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Reaction Kinetics of End-Functionalized Chains at a Polystyrene/Poly(methyl methacrylate) Interface

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ABSTRACT: Forward recoil spectrometry (FRES) has been used to monitor the extent of reaction between model end-functional polymers at a PS/PMMA interface. Bilayer samples comprising a high molecular weight polystyrene layer containing ∼8.5 wt % of amino-terminal deuterated polystyrene (dPS-NH_2) on an anhydride-terminal poly(methyl methacrylate) (PMMA-anh) layer were annealed at 174 °C for various periods. Significant reaction with the PMMA-anh, indicated by an interfacial excess, was observed with three molecular weights ($M = 22\,000$, 37 000, and 92 000 g/mol) of dPS-NH_2. The measured growth of the interfacial excess with time for all three molecular weights could not be well described with recent theories of diffusion-controlled interfacial reactions. A model that incorporates polymer chain reactivity fit the data better, with reaction rate constants $k = 0.20$, 0.055, and 0.042 kg mol^{-1} s^{-1} for dPS-NH_2-22, -37, and -92, respectively. Furthermore, a novel trilayer sample geometry showed that the reactive dPS chains can diffuse throughout the PS matrix and sample the PS/PMMA interface several times before a significant amount of reaction occurs. The results of this study are consistent with other experimental systems where the in situ copolymer formation is limited by reaction rate, rather than the diffusion of reactive chains through the bulk.

I. Introduction

Intermolecular reactions at polymer interfaces are central to reactive compatibilization, where mixtures of two immiscible polymers are stabilized through the in situ formation of block or graft copolymers. Recent experimental studies of reactive compatibilization have emphasized the effect of interfacial reaction on morphology development and the resulting material properties of the blend.[1−4] However, it can be difficult to determine the rate of reaction or the amount of copolymer formed in such experiments, for several reasons. The reactive polymers in these studies are typically heterogeneous in both degree of functionality and molecular weight. Highly functionalized polymers can form densely grafted copolymers or even cross-linked structures at the interface. Furthermore, the complex flow profiles in mixers and extruders may contribute substantially to the kinetics and extent of reaction.[1,4−6]

In contrast, theoretical analyses of polymer−polymer interfacial reactions have explored relatively simple cases, such as the irreversible reaction between end-functionalized polymers at a planar interface illustrated in Figure 1. For example, Fredrickson[7] and O'Shaughnessy and Sawhney[8] independently treated interfacial reactions in the absence of flow and where only a small fraction of the polymer chains in each phase were end-functionalized. Both theories predict that copolymer formation at an interface is described by a reaction rate constant

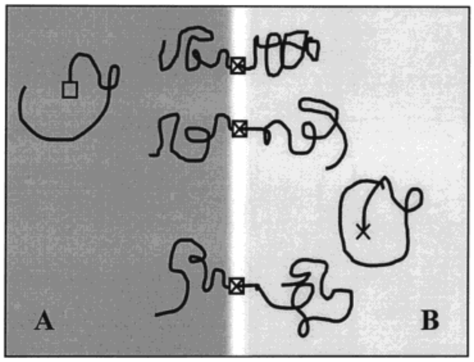

Figure 1. Schematic of reaction between end-functionalized polymer chains to create diblock copolymer at an interface between two immiscible polymers A and B.

$$k \approx DR_g(2R_gS_V/\ln N) \tag{1}$$

where D, R_g, and N are the diffusion coefficient, radius of gyration, and degree of polymerization of a reactive chain, respectively. S_V is the ratio of interfacial area to total volume, and the term $2R_gS_V/\ln N$ represents the volume fraction of the interfacial region accessible to reaction. The factor of $1/\ln N$ is associated with subdiffusive Rouse dynamics on the time scale that local equilibrium is achieved in the interfacial region.[7] In a subsequent paper, Fredrickson and Milner[9] indicate that this local reaction rate applies only to relatively short times, before a depletion of reactants around the interface leads to a diffusion-controlled reaction. As time progresses, the interface eventually fills with copolymer, and the resulting formation of a polymer brush further impedes the reaction. Müller investigated the first two

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time regimes of Fredrickson and Milner's theory using Monte Carlo simulations and found that the theory and simulation agreed during the intermediate diffusion-controlled regime. During the first regime of the reaction, however, the simulation indicated a higher reaction rate than predicted by the theory.[10]

There have been few experimental studies of this fundamental diffusion−reaction problem for planar polymer interfaces in the absence of flow. Some depth-profiling experiments have monitored the interaction of end-functionalized chains with a surface of immobile reactive sites. For example, Clarke et al. observed the physical adsorption of deuterated polystyrene end-functionalized with carboxylic acid (dPS-COOH) from polystyrene matrices of various molecular weights to the native oxide layer of a silicon substrate.[11] Depletion zones in the concentration profile of the functionalized chains persisted for up to 4 times longer than necessary for the chains to diffuse the distance from surface to interface. Consequently, these profiles could not be explained simply in terms of the diffusion of the functionalized chains. Norton et al. examined the reaction of dPS-COOH chains with functionalized epoxy networks (both amine-rich and epoxy-rich) as a function of time.[12] This system also represents a case where the reactive sites are fixed in space. A straightforward diffusion-controlled reaction model overestimated the observed extent of reaction between the dPS-COOH chains and the epoxy network.[13] Kramer therefore considered a model where the reaction kinetics were limited by a bimolecular rate constant and the concentration of reactive end groups in the interfacial region. This model fit the same dPS-COOH/epoxy data with a rate constant $k = 0.18$ kg s^{-1} mol^{-1}. This result was deemed to compare reasonably well with $k = 9.9 \times 10^{-3}$ kg s^{-1} mol^{-1} determined by Guégan et al. for a homogeneous PS-COOH/PS-epoxide reaction during blending at the same temperature (160 °C).[5]

Others have monitored interfacial reactions in systems where all the reactants were mobile. For example, Jiao followed the reaction between dPS end-functionalized with an amine group (dPS-NH$_2$) and commercial poly(styrene-*r*-maleic anhydride) (PSMA) using forward recoil spectrometry, transmission electron microscopy, and atomic force microscopy.[14] The low molecular weight dPS-NH$_2$ ($N = 33$, 55, and 270) formed a graft copolymer with the PSMA. At high extents of reaction the PS/PSMA interface became unstable, attributed to the decrease in interfacial tension with increased copolymer concentration at the interface. A version of Kramer's reaction rate-controlled model was necessary to describe the extent of reaction as a function of time. Jiao inferred a reaction rate constant $k = 3.4 \times 10^{-3}$ kg mol^{-1} s^{-1} at 180 °C for $N = 270$.

