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Flow-Induced Reactive Self-Assembly

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Most polymer−polymer pairs are immiscible. However, if one polymer is properly dispersed within another, unique morphologies can be created with synergistic properties.[1] For example, sheets of a low permeability polymer can greatly increase the barrier performance of a layered composite,[2] while submicron size droplets of a rubbery phase can improve toughness 10-fold[3] in a glassy or semicrystalline plastic.

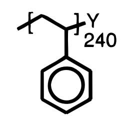
The key to these property improvements is creation and stabilization of the desired composite morphology. Intensive mixing as the polymers melt can create thin sheets, and subsequently fine droplets,[4] of the minor component. However, these small droplets rapidly coalesce since they are far from thermodynamic equilibrium.[4,5] The most successful strategy for stabilizing or compatibilizing these nonequilibrium structures is to fix complementary functional groups on the two polymers that can couple at the interfaces forming a graft or block copolymer during mixing.[6] This copolymer provides a physical barrier against coalescence[5,7−10] and also increases adhesion between the two phases, improving mechanical properties.[11,12]

In most previous studies and commercial processes graft or cross-linked copolymers were produced.[6] Such branched and network structures tend to inhibit interfacial deformation, thereby restricting further area generation. We have prepared polymer chains with a single functional group on just one end. These terminally functional polymers can only form diblock copolymers. With a moderate chemical reactivity these functional groups produce relatively fine, stable droplets[7] similar to results with reactively formed graft or cross-linked copolymers.[3,5,6,9,13] However, we have recently discovered that very fast reaction rates lead to coupling of *all* the reactive chains when the mixture is shear processed. The resulting block copolymer self-assembles into a nanostructured morphology.

Three different types of heterogeneous blends were studied in our experiments, each prepared with 70 wt % polystyrene (**I**) and 30 wt % of polyisoprene (**II**) (or polybutadiene). The first set of blends did not contain functional groups, while the second set involved a cyclic anhydride (**III**) attached to the polydiene,[14] reacting with a primary aromatic amine (**IV**) at the terminus of the polystyrene.[15] For the third set a primary aliphatic amine (**V**) was substituted for the aromatic amine of the second mixture.[16] The blends were prepared by shear mixing in the molten state.[17] The polydiene minor phase is expected to break up into droplets.[4,5]

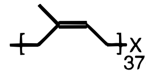
Conversion of the reaction was determined by gel permeation chromatography (GPC) using a UV detector sensitive only to the polystyrene as it eluted from the columns. Since the polymers were relatively monodisperse,[18] the amount of coupled chains could easily be distinguished and quantified.[7] Phenyl isocyanate was added to the samples before dissolving in THF to quench all remaining amino groups. This prevented further reaction in solution and prevented adsorption of the amino groups to the chromatographic columns.

(**I**)

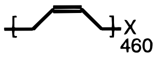


polystyrene
25,000 g/mol

(**II**)

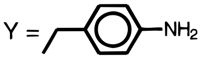


1,4-polyisoprene
25,000 g/mol



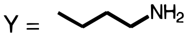
1,4-polybutadiene
25,000 g/mol

(**IV**)

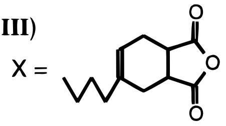


or

(**V**)



(**III**)



At high temperatures a primary amine reacts essentially irreversibly with a cyclic anhydride to produce a cyclic imide plus water.[19] The reaction of the aromatic amine with cyclic anhydride is relatively slow, while the reaction of the aliphatic amine is extremely fast compared to the blending process time scale. Comparative rates of reaction were measured by preparing *homogeneous* blends of reactive polystyrene containing the complementary functional groups in a stoichiometric ratio. The aromatic amine reaction reached a maximum conversion of 36% at 180 °C over the 20 min mixing time employed in these experiments. The aliphatic amine reaction reached essentially complete conversion to coupled chains in less than 1 min, i.e., when the first sample was removed from the mixer (see Figure 1a). Approximate rates of generation of block copolymer can be determined from the data in Figure 1a using the initial slopes. For the aromatic amine reaction we get

$$\frac{dC}{dt} \approx \frac{\Delta C}{\Delta t} = \frac{16\%}{120\ \mathrm{s}} \Rightarrow 1.3 \times 10^{-5}\ \frac{\mathrm{mol}}{\mathrm{L{\cdot}s}} \qquad (1)$$

and for the aliphatic amine

$$\frac{dC}{dt} \approx \frac{\Delta C}{\Delta t} > \frac{100\%}{60\ \mathrm{s}} \Rightarrow >1.7 \times 10^{-4}\ \frac{\mathrm{mol}}{\mathrm{L{\cdot}s}} \qquad (2)$$

