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Diffusion-Controlled Reactive Coupling at Polymer−Polymer Interfaces

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Reactive coupling of an end-functionalized polymer A with another end- or chain-functionalized polymer B at an A−B interface is technologically referred to as reactive compatibilization. It is a proven means by which to reduce interfacial tension and improve adhesion between domains in polymer blends.[1] In reactive systems, whether small-molecule or macromolecular in nature, the two regimes that generally describe the rate-limiting mechanism of the reaction are classified as diffusion- and reaction-controlled (DC and RC, respectively) regimes.[2] A dimensionless Damkohler number (N_{Da}) as defined below can be used to determine which regime dominates a particular reaction.[3]

$$N_{\mathrm{Da}} \equiv \frac{\tau_{\mathrm{M}}}{\tau_{\mathrm{R}}} \tag{1}$$

Here, τ_{M} and τ_{R} are the characteristic time scales for mass transfer and reaction, respectively. This can be considered a measure of the ability of reactive groups to locate each other as compared to their ability to couple (i.e., form a strong bond). When $\log(N_{\mathrm{Da}}) \rightarrow \infty$, the system is strongly DC, whereas the system is strongly RC as $\log(N_{\mathrm{Da}}) \rightarrow -\infty$.[2] This can be a useful guide for choosing pertinent experimental parameters, including reaction temperature and molecular weight of the polymers.

The DC mechanism for macromolecular systems was theoretically detailed by de Gennes[4] for bulk miscible systems, and the rate of chain coupling was shown to be directly proportional to the self-diffusivity (chain mobility) of the functionalized polymers involved. A similar relationship between chain coupling rates and self-diffusivity has been proposed for DC reactions conducted at the interfaces of immiscible polymers.[5,6] Recent experimental investigations of reactive coupling at interfaces commonly rely on planar films,[7,8] where detection and quantitation of copolymer formation can be straightforward using real-space depth profiling techniques.[9] These studies[7,8] have concluded that the interfacial reactions examined, although involving relatively slowly diffusing polymers[10] and highly reactive functional groups,[11] appear to be RC. For reactive coupling of polymers at an immiscible polymer−polymer interface, direct observation of DC reactions has remained elusive. The absence of reliable observation and characterization of DC reactions across polymer−polymer interfaces, which can be partially attributed to depth resolution limitations in experimental techniques,[9] has limited the progress in understanding and furthering theoretical development of macromolecular reactions and has therefore motivated the present study.

For DC reactive coupling, the progression of interfacial copolymer formation is controlled by the physics of mass transfer rather than chemical bonding mechanisms.[12,13] Various interfacial phenomena can create conflicting experimental observations and must be delineated to allow proper characterization of reactive coupling. For systems where the interface does not become thermodynamically unstable,[7] DC reactions can be separated into two clear stages. Early stage reactions are unhindered by an excess of copolymer formed at the

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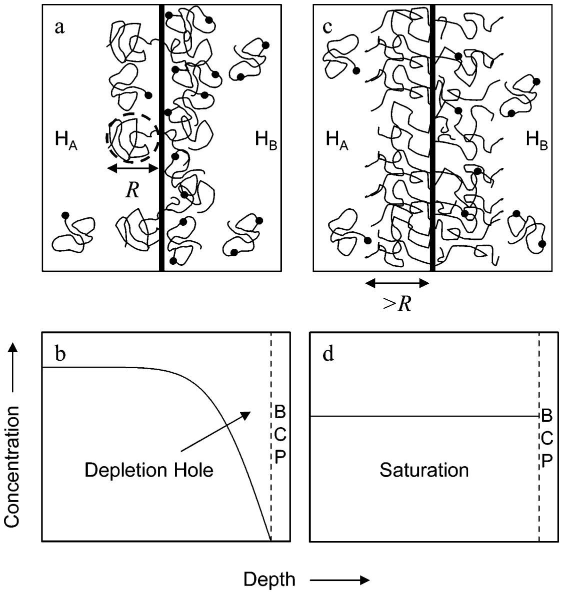