In this work, we have used forward recoil spectrometry to measure the extent of reaction at a polystyrene/poly(methyl methacrylate) interface. PS/PMMA interfaces have been studied extensively in the literature,[5,15−19] and model end-functionalized polymers with narrow molecular weight distributions can be synthesized.[20,21] In these experiments, dPS with an amine end group (dPS-NH$_2$) reacts with PMMA with an anhydride end group (PMMA-anh) to form a diblock copolymer through the mechanism shown in Figure 2. Previous studies demonstrated that the amic acid intermediate is short-lived at temperatures above the glass transition temperature T_g ($T_{g,PS} \approx 100$ °C, $T_{g,PMMA} \approx 125$ °C); i.e., the reaction goes irreversibly to the imide.[22] Orr et al. also found this reaction to be rapid under flow: complete conversion of reactants to products was attained in several minutes at 180 °C in a mixer with a typical shear rate of ca. 80 s^{-1}.[6,23] We are able to test Fredrickson and Milner's theory of interfacial reaction by measuring the interfacial excess that results at the PS/PMMA interface from polymer coupling, using the sample geometry shown in Figure 3a. Furthermore, the novel sample geometry in Figure 3b allowed us to observe independently the diffusion of dPS-NH$_2$ chains through the PS matrix as well as the eventual reaction with the PMMA-anh. The concentration profiles obtained from these two types of samples indicate whether the diblock copolymer formation is limited by reaction rate or by the diffusion of the reactive chains through the bulk.

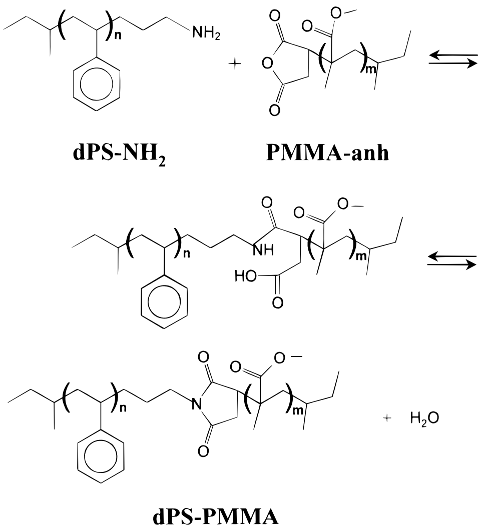

Figure 2. Perdeuterated polystyrene with an amine end group reacts with poly(methyl methacrylate) with an anhydride end group to form a dPS−PMMA diblock copolymer. The amic acid intermediate is short-lived at temperatures above the glass transition, and the reaction goes irreversibly to the imide.[22]

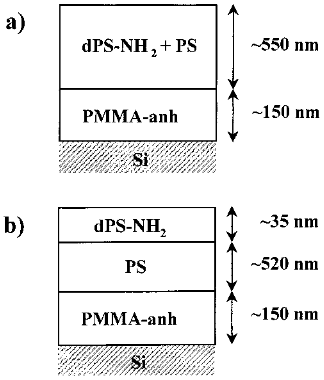

Figure 3. Two sample geometries were used in these experiments. (a) Bilayer samples were prepared by floating films containing dPS-NH$_2$ (8.4 wt %) and PS onto PMMA-anh layers that had been spun from solution onto a Si wafer. (b) Trilayer samples were prepared by first floating a PS film onto a PMMA-anh layer, followed by floating a thinner dPS-NH$_2$ film on top of the PS.

II. Experimental Section

Polymer Synthesis and Characterization. The characteristics of the polymers used in this study are shown in Table

Table 1. Materials Used

polymer	$M_n \times 10^{-3}$	M_w/M_n	*f* ^{1}H NMR	titration	TLC/FID
PS[a]	230	1.06			
dPS-NH$_2$-22	22	1.04	0.59	0.84	0.93
dPS-NH$_2$-37	37	1.06	0.72	0.98	0.95
dPS-NH$_2$-92	92	1.06	0.24	0.70	
PMMA-anh	35	1.07	0.84[b]		

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

1. A polystyrene standard, PS-230 ($M = 2.3 \times 10^5$ g/mol), purchased from Pressure Chemical was used as a matrix in these experiments. Three perdeuterated polystyrenes end-functionalized with an aliphatic amine group (dPS-NH$_2$) were synthesized.[20] The molecular weights were confirmed via gel permeation chromatography combined with low-angle laser light scattering. Functionality was checked by a variety of methods. At the time of synthesis, thin-layer chromatography/flame ionization detection (TLC/FID) showed >90% functionality on the dPS-NH$_2$-22 and dPS-NH$_2$-37 polymers. Later TLC experiments (without FID analysis) qualitatively indicated that all three dPS-NH$_2$ polymers were completely functional. The dPS-NH$_2$ polymers were 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.[24] These titration experiments also indicated relatively high functionality for all three dPS-NH$_2$ polymers, as shown in Table 1. Functionality was also estimated by comparing the signals from the aliphatic protons near the terminal amine group to those proton signals from the *sec*-butyllithium initiator in 500 MHz ^{1}H NMR. The ratio of these signals for a completely functionalized dPS-NH$_2$ polymer should be 2:6. Although this method should in principle be the most direct measure of functionality, the high molecular weight reduces the signal-to-noise and the accuracy of the signal integration. Given this difficulty, we consider the NMR results to underrepresent the level of functionality. Because the titration and TLC methods seem most reliable and reproducible, we used the average of the functionality obtained from these methods for later calculations.