The aliphatic amine reaction is possibly orders of magnitude faster since the reaction was virtually complete at the time of the first sampling. In the case of the aromatic amine, if the reaction had continued at this same initial rate it would require over 12 min to achieve complete conversion. Instead, the rate of reaction is seen to decrease as conversion proceeds.

Conversion measured in the *heterogeneous* polystyrene/polyisoprene blends is shown in Figure 1b; conversion in the polybutadiene blends was comparable. As in the homogeneous case the reaction of the aliphatic amine terminal polyisoprene is much faster than the aromatic amine. Polymer blend morphologies were analyzed by transmission electron microscopy (TEM).[20] TEM micrographs of the three different blends involving polyisoprene are shown in Figure 2. Nonreactive blends contained dispersed phase particles from 5 to 30 μm in diameter, and the polybutadiene blend (not shown) included some large cocontinuous regions. Blends

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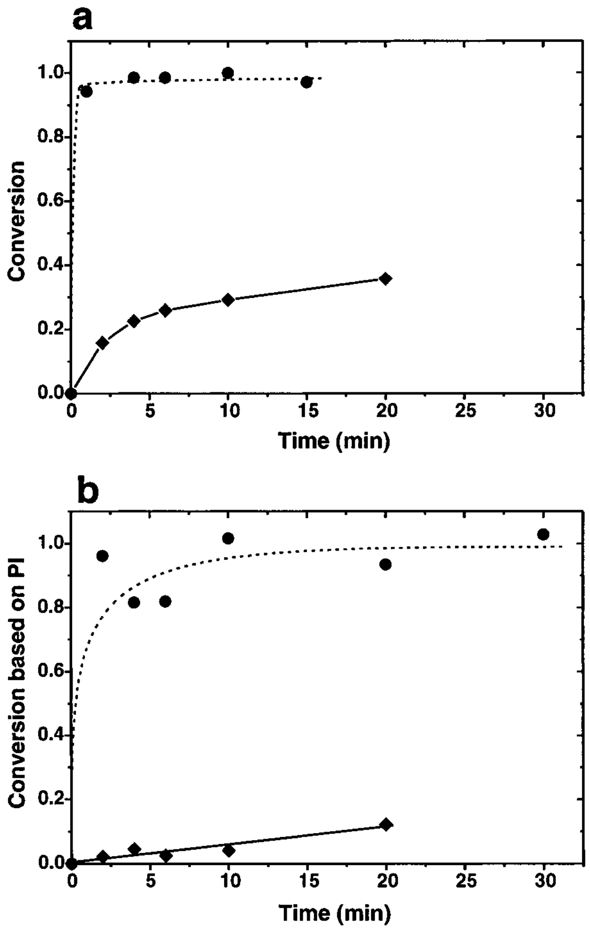

Figure 1. Representative conversion to diblock copolymer for aliphatic amine (●) and aromatic amine (◆) reactions conducted at 180 °C. (a) Homogeneous reactions of polystyrene (PS) containing a stoichiometric ratio of complementary functional groups. (b) Heterogeneous blends of 70 wt % polystyrene and 30% polyisoprene (PI) showing conversion based on the minor polyisoprene phase. Scatter in the data is attributed to the concentration inhomogeneities in the mixer when the sample was removed. The conversion acquired from the GPC technique is repeatable to ±0.5% for each sample but varies for different samples taken separately from the mixer.