Figure 1. Homopolymer A (H_A) contains a fraction of end-functionalized polymers, while homopolymer B (H_B) contains 100% chain-functionalized polymers. During early stages (a) the buildup of the copolymer is not significant enough to hinder diffusion of reactive H_A to the interface. During the late stages (c) copolymer coverage limits replenishment of reactive H_A to the interface. Here R is the RMS end-to-end distance of a single chain. Ideal Fickian diffusion profiles[26] of functionalized, unreacted H_A (concentration vs depth) are shown as examples of (b) the early stages when an infinite sink for functionalized H_A at the interface causes a depletion hole near the interfacial block copolymer (BCP), whereas in the bulk the constant initial concentration is still observed, and (d) during the late stages when the interface does not serve as a strong sink anymore and this gradient is not present.

interface and are characterized by Fickian diffusion of reactive species[13–16] and $\Gamma \sim t^{1/2}$ (see Figure 1a,b), where Γ is the interfacial excess of copolymer (sometimes referred to as Z^*[7,8]) and t is the real time of reaction. According to many theories,[13,14] late stage reactions are significantly hindered by the chemical potential of the brush that is forming,[17,18] with the time scales and coverage set by the onset of chain stretching[19] at $\Gamma_c \approx R$ (see Figure 1c,d), where Γ_c is the critical excess and R is the RMS end-to-end distance[20] of a reactive polymer chain.

Here we provide direct evidence of DC reactive coupling at an interface between highly immiscible polystyrene (PS) and poly(methyl methacrylate) (PMMA). Real-space depth profiles are generated for reactions conducted at relatively low temperatures with highly reactive functional groups using dynamic secondary ion mass spectrometry (DSIMS). DSIMS provides a significant improvement in depth resolution over previously employed depth profiling techniques such as forward recoil spectrometry (FRES).[9,21] The experimental profiles clearly reveal a depletion hole in the reactive polymer concentration profile, as depicted schematically in Figure 1b, with a subsequent disappearance of this gradient at long times (see Figure 1d).

Deuterated hydroxy-terminated PS (dPS-OH, M_w = 76.6 kDa, M_w/M_n = 1.05, >95% end-functionalized) and PS (M_w = 73.0kDa, M_w/M_n = 1.04) were purchased from Polymer Source and used as received. A random copolymer of methyl methacrylate and methacrylic acid (P(MMA-*co*-MAA), $M_w \approx$ 34 kDa, $M_w/M_n \approx$ 2.3) was purchased from Sigma-Aldrich. The monomer fraction of MAA was determined to be 1.2% using acid–base titration. The P(MMA-*co*-MAA) was dissolved in anhydrous toluene in a desiccated vial, and 50× molar excess of oxalyl chloride ($(COCl)_2$) was added to convert the carboxy groups of the MAA to highly reactive acyl chloride,[22] thereby resulting in a random copolymer of methyl methacrylate and methacryloyl chloride (P(MMA-*co*-MAC)). After allowing 24 h for complete conversion, the P(MMA-*co*-MAC) solution was cast onto hydrogen-passivated Si wafers. The samples were immediately annealed after spin-casting at 135 °C under vacuum for 30 min to remove all solvent, including excess $(COCl)_2$, yielding a 60 nm P(MMA-*co*-MAC) bottom layer, as determined by ellipsometry. On the basis of the diffusion coefficient of toluene in PMMA,[23] the $(COCl)_2$ is expected to be completely removed in $\ll$1 min. After annealing, a 150 nm top layer was immediately cast directly onto the P(MMA-*co*-MAC) layer from a solution of dPS-OH/PS (15% v/v) in anhydrous 1-chloropentane, which serves as a selective solvent for PS relative to PMMA.