Poly(methyl methacrylate) end-functionalized with anhydride (PMMA-anh) was also synthesized.[21] The molecular weight was determined by gel permeation chromatography/light scattering. 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. 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 was then separated from the excess poly(ethylene oxide) using GPC. 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.[21] This procedure indicated the PMMA-anh to be ca. 84% functional. The error in this analysis is estimated to be ±10%.

Sample Preparation. PMMA-anh was dissolved in toluene (~4.5 wt % PMMA) and spun at 1000 rpm onto silicon wafers. Ellipsometry indicated these films to be approximately 150 nm thick.

The bilayer samples depicted in Figure 3a were prepared by first dissolving mixtures of dPS−NH$_2$ (8.4 wt %) and PS-230 in toluene to form a ~4.5 wt % polymer solution. This solution was then spun onto mica substrates at 1000 rpm. After scoring the mica substrates with a razor blade, the films (approximately 550 nm thick) were floated off onto deionized water and picked up with the PMMA-coated silicon wafers. The samples were allowed to dry overnight and then annealed at 174 °C under vacuum (<20 mTorr) for various periods.

To prepare the trilayer samples as in Figure 3b, a PS/toluene solution (~4.5 wt % PS) was first spun onto mica and floated onto PMMA-coated silicon wafers as above and allowed to dry overnight. A dPS-NH$_2$/toluene solution (~1 wt % dPS-NH$_2$) was then spun at 1000 rpm onto a mica substrate, scored with a razor blade, and floated onto the now PS/PMMA-coated silicon wafers. Ellipsometry indicated these dPS-NH$_2$ films were 30−40 nm thick. The samples were left to dry and then annealed at 174 °C under vacuum for various periods. Because of their low viscosity and high brittleness, dPS-NH$_2$-22 and -37 films could not readily be floated onto water to make trilayer samples; only dPS-NH$_2$-92 trilayer samples were tested.

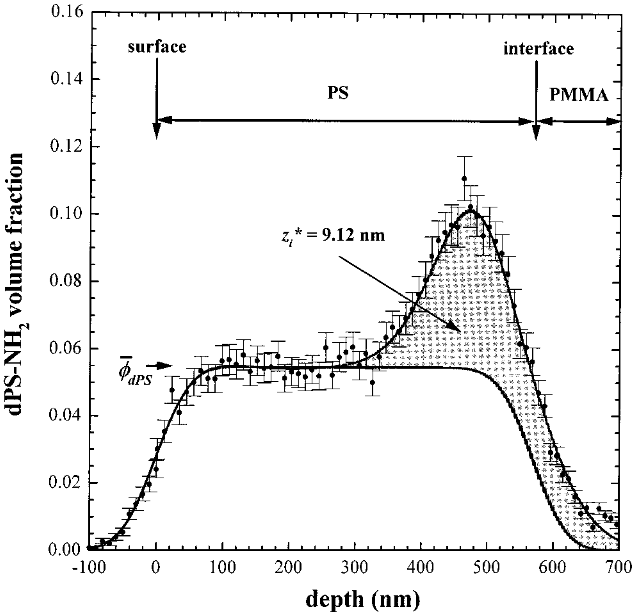

Figure 4. Concentration profile of a dPS-NH$_2$-37 bilayer sample obtained with FRES. An interfacial excess z_i^* (shaded area) of 9.12 nm ($z_i^*/R_g = 1.81$, $\Sigma = 0.168$ chains/nm^2) is observed after annealing at 174 °C for 48 h.

Forward Recoil Spectrometry. FRES was performed at the Ion Beam Analysis Facility at the University of Minnesota Center for Interfacial Engineering. 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 collected for each spectrum, over 20−25 min. In general, two spots on each sample were tested, and two samples were constructed and annealed under identical conditions. On a few samples, spectra were collected in four different spots for 5 μC each and added together. The spectra from these samples resulted in concentration profiles that were indistinguishable from profiles obtained from a 20 μC test of a sample that had experienced identical annealing conditions. The spectra were converted from yield vs energy data to volume fraction vs depth using usual FRES analysis procedures.[25] 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.

III. Results

A typical FRES concentration profile of an annealed bilayer sample is shown in Figure 4. For all three molecular weights of dPS-NH$_2$, peaks near the PS/PMMA interface were ultimately observed. This interfacial excess is evidence of copolymer formation from the reaction of the dPS-NH$_2$ with the PMMA-anh chains. For all three molecular weights, the peak at the interface increased in amplitude with time, while the free surface volume fraction correspondingly decreased. The evolution of the interfacial excess as a function of