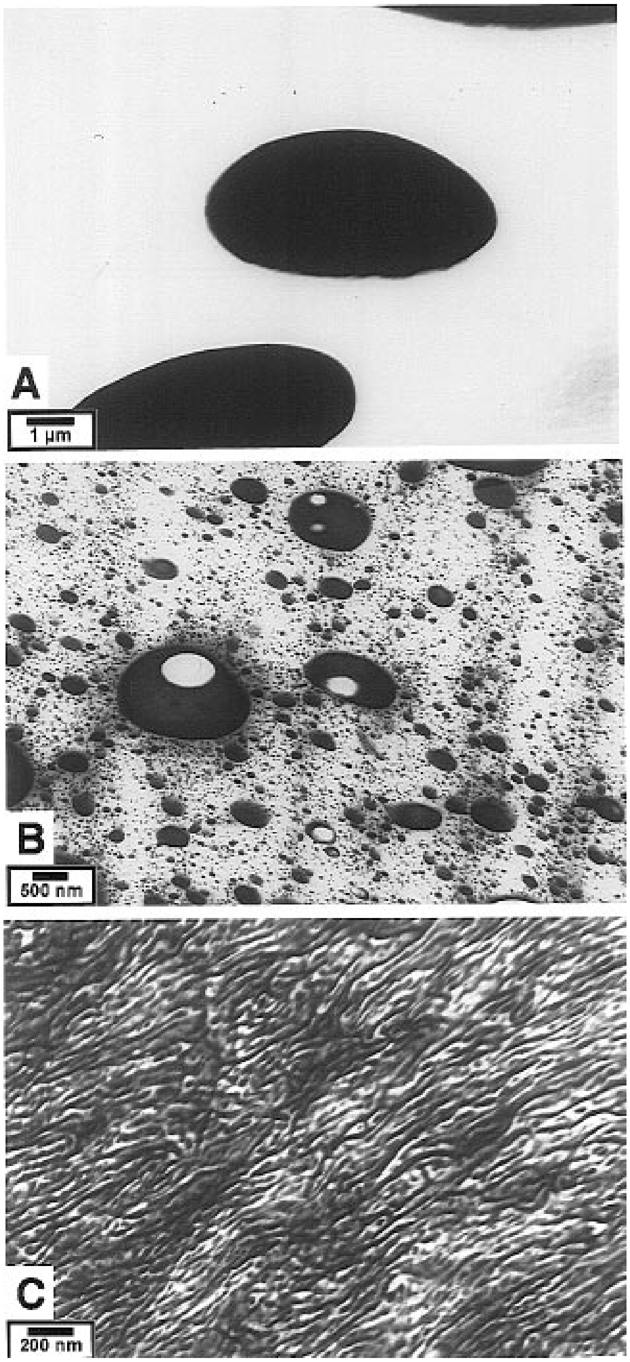

Figure 2. Representative transmission electron microscopy (TEM) images of the morphologies produced after mixing functionalized PS (70%) and PI (30%) at 180 °C for 20 min. (a) Blends with no functional groups. (b) Aromatic amine terminal PS with anhydride terminal PI. Particles range in size from 2 μm down to the limiting case of micelles. Inclusions of polystyrene are also seen in some large polyisoprene particles. (c) Aliphatic amine terminal PS with the same anhydride terminal PI. Even after 2 min of mixing a similar morphology was obtained from this very fast coupling reaction. TEM micrographs were obtained by staining ultrathin sections with OsO_4 vapor which selectively stains the PI.

containing the aromatic amine were composed of dispersed phase particles of 0.2−0.3 μm average diameter and ~5 vol % block copolymer, similar to what was obtained in prior work.[3,5,7,9,13] By image analysis of Figure 2b, about 2 vol % of block copolymer resides in spherical micelles. Blends made with the aliphatic amine showed complete conversion of the minor phase to diblock copolymer in 10 min or less (see Figure 1b). TEM micrographs (Figure 2c) taken after 20 min show a uniform morphology with molecular scale self-assembly into cylindrical micelles over the entire sample. Complete conversion of the minor phase to diblock corresponds to 60 wt % diblock and 40 wt % polystyrene homopolymer due to the stoichiometric excess of the latter. A TEM micrograph taken after 2 min and only 70% polyisoprene conversion (40 wt % diblock) shows similar molecular scale structures. The blends with the slower aromatic amine reaction did not show high conversions or molecular scale morphology even after 90 min of mixing.

