1893.
(19) Cernohous, J. J.; Macosko, C. W.; Hoye, T. R. *Macromolecules* **1997**, *30*, 5213.
(20) Schulze, J. S. Ph.D. Thesis, University of Minnesota, 2000.
(21) Doyle, B. L.; Brice, D. K. *Nucl. Instrum. Methods* **1988**, *B35*, 301.
(22) Mallakin, A.; Dixon, D. G.; Greenberg, B. M. *Chemosphere* **2000**, *40*, 1435.
(23) Kramer, E. J. *MRS Bull.* **1996**, *21*, 37.
(24) Jones, T. D. Ph.D. Thesis, University of Minnesota, 2000.
(25) Anastasiadis, S. H.; Russell, T. P.; Satija, S. K.; Majkrzak, C. F. *J. Chem. Phys.* **1990**, *92*, 5677.
(26) Lyu, S.-P.; Cernohous, J. J.; Bates, F. S.; Macosko, C. W. *Macromolecules* **1999**, *32*, 106.
(27) Jiao, J.; Kramer, E. J.; de Vos, S.; Möller, M.; Koning, C. *Polymer* **1999**, *40*, 3585.
(28) Schulze, J. S.; Lodge, T. P.; Macosko, C. W. *Mater. Res. Soc. Symp. Proc.* **2000**, *629*, in press.
(29) Green, P. F.; Kramer, E. J. *Macromolecules* **1986**, *19*, 1108.
(30) Fredrickson, G. H.; Milner, S. T. *Macromolecules* **1996**, *29*, 7386.
(31) Fredrickson, G. H. *Phys. Rev. Lett.* **1996**, *76*, 3440.
(32) O'Shaughnessy, B.; Sawhney, U. *Phys. Rev. Lett.* **1996**, *76*, 3444.
(33) O'Shaughnessy, B.; Sawhney, U. *Macromolecules* **1996**, *29*, 7230.
(34) Jiao, J. Ph.D. Thesis, Cornell University, 1997.

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