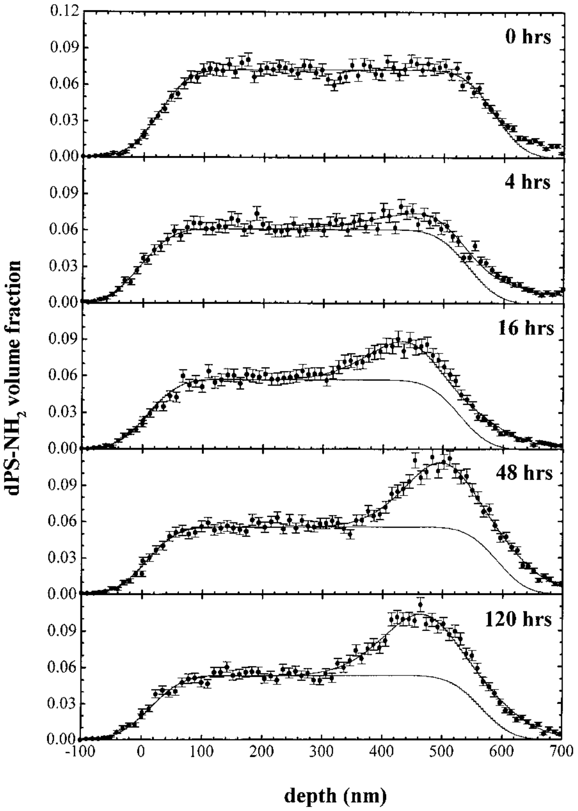

Figure 5. FRES concentration profiles showing the evolution of interfacial excess with annealing time of dPS-NH$_2$-22 bilayer samples at 174 °C.

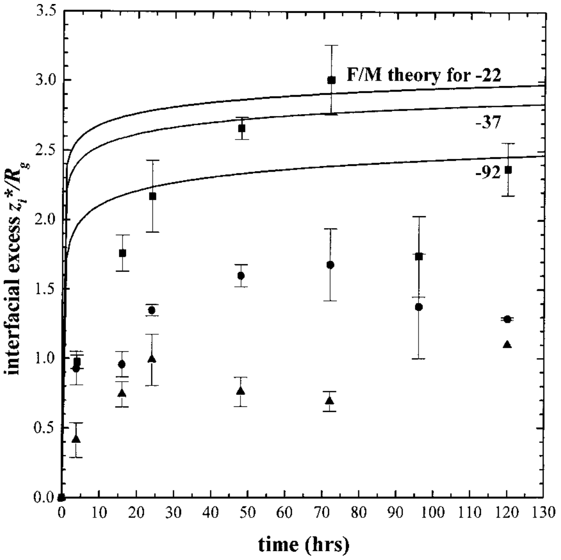

Figure 6. Normalized interfacial excess z_i^*/R_g as a function of time at 174 °C from bilayer samples of the following: dPS-NH$_2$-22 (■), dPS-NH$_2$-37 (●), and dPS-NH$_2$-92 (▲). Fredrickson and Milner's theoretical predictions for polymer−polymer interfacial reactions are also shown.[9] Note the difference in initial slope between the experimental data and the theoretical prediction.

time for dPS-NH$_2$-22 is illustrated in Figure 5. In contrast to the concentration profiles of dPS-COOH in high molecular PS matrices investigated by Clarke et al.,[11] no depletion zones were observed in any of the concentration profiles of the bilayer samples. As discussed in detail below, this implies that the dPS-NH$_2$ chains were in a diffusion equilibrium with the interfacial region.

To analyze the concentration profiles of the bilayer samples quantitatively, the spectra were fit to a profile that is a sum of a Gaussian function, representing the interfacial excess, and a rectangular block, representing the uniform distribution of dPS in PS. The peak position of the Gaussian function coincides with the edge of the rectangular block. This profile was then convoluted with another Gaussian representing the instrumental response function (resolution 90 nm) and fit to the data by minimizing the χ^2 statistical parameter. The normalized χ^2 parameter for the fits typically ranged from 0.8 to 1.2.[26] After the data were fit, a quantity $\bar{\phi}_{dPS}$ that represents the volume fraction of unreacted dPS-NH$_2$ chains far from the PS/PMMA interface was then calculated.[27] $\bar{\phi}_{dPS}$ has the same magnitude as the height of the rectangular block used to fit the data. Because the distance from the free surface to the interface (i.e., the "thickness" of the film containing the unreacted dPS-NH$_2$ chains) that determines the width of the rectangle of height $\bar{\phi}_{dPS}$ is not unambiguously defined, we chose to calculate $\bar{\phi}_{dPS}$ and the corresponding interfacial excess by three different methods and then average the results. We first used the experimentally determined thickness of an unannealed sample; however, slight variations among samples resulted in some unannealed samples being thicker than the annealed samples. The second method for determining the thickness relied on a rule of conservation of area from unannealed sample to annealed sample. The unannealed and annealed samples were constructed from the same solution and thus should have the same relative amount of dPS-NH$_2$ to PS. For an unannealed sample, the value of $\bar{\phi}_{dPS}$ multiplied by the surface-to-interface distance equals the area under the data. A corresponding distance for an annealed sample was then determined as

$$\frac{(\text{thickness})_{\text{annealed}}}{(\text{thickness})_{\text{unannealed}}} = \frac{\int_{\text{annealed}}\phi(x)\,\mathrm{d}x}{\int_{\text{unannealed}}\bar{\phi}_{dPS}(x)\,\mathrm{d}x} \tag{2}$$

Finally, other workers have defined the surface-to-interface distance by the position of the half-height of the peak that lies nearer to the interface.[14,28] For the dPS-NH$_2$ annealed bilayer samples in this study, the surface-to-interface distance and the area beneath $\bar{\phi}_{dPS}$ were determined using all three methods (where applicable). The fits shown in Figures 4 and 5 are those obtained from setting the interface at the position of the half-height of the peak. The interfacial excess z_i^* corresponding to the shaded area shown in Figure 4 was then calculated using the following integral:

$$z_i^* = \int_{-\infty}^{+\infty} (\phi(x) - \bar{\phi}_{dPS})\,\mathrm{d}x \tag{3}$$

where $\phi(x)$ is the volume fraction from the fit to the data at depth x, and $\bar{\phi}_{dPS}$ is the function calculated using one of the three methods described. Interfacial excess values from the three methods agreed to within 15%. These interfacial excess values were then normalized by dividing by the radius of gyration R_g of the dPS-NH$_2$ polymer, calculated using $R_g = (Na^2/6)^{0.5}$, with the statistical segment length $a = 0.68$ nm.[16] Values of the normalized interfacial excess z_i^*/R_g calculated by the above three methods were first averaged across replicate samples and then averaged across the three methods. These average z_i^*/R_g values are plotted as a function of time in Figure 6. The error bars represent one