The final diblock morphologies that we observe are essentially equilibrium structures. The polybutadiene blend assembled into spherical micelles, while the polyisoprene blend showed cylindrical micelles (Figure 2c). Here we note that the polystyrene phase is swollen with 40 wt % polystyrene homopolymer. A previous study of the phase diagram of polystyrene−polydiene diblocks with excess homopolymer polystyrene found similar results.[21] Our blends lie on their phase diagram at the estimated intersection between cylindrical micelles, disordered micelles, and phase separation. Samples taken from the mixer after 20 min were also solvent cast and then annealed for 30 min at 120 °C. TEM showed that the unreacted polystyrene separated into isolated domains and the remaining polymer displayed a random lamellar morphology, as anticipated for a neat symmetric diblock material. In the reactively assembled blends (Figure 2c) macroscopic ordering was not observed. This is probably due to the fact that these samples were quenched in a stressed state.

We can estimate whether diffusion of reactive groups to the interface limits the overall rate of coupling. Since nearly every chain has a terminal functional group, diffusion over approximately a radius-of-gyration (R_g) of the polymer chain is the longest distance required to be traversed by a chain end to reach the interface. For PS with $M = 25\,000$ g/mol, $R_g = 4.4$ nm, and the self-diffusion coefficient at 180 °C is $D_s \cong 2 \times 10^{-11}$ cm^2/s.[22] Applying Fick's law for whole chain motion over this distance yields a characteristic diffusion time of 1.6 ms, which is much faster than our experimental time of one or more minutes. This suggests that the rate of interfacial area generation rather than diffusion controls the evolution of block copolymer and morphology.

In going from PS and PI homopolymers to the ordered block copolymer a tremendous amount of interface is created. The minimum energy per unit volume required to create interfacial area in our PS–PI system can be roughly estimated from $\Gamma/R_g \cong 2 \times 10^5$ J/m^3, where $\Gamma \cong 1.0$ mN/m is the interfacial tension for PS–PI.[23] The energy input rate through viscous dissipation during mixing is about 10^5 J/(m^3 s) based on a viscosity of 100 Pa·s (for the polystyrene) and an average shear strain rate in the mixer $\bar{\dot{\gamma}} = 40$ s^{-1}. If all the mixing energy could be channeled into generating an interface, it would only take about 2 s of stirring to produce the microstructure shown in Figure 2c based on these estimated parameters. Therefore interface generation is not limited by energy input requirements.

Is the rate of reaction fast enough to cover the interface as fast as it is generated? The interfacial area per unit volume can be estimated by assuming cylinders of PI in PS. From TEM micrographs we estimate the average cylinder diameter at ~17 nm. This gives an interfacial area of 70 m^2/cm^3. Assuming all the interface is created in 2 min gives a rate of area generation

$$\frac{dA}{dt} \approx \frac{\Delta A}{\Delta t} = 600 \frac{\text{m}^2}{\text{L}\cdot\text{s}} \qquad (3)$$

Each PS–PI diblock occupies 6.25 nm^2 of the interface or $\Sigma = 0.16$ chain/nm^2.[24] Thus to cover the area requires that diblock be formed at a rate of

$$\frac{dC}{dt} \approx \frac{\Delta C}{\Delta t} = \Sigma\frac{\Delta A}{\Delta t} = 1.6 \times 10^{-4} \frac{\text{mol}}{\text{L}\cdot\text{s}} \qquad (4)$$

Comparing eq 2 we see the reaction is indeed fast enough.