In a desiccated vial 1 mL of anhydrous deuterated chloroform ($CDCl_3$) and an identical amount of $(COCl)_2$ used to convert the P(MMA-*co*-MAA) were added. After 24 h the solution was analyzed with nuclear magnetic resonance (NMR) spectroscopy. The ^{13}C NMR revealed significant $(COCl)_2$ present in the solution, demonstrating that water sensitivity was indeed minimized significantly. In another desiccated vial 50× excess of $(COCl)_2$ was added to a phenylacetic acid and $CDCl_3$ solution, which had been dried over molecular sieves. After 24 h, ^1H NMR revealed >80% conversion of the phenylacetic acid to phenylacetyl chloride. This carboxy group is known to be quite difficult to convert to an acyl chloride using $(COCl)_2$,[22] and as such, this technique should provide >80% conversion of MAA to MAC. The reactive bilayers will therefore have at least 40× molar excess of methacryloyl chloride groups relative to hydroxy end groups of the dPS-OH at the interface, and the observed reaction kinetics are dominated by the properties of the PS layer. Samples were annealed at a constant temperature to within ±0.2 °C using an Instec STC200 controlled hot stage after a nitrogen purge.

Depth profiles were generated using a CAMECA IMS-6F magnetic sector spectrometer using a 20 nA, 5.5 keV O_2^+ primary beam rastered over a 180 μm × 180 μm area with detection of positive secondary ions from a 60 μm diameter circle at the center. A 50 nm PS sacrificial layer was added to the surface of each sample after the reaction to ensure that uniform matrix secondary ion yield is achieved before sputtering through the PS layer, and a 20 nm gold film was deposited onto this sacrificial layer to reduce artifacts associated with charging of these insulators. The DSIMS conditions were optimized with consideration of signal-to-noise ratio, charging effects, depth resolution, and, most importantly, constant matrix species through the PS–PMMA interface. The deuterium signal was normalized to the carbon signal.

Relevant time scales for determination of the Damkohler number include the disentanglement time τ_d for the characteristic time of mass transfer[24]

$$\tau_M \equiv \tau_d = \frac{R^2}{3\pi^2 D} \sim N^3 \tag{2}$$

and for the characteristic reaction time, $\tau_R \equiv Q^{-1}$, where Q is the local or bare reactivity between two comple-

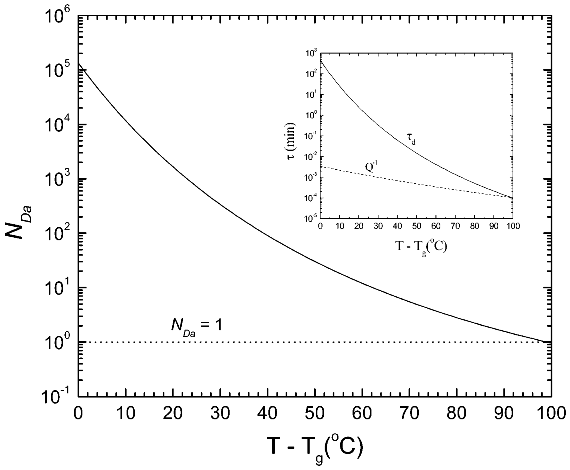

Figure 2. A plot of N_{Da} vs $(T - T_g)$, where T_g is the glass transition temperature of PS (104 °C). This was determined from eq 3 using the known diffusivities of 73 kDa PS[10] and reaction constants reported for ethanol and acetyl chloride[25] after conversion to a solvent free basis. From this "map" the DC and RC regimes can be predicted. The inset shows the characteristic reaction (Q^{-1}) and diffusion (τ_d) times.

mentary reactive groups.[12] This provides a simple expression for N_{Da} as a function of D and Q from eq 1:

$$N_{\mathrm{Da}} = \frac{R^2 Q}{3\pi^2 D} \sim N^3 \tag{3}$$

This is a molecular interpretation of N_{Da}, and it represents the ability of an entangled chain to provide a reactive group for chemical bonding relative to the intrinsic reactivity of a reaction pair.