Table 2. Estimated Diffusion Times at 174 °C

polymer	D^* (cm^2/s) (ref 30)	time (h) to diffuse 550 nm ($t = x^2/4D^*$)
dPS-NH$_2$-22	1.6×10^{-11}	0.01
dPS-NH$_2$-37	5.5×10^{-12}	0.04
dPS-NH$_2$-92	8.9×10^{-13}	0.24

standard deviation of the average z_i^*/R_g values. The normalized interfacial excess z_i^*/R_g is directly proportional to the interfacial coverage Σ (chains/nm^2):

$$\Sigma = \left(\frac{z_i^*}{R_g}\right)\frac{\rho_0 R_g}{N} \tag{4}$$

where ρ_0 is the dPS segment density.

Estimating the time required for the dPS-NH$_2$ chains to diffuse 550 nm, the average thickness of the samples, provides a preliminary observation concerning the limiting factor in these interfacial reactions. Characteristic times for diffusion, $x^2/4D^*$, where D^* is the self-diffusion coefficient for dPS at 174 °C and x is 550 nm, are shown in Table 2.[29] The self-diffusion coefficient $D^* = 2.5 \times 10^{-12}$ cm^2/s was reported for dPS-55 in entangled PS matrices at 174 °C.[30] The diffusion coefficients for dPS-NH$_2$-22, -37, and -92 in Table 2 were estimated by scaling this value by the molecular weight raised to the -2.0 power. We have also observed the diffusion of nonfunctional dPS-86 through PS-90 at 174 °C using FRES. Fickian concentration profiles with a diffusion coefficient of 5.9×10^{-13} cm^2/s fit these data, within a factor of 2 of the literature D^* value scaled for molecular weight. The scaled literature value of D^* was also similar to the value obtained from fitting trilayer dPS-NH$_2$-92 samples as will be discussed below. The fact that the characteristic diffusion times in Table 2 are all less than 1 h implies that the dPS-NH$_2$ chains are in a diffusion equilibrium with the interface and also indicates that the reactive chains may enter the interfacial region many times before reaction is observed. Thus, it appears that diffusion of the dPS-NH$_2$ chains through the PS matrix does not the limit the rate of interfacial reaction.

IV. Discussion

As shown in Figure 6, the reaction of dPS-NH$_2$-37 and -92 with PMMA-anh appears to slow before the dPS-NH$_2$-22. One possible explanation for this behavior is that the interface becomes saturated with copolymer, and the formation of a dense copolymer brush inhibits further reaction. Any unreacted chains entering a dense brush have to adopt a low-entropy stretched configuration and localize the reactive end group at the interface before gaining the free energy of reaction.[13] The copolymer interfacial coverages at long time (72 h) were first compared to the chains per area of a pure diblock copolymer, a reasonable first approximation of the number of chains per area consistent with a saturated interface. (This procedure assumes the coupling reaction results in a lamellar copolymer, which might not be the case for any asymmetric copolymer formed. For example, the reaction between the dPS-NH$_2$-92 and PMMA-anh-35 results in a copolymer with a PS volume fraction of 0.66, which might not be lamellar.) The number of chains per area for a diblock copolymer $\Sigma_{\rm diblock}$ was determined from values of the lamellar spacing of PS−PMMA block copolymers obtained by neutron reflectivity.[16] The lamellar spacing was scaled for molecular weight with an exponent of 0.66.

For dPS-NH$_2$-22, the average interfacial coverage after 72 h of annealing ($\Sigma = 0.362$ chains/nm^2) was greater than that calculated from the data of Anastasiadis et al. for a diblock copolymer of the same molecular weight ($\Sigma_{\rm diblock} = 0.171$ chains/nm^2). The relatively large values of the z_i^*/R_g (or Σ) obtained for the dPS-NH$_2$-22 may indicate "interfacial roughening" is occurring.[19,31] However, more rigorous measurements of the interfacial structure using transmission electron microscopy and atomic force microscopy would be necessary to establish this. For dPS-NH$_2$-37, the average interfacial coverage at 72 h ($\Sigma = 0.156$ chains/nm^2) was essentially equal to that expected for a pure diblock of the same molecular weight, $\Sigma_{\rm diblock} = 0.155$ chains/nm^2. For this molecular weight, then, the reaction being slowed or brought to a steady state as a result of a saturated interface is reasonable. The average interfacial coverage for dPS-NH$_2$-92 at 72 h was one-third of that expected for the same molecular weight diblock: $\Sigma = 0.0407$ chains/nm^2 < $\Sigma_{\rm diblock} = 0.125$ chains/nm^2. However, the dPS-NH$_2$-92 coverage at 72 h is within a factor of 2 of the coverage at which the chemical potential of the copolymer is of order k_BT, as predicted by self-consistent mean field theory ($z_i^*/R_g = 0.80$).[32]

The molecular weight of the diblock copolymer formed at the interface may explain the observed values of the interfacial coverage at long times. Self-consistent mean field theory predicts that lower molecular weight diblock copolymers will have a greater ability to reduce the interfacial tension at a given chemical potential or interfacial excess.[33] Lower molecular weight diblock copolymers are also more susceptible to thermal fluctuations, an observation which was used to explain the interfacial roughening observed in a similar PS/PMMA reactive system with high concentrations of slightly lower molecular weight reactants.[19] Thus, an interface saturated with low molecular weight diblock copolymers, disrupted by both thermal fluctuations and a decrease in interfacial tension, may contain a higher coverage of copolymers than expected from a calculation of $\Sigma_{\rm diblock}$ (without the interfacial tension being zero). In short, an interface saturated with low molecular weight diblocks may be less "rigid" than an interface saturated with high molecular weight copolymers. As diblock molecular weight increases, the interface becomes less susceptible to thermal fluctuations, and steady-state coverage is determined by a coverage corresponding to a chemical potential on the order of k_BT.

The degree of diblock copolymer coverage at the interface raises the question of the magnitude of the corresponding decrease in interfacial tension. As block copolymer is added to a polymer−polymer interface, the interfacial tension is expected to decrease. If the interfacial tension is driven to zero, a microemulsion consisting of small droplets of one phase in the other, or a corrugated interface, may form between the two phases.[34−36] Reduction of the interfacial tension has been the reason given for interfacial roughening observed in similar reactive systems.[31] Self-consistent mean field theory for end-adsorbed polymer brushes in polymeric matrices allows estimates of the copolymer coverage required to drive the interfacial tension to zero.[32] The critical interfacial excess for each molecular weight was calculated using Shull's tabulated values of the change in interfacial tension, $\Delta\gamma$, and Helfand and

Tagami's prediction of the interfacial tension between two high molecular weight homopolymers, γ_0,[37] following a similar procedure found in the literature:[14,31]

$$\frac{-\Delta\gamma}{\gamma_0} = \frac{1}{\sqrt{\chi N}}\int_{-\infty}^{\mu}\mu\left(\frac{z_i^*}{R_g}\right)\mathrm{d}\mu \qquad (5)$$

where N is the degree of polymerization of the dPS-NH_2 chain, and μ is the chemical potential of a grafted chain for a dry brush situation ($N_{\mathrm{matrix}}/N = 8$). The interaction parameter χ for PS−PMMA has been measured to be 0.0367 at 174 °C.[15] Equation 5 indicates that the interfacial tension is zero when the right-hand side is unity. For dPS-NH_2-22, this occurs when z_i^*/R_g equals 1.60, which is less than any value of z_i^*/R_g after 16 h of annealing. Again, it will be worthwhile to examine directly the interface of the dPS-NH_2-22 bilayer samples to determine whether significant interfacial roughening is occurring in this system. Mean-field theory predicts $\gamma = 0$ at z_i^*/R_g of 1.75 and z_i^*/R_g of 2.25 for dPS-NH_2-37 and -92, respectively, and therefore it seems unlikely that the interfacial tension has decreased to zero in these particular samples.

The final, and perhaps most important, issue to be considered for this experiment is whether the observed reaction kinetics are controlled by diffusion or by reaction. As mentioned in the Introduction, several theoretical treatments have assumed that the interfacial reaction between two immiscible polymers is predominately a diffusion-controlled process over most time scales; i.e., the reaction between functionalized chains is much faster than the diffusion of the chains over large distances. However, our experiments are consistent with other experimental studies where the observed formation of copolymer at the interface is better described by reaction rate kinetics.[5,13,14,23] As described above, the diffusion times shown in Table 2 reveal the influence of the reaction rate of the two end-functionalized polymers. Given that the thickness of the PS layer is approximately 550 nm and the dPS-NH_2 diffusion coefficients are known or can be scaled from literature values, the time for a dPS-NH_2 chain to diffuse across the PS matrix at 174 °C can be determined. Table 2 shows these diffusion times are much less than the time at which significant reaction is observed. This result suggests that the reactive polymers can cross the PS matrix and sample the PS/PMMA interface many times before a significant amount of reaction occurs.

The trilayer experiment shown in Figure 7 exposes this fact more directly. At $t = 0$, the reactive dPS-NH_2-92 chains are all located in a thin film (~35 nm thick) on top of a PS matrix that covers a PMMA-anh layer. After annealing the sample at 174 °C for 15 and 30 min, some dPS-NH_2-92 has diffused throughout the PS matrix. These concentration profiles can be fit with a solution to Fick's law for a thin film of initial thickness h diffusing to a reflecting boundary:

$$\phi(x) = \frac{1}{2}\sum_{n=-\infty}^{\infty}\left\{\mathrm{erf}\left[\frac{h + 2nl - x}{\sqrt{4D^*t}}\right] + \mathrm{erf}\left[\frac{h - 2nl + x}{\sqrt{4D^*t}}\right]\right\} \qquad (6)$$

where D^* is the tracer diffusion coefficient, and l is the location of the PS/PMMA interface.[29] A small Gaussian function with a peak position near the surface and width 2σ equal to the instrumental resolution is added to the Fickian diffusion profile to account for the small surface excess observed at 4 h. This small surface excess may result from the deuterated functionalized chains having a slight affinity for the vacuum/PS surface. The diffusion coefficient D^* obtained from fitting the profiles at 15 and 30 min is 3.0×10^{-13} cm^2/s, which is similar to the literature value mentioned in the Results section.[30] Between 1 and 2 h in this experiment, the dPS-NH_2 chains are essentially dispersed throughout the PS matrix. However, 24 h of annealing is necessary in order to observe a significant peak at the PS/PMMA interface, indicating that the reaction has occurred. The z_i^*/R_g at $t = 24$ h is 0.867, which agrees with the z_i^*/R_g observed in the bilayer dPS-NH_2-92 samples at this annealing time. This trilayer experiment establishes directly that the dPS-NH_2-92 chains are indeed in a diffusion equilibrium with the interface, as expected from the calculations shown in Table 2.