The value of D for PS has been reported elsewhere as a function of molecular weight and temperature,[10] and Q is approximated from the reaction constants reported for ethanol and acetyl chloride[25] after conversion to a solvent free basis. According to the predictions of eq 3 presented in Figure 2, the system employed here should be strongly DC at temperatures <145 °C (N_{Da} > 100). To provide a sufficiently large range of experimentally accessible times in which to fully characterize the interfacial reactions using DSIMS, we have chosen 120 °C as our primary reaction temperature, with $N_{\mathrm{Da}} \approx 3500$. This temperature is 16 °C above the inflection point glass transition temperature (T_g) of the PS and dPS-OH and 3 °C above the T_g of the P(MMA-*co*-MAA), as determined by differential scanning calorimetry.

Figure 3 shows the concentration vs depth profiles for t = 0, 3, 6, 12, 24, and 100 h at 120 °C, with a depth resolution of ≈10 nm. At the reactive PS–PMMA interface, formation and growth of a depletion hole is readily apparent from 0 to 24 h as shown in Figure 3a–e, which is direct evidence of a DC reaction.[13,14] The peak arises due to the localization of copolymer molecules consisting of dPS grafted to the PMMA chain (PMMA-*g*-dPS), which resides at the interface because of enthalpic constraints. After 24 h of reaction (Figure 3e), the depletion hole has a width ~40 nm. This is approximately half the RMS diffusion length[4] ($\langle x^2\rangle^{1/2} = (2Dt)^{1/2} \simeq 70$ nm) for this annealing time and temperature. Although these two lengths cannot be compared directly due to the buildup of interfacial excess and the subtleties of the Fickian profile, they imply an effective diffusivity in our thin film systems somewhat lower than the bulk tracer diffusivity.[10] After 100 h of reaction at 120 °C shown in Figure 3f, the dPS-OH/PS layer approaches diffusion equilibrium, directly evident by the disappearance of the Fickian-type diffusion profile[26] (see Figure 1b,d) of the dPS-OH that at prior times was exhibited in Figure 3b–e. At this point, the further formation of copolymer would show an apparent RC-type behavior, although the reactivity of the complementary reactive groups has not changed.

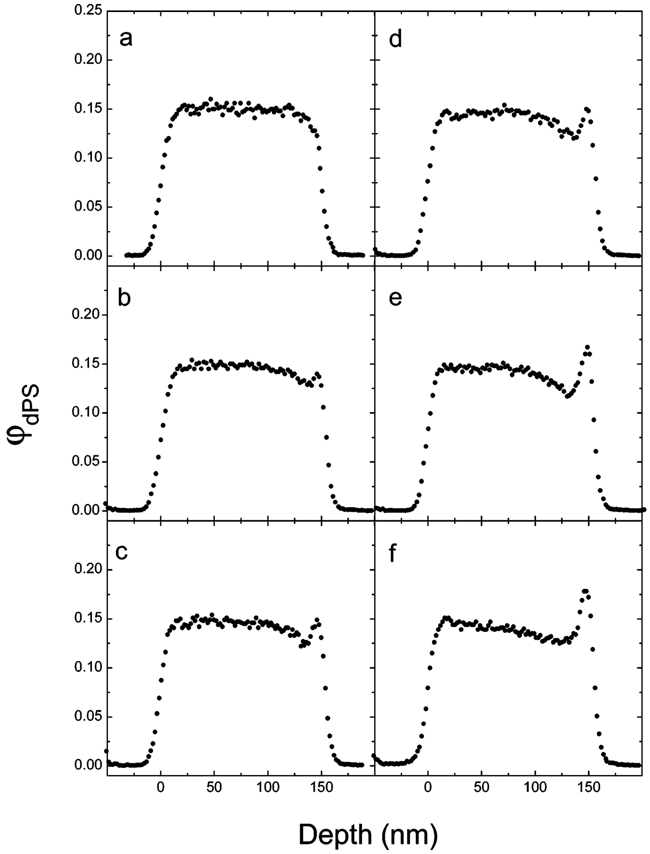

Figure 3. Real-space DSIMS depth profiles of the dPS volume fraction (φ_{dPS}), including both unreacted dPS-OH within the PS layer and PMMA-*g*-dPS located at the interface, are shown as a function of sample depth for (a) 0, (b) 3 h, (c) 6 h, (d) 12 h, (e) 24 h, and (f) 100 h at 120 °C. Profiles were generated using O_2^+ DSIMS with a depth resolution of ≈10 nm. Over a 24 h period, a Fickian-type profile[26] is observed with formation and subsequent growth of a depletion hole. Crossover to late stage is apparent after ≈100 h.