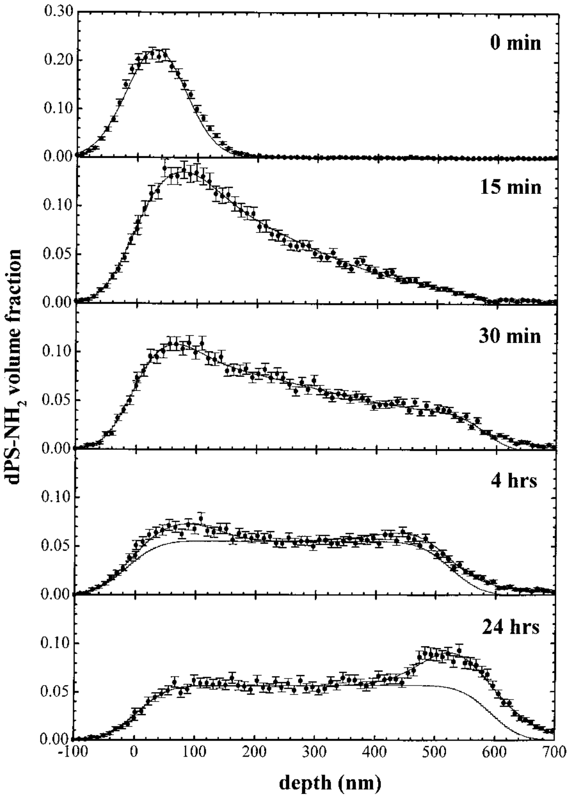

Figure 7. Diffusion of dPS-NH_2-92 through PS to a PMMA-anh layer at 174 °C. Normalized interfacial excess z_i^*/R_g is 0.867 at 24 h.

The recent theoretical work by Fredrickson and Milner identifies three regimes in the reaction of end-functionalized polymers at an interface.[9] In the first regime, the growth of the interfacial excess $\xi = z_i^*/R_g$ with time is determined by second-order reaction kinetics:

$$\xi(t) = \left(\frac{N}{R_g\rho_0}\right)k\nu_0^{\,2}t = 40.7\left(\frac{N}{R_g\rho_0}\right)\frac{R_g^{\,4}}{\tau\ln(\tau/\tau_0)}\,\nu_0^{\,2}t \qquad \text{for } t < \frac{4D^*}{\pi\nu_0^{\,2}k^2} \qquad (7)$$

where τ_0 is the longest Rouse time, τ is the reptation time, and ν_0 is the number density of functionalized chains in each phase. N, R_g, and ρ_0 are respectively the degree of polymerization, radius of gyration, and segment density of the dPS-NH_2 chains. This first regime thus describes the reaction of the chains that are initially in the interfacial region. Because the rate constant k in eq 7 is determined solely by chain relaxation times (τ_0, τ), this regime quickly crosses over to a diffusion-controlled reaction at a time on the order of seconds:

$$\xi(t) = \left(\frac{2}{\pi^{1/2}}\right)\left(\frac{N}{R_g\rho_0}\right)\nu_0(D^*t)^{1/2} \qquad \text{for } \frac{4D^*}{\pi{\nu_0}^2k^2} \le t < \frac{(\xi_m R_g\rho_0)^2}{D^*(\nu_0 N)^2} \quad (8)$$

This diffusion-controlled regime can last for several minutes. The last regime begins when the interfacial excess reaches ξ_m, the excess that corresponds to a chemical potential barrier of order k_BT. We used Shull's SCMF dry brush result of $z_i^*/R_g = 0.80$ for $\mu/k_BT = 1$ to evaluate ξ_m. The interfacial excess grows much more slowly with time in this regime:

$$\xi(t) = \xi_m\sqrt{\ln\left(\frac{N^{1/2}t}{\tau_\xi \ln N}\right)} \quad \text{for } t \ge \frac{(\xi_m R_g\rho_0)^2}{D^*(\nu_0 N)^2} \qquad (9)$$

where τ_ξ is the crossover time to the third regime. Equations 7−9 are plotted in Figure 6. Fredrickson and Milner's theory clearly overestimates the rate of interfacial reaction observed in these experiments.

A more recent theory by O'Shaughnessy and Vavylonis may provide a better description of polymer−polymer interfacial reactions.[38,39] These authors state that because the amine/anhydride and carboxylic acid/epoxy reactions studied by Macosko and co-workers[5,6,23] are sufficiently "weak" reactive pairs, linear second-order reaction kinetics should apply until the interface saturates with copolymer and a transition to diffusion-controlled reaction kinetics will not be observed. O'Shaughnessy and Vavylonis describe the relative reactivity of end-functionalized polymer chains with a dimensionless parameter Qt_a, where Q is a local chemical reactivity and t_a is a monomer relaxation time. Qt_a values for the above reactive pairs range from 10^{-6} to 10^{-11}.[38,39] These Qt_a values and an estimate of t_a of 5×10^{-8} s indicate that the time at which the PS/PMMA interface should saturate ranges from 0.5 to 10^4 h. Our experimental results indicate that the saturation of the PS/PMMA interface occurs on the order of 10^1−10^2 h, which is well within the range of the theoretical prediction. Because of the absence of numerical prefactors, this theory could not be compared to our experimental data more quantitatively.

Our findings are similar to those observed in systems where end-functionalized chains grafted to a fixed network of reactive sites or reacted to form graft copolymer at an interface.[13,14,31] A straightforward model for reaction rate-limited grafting kinetics where the polymer chains must overcome a potential barrier before reacting was proposed by Kramer.[13] However, this model assumes an infinite amount of functionalized chains are available for reaction, and it does not describe the buildup of a copolymer brush from an initially bare interface. Jiao[14] included these effects in the following model for interfacial reactions limited by reaction rate:

$$\frac{d\xi}{dt} = k\phi_{dPS}[-\text{anh}]\left(1 - \frac{R_g}{h\phi_{dPS}}\,\xi\right)\left(\frac{\delta}{R_g}\right)^{2.1}\left(1 - \frac{\xi}{\xi_m} + \frac{\xi}{\xi_m}\exp\left(-\frac{\bar{\mu}(\xi_m)}{k_BT}\right)\right) \quad \text{for } \xi < \xi_m \quad (10a)$$