Interfacial reactive coupling was analyzed with the same system after 4 h at 140 °C, as shown in Figure 4. At this temperature the reaction is expected to be DC ($N_{\mathrm{Da}} \approx 150$), although characteristic diffusion times will increase ≈50× from 120 °C (i.e., 4 h reaction at 140 °C is equivalent to ≈ 200 h at 120 °C). Quantitation of copolymer coverage is straightforward once diffusion equilibrium is attained because no assumptions must be made regarding the diffusion profile or the ability of the interface to act as a truly perfect sink for mass transfer of reactive polymer.[26,27] The profile is fit to two Gaussian error functions to account for the convoluted dPS-OH profile and a superimposed Gaussian peak for the dPS block at the interface. The area under the Gaussian peak in Figure 4 yields $\Gamma = 0.083R$, which is significantly less than Γ_c ($\approx R$), yet the ester-forming condensation reaction is completely irreversible under the conditions implemented here.[25,28]

This low Γ observed for diffusive equilibrium suggests that complete saturation of the interface is not required

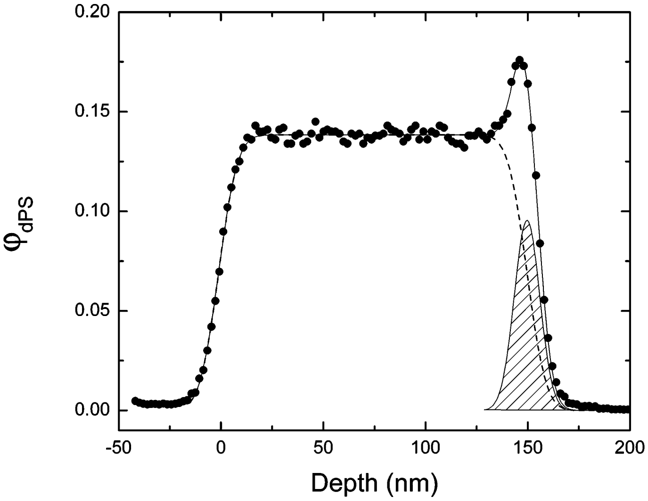

Figure 4. DSIMS depth profile after 4 h reaction at 140 °C. This shows the late stage as depicted in Figure 1d, with high coverage of copolymer at the interface and consequently no depletion hole. The profile has been fit to two Gaussian error functions for the convoluted dPS-OH profile and a superimposed Gaussian peak for the dPS in the PMMA-*g*-dPS copolymer at the interface. The crosshatched area represents the interfacial excess ($\Gamma = 0.083R$) of the dPS in the copolymer. This is far less than Γ_c ($\approx R$), which is required for chain stretching[19] as shown in Figure 1c.

to significantly hinder interfacial reactions in highly reactive systems, a conclusion that can be directly drawn from the disappearance of the depletion hole in the dPS depth profiles. This means that reactive coupling at polymer−polymer interfaces may not be governed simply by the intrinsic reactivity of the complementary reactive pairs, the bulk diffusivity, or the chemical potential of a brush forming at the interface. The low Γ directly translates into much shorter time scales than previously envisioned for the ideal case in which DC reactions become significantly hindered by a copolymer brush,[13,14] even though the bulk diffusivity and intrinsic reactivity remain unchanged during the course of the reaction. Because of these complexities, if the early stage is not included within the range of characterization times for DC reactions or a depletion hole cannot be resolved due to intrinsic limitations of the characterization technique,[9] then results can be interpreted as a simple RC mechanism. This makes the Damkohler number analysis a powerful tool for decoupling true RC and DC mechanisms from other interfacial phenomena.

We have provided direct evidence of DC reactive coupling at an immiscible polymer−polymer interface using high depth resolution real-space depth profiling and relatively low annealing temperatures. The location of the DC regime with respect to temperature, molecular weight, and reactive groups employed has been predicted using the dimensionless Damkohler number with independently determined parameters. The formation and growth of a depletion hole during early-stage DC reaction and subsequent remission of this depletion have been observed over the course of 100 h at 120 °C. In addition, the critical copolymer excess required to hinder reactive coupling[13−15] has been discerned. Quantitative characterization of DC reactive coupling at polymer−polymer interfaces is a prerequisite for the future development of theoretical formalisms that can provide fundamental insight and predictive capabilities into the mechanisms of reacting polymers within confined environments.

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References and Notes

(1) Pernot, H.; Baumert, M.; Court, F.; Leibler, L. *Nat. Mater.* **2002**, *1*, 54.
(2) Astarita, G. *Mass Transfer with Chemical Reaction*; Elsevier: New York, 1967.
(3) Rosner, D. E. *Transport Processes in Chemically Reacting Flow Systems*; Butterworth: Boston, 1986.
(4) de Gennes, P. G. *J. Chem. Phys.* **1982**, *76*, 3322.
(5) Durning, C.; O'Shaughnessy, B. *J. Chem. Phys.* **1988**, *88*, 7117.
(6) Fredrickson, G. H. *Phys. Rev. Lett.* **1996**, *76*, 3440.
(7) Jiao, J. B.; Kramer, E. J.; de Vos, S.; Moller, M.; Koning, C. *Macromolecules* **1999**, *32*, 6261.
(8) Schulze, J. S.; Cernohous, J. J.; Hirao, A.; Lodge, T. P.; Macosko, C. W. *Macromolecules* **2000**, *33*, 1191.
(9) Kramer, E. J. *Physica B* **1991**, *173*, 189.
(10) Antonietti, M.; Coutandin, J.; Sillescu, H. *Makromol. Chem. Rapid Commun.* **1984**, *5*, 525.
(11) Orr, C. A.; Cernohous, J. J.; Guegan, P.; Hirao, A.; Jeon, H. K.; Macosko, C. W. *Polymer* **2001**, *42*, 8171.
(12) O'Shaughnessy, B.; Sawhney, U. *Phys. Rev. Lett.* **1996**, *76*, 3444.
(13) O'Shaughnessy, B.; Vavylonis, D. *Macromolecules* **1999**, *32*, 1785.
(14) Fredrickson, G. H.; Milner, S. T. *Macromolecules* **1996**, *29*, 7386.
(15) Yeung, C.; Herrmann, K. A. *Macromolecules* **2003**, *36*, 229.
(16) Muller, M. *Macromolecules* **1997**, *30*, 6353.
(17) Milner, S. T. *Science* **1991**, *251*, 905.
(18) Shull, K. R. *J. Chem. Phys.* **1991**, *94*, 5723.
(19) de Gennes, P. G. *Macromolecules* **1980**, *13*, 1069.
(20) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(21) Schwarz, W. A.; Wilkens, B. J.; Pudensi, M. A. A.; Rafailovich, M. H.; Sokolov, J.; Zhao, X.; Zhao, W.; Zheng, X.; Russell, T. P.; Jones, R. A. L. *Mol. Phys.* **1992**, *76*, 937.
(22) Adams, R.; Ulich, L. H. *J. Am. Chem. Soc.* **1920**, *42*, 599.
(23) Arnould, D.; Laurence, R. L. *Ind. Eng. Chem. Res.* **1992**, *31*, 218.
(24) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford University Press: New York, 1986.
(25) Branch, G. E. K.; Nixon, A. C. *J. Am. Chem. Soc.* **1936**, *58*, 2499.
(26) Crank, J. *The Mathematics of Diffusion*, 2nd ed.; Oxford University Press: New York, 1975.
(27) Clarke, C. J.; Jones, R. A. L.; Clough, A. S. *Polymer* **1996**, *37*, 3813.
(28) Sonntag, N. O. V. *Chem. Rev.* **1953**, *52*, 237.

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