$$\frac{d\xi}{dt} = k\phi_{dPS}[-\text{anh}]\left(1 - \frac{R_g}{h\phi_{dPS}}\,\xi\right)\left(\frac{\delta}{R_g}\right)^{2.1}\exp\left(-\frac{\bar{\mu}(\xi_m)}{k_BT}\right) \quad \text{for } \xi \ge \xi_m \quad (10b)$$

where ξ is the interfacial excess z_i^*/R_g, ϕ_{dPS} and h are respectively the initial volume fraction and film thickness of dPS-NH_2 in the sample, [−anh] is the concentration of anhydride in the PMMA layer, and k is the bimolecular reaction rate constant. δ is the interfacial thickness from Helfand and Tagami,[37] and the quantity $(\bar{\mu}(\xi)/k_BT)$ is the chemical potential of the dPS chains as tabulated by Shull.[32] Equation 10a describes the rate of reaction at coverages less than ξ_m, when the interface is relatively bare. Equation 10b describes the rate of reaction once chains must overcome a potential barrier on the order of k_BT in order to react: $\xi_m = (z_i^*/R_g)_m = 0.80$. When this model is fit to our data by adjusting the value of k, rate constants of 0.20, 0.055, and 0.042 kg mol^{-1} s^{-1} are found for the dPS-NH_2-22, -37, and -92 reactions, respectively. The fits to the data are shown in Figure 8. Although the fits do not perfectly describe the data, we believe they provide reasonable estimates of the reaction rate constant. These results indicate that the amine/anhydride reaction is slightly faster than the carboxylic acid/epoxy reaction ($k = 0.04$ kg mol^{-1} s^{-1} at 180 °C) for reactants of similar molecular weight.[5] However, these reaction rate constants are an order of magnitude larger than those observed by Jiao: for dPS-NH_2 ($M = 30\,000$) reacting with poly(styrene-*r*-maleic anhydride) at 180 °C, $k = 3.4 \times 10^{-3}$ kg mol^{-1} s^{-1}.[14] Furthermore, the rate constants obtained from the model above are much less than those implied from previous mixing studies, where complete conversion of reactants was achieved in several minutes at a typical shear rate of ca. 80 s^{-1}.[6,23] These discrepancies warrant further study of the reaction kinetics of this particular system.

Finally, the molecular weight dependence of the reaction rates in this study does not necessarily violate Flory's principle of equal reactivity.[40] Rather, we believe the molecular weight dependence arises from physical, rather than chemical, restrictions.

V. Conclusions

We have measured the amount of reaction that occurs between model end-functional polymers at a PS/PMMA interface. Samples comprising a layer containing dPS-NH_2 in a high molecular weight PS placed on a PMMA-anh layer were annealed at 174 °C for various periods. Forward recoil spectrometry was then used to measure the interfacial excess z_i^*/R_g, indicating the coupling between three molecular weights of dPS-NH_2 and PMMA-anh. Previous studies indicated this polymer reaction to be extremely fast, and we anticipated that this system would be diffusion-controlled in the absence of external convection.[6,23] For the lowest molecular weight, dPS-NH_2-22, interfacial coverages higher than the estimated coverage of a pure diblock were achieved, warranting further investigation into the interfacial structure. The measured growth of the interfacial excess

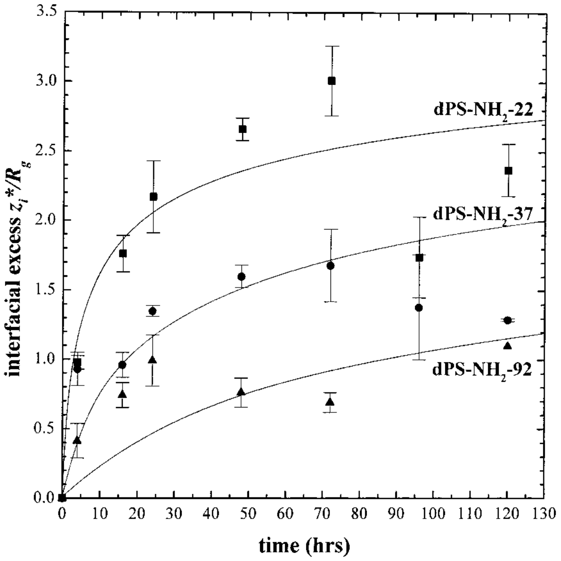

Figure 8. Normalized interfacial excess z_i^*/R_g as a function of time at 174 °C from bilayer samples of the following: dPS-NH$_2$-22 (■), dPS-NH$_2$-37 (●), and dPS−NH$_2$-92 (▲). Jiao's model for reaction rate-limited interfacial reaction is also shown fit to the data.[14]

with time for all three molecular weights could not be described with a theoretical treatment of diffusion-controlled interfacial reaction proposed by Fredrickson and Milner.[9] A model that incorporates polymer chain reactivity better fit the data,[14] with reaction rate constants $k = 0.20$, 0.055, and 0.042 kg mol^{-1} s^{-1} for dPS-NH$_2$-22, -37, and -92, respectively. These results are consistent with other experimental systems where copolymer formation is limited by the reaction rate, rather than the bulk diffusion of reactive chains.[5,13,14,23] However, these reaction rates are much smaller than those implied from previous mixing experiments involving the amine/anhydride reaction.[6,23] Furthermore, a novel trilayer sample geometry showed that the reactive dPS chains can diffuse throughout the PS matrix and sample the PS/PMMA interface several times before a significant amount of reaction occurs. Concentration profiles of these trilayer samples indicate that the dPS-NH$_2$ can disperse itself over 550 nm in about 1 h at 174 °C but that significant reaction is not observed until a further 24 h elapse. These results demonstrate that diffusion in the bulk of the polymer does not limit the rate of reaction. Rather, the diffusion and reaction that takes place within the interfacial zone are paramount.

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