Is the shear deformation in the mixer sufficient to generate the required interfacial area? Our cup-and-rotor type mixer is only capable of simple shear flow. Tadmor and Gogos[25] show that in simple shear flow of two liquids of matched viscosity with random orientation of the initial interfaces (A_o), and no interfacial effects, the change in interfacial area is half the accumulated strain

$$\frac{A}{A_o} = \frac{\gamma}{2} = \frac{\bar{\dot{\gamma}}t}{2} \qquad (5)$$

In our mixer we place all the polystyrene in a layer on top of the polyisoprene so the initial interfacial area per unit volume is about 1×10^{-4} m^2/cm^3. Applying eq 5 with the average shear rate of 40 s^{-1} for 2 min gives 0.48 m^2/cm^3. This result is less than 1% of the interfacial area needed to give the morphology observed in Figure 2c. Furthermore, eq 5 *over*estimates the area generation since the initial interfaces are almost parallel to the shear direction rather than randomly oriented. Thus there must be another mechanism than simple shear which contributes to area generation.

A theoretical treatment of such a reactive system has recently been published.[26] If the reaction is much faster than diffusion and there is no shear, the reaction rate is predicted to be exponentially depressed as the interface is saturated with copolymer. In our case, apparently, the external shear field does not allow saturation of the interface to slow the conversion rate. Shear studies on lamellar block copolymers show that they tend to rotate to align their interfaces with respect to the plane of the shear gradient.[27] This rotation generates more interface and may be the mechanism which leads to flow-induced reactive self-assembly. Recent experiments show that even quiescent reactive interfaces spontaneously fold and form micelles but extremely slowly.[28] We are pursuing such experiments as well as model flow studies[29] with these fast coupling polymers.

We have shown how employing a very fast coupling reaction can transform immiscible reactive homopolymers into diblock copolymer during reactive blending. With the extremely fast cyclic anhydride–aliphatic amine reaction reported here, molecular scale morphologies were observed in less than 2 min of mixing. To the best of our knowledge, this is the first example of flow-induced molecular ordering of reactive polymers. This method has potential to rapidly produce current self-assembled structures like pressure sensitive adhesives or new structures such as selective membranes.

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References and Notes

(1) Utracki, L. *Polymer Alloys and Blends*; Hanser: New York, 1989.
(2) Subramanian, P. M. *Polym. Eng. Sci.* **1985**, *25*, 483.
(3) Wu, S. *Polymer* **1985**, *26*, 1855.
(4) Scott, C. E.; Macosko, C. W. *Polym. Bull.* **1991**, *26*, 341. Sundararaj, U.; Macosko, C. W.; Rolando, R. J.; Chan, H. T. *Polym. Eng. Sci.* **1992**, *32*, 1814. Scott C. E.; Macosko, C. W. *Polymer* **1995**, *36*, 461. Sundararaj, U.; Macosko, C. W.; Nakayama, A.; Inoue, T. *Polym. Eng. Sci.* **1995**, *35*, 100. Sundararaj, U.; Dori, Y.; Macosko, C. W. *Polymer* **1995**, *36*, 1957. Levitt, L.; Macosko, C. W.; Pearson, S. D. *Polym. Eng. Sci.* **1996**, *36*, 1647.
(5) Sundararaj, U.; Macosko, C. W. *Macromolecules* **1995**, *28*, 2647.
(6) Brown, S. B. *Annu. Rev. Mater. Sci.* **1991**, *21*, 409. Liu, N. C.; Baker, W. E. *Adv. Polym. Technol.* **1992**, *11* (4), 249.
(7) Guégan, P.; Macosko, C. W.; Ishizone, T.; Hirao, A.; Nakahama, S. *Macromolecules* **1994**, *27*, 4993; Nakayama, A.; Inoue, T.; Hirao, A.; Guégan, P.; Khandpur, A. K.; Macosko, C. W. *Polym. Process. Soc. Proc.* **1996**, *12*, 179.
(8) Macosko, C. W.; Guégan, P.; Khandpur, A. K.; Nakayama, A.; Marechal, P.; Inoue, T. *Macromolecules* **1996**, *29*, 5590.
(9) Tan Beck, N. C.; Tai, S. K.; Briber, R. M. *Polymer* **1996**, *37*, 3509.
(10) Milner, S. T.; Xi, H *J. Rheol.* **1996**, *40*, 663.

(11) Norton, L. J.; Smigolova, V.; Pralle, M. U.; Hubenko, A.; Dai, K. H.; Kramer, E. J.; Hahn, S.; Berglund, C.; DeKoven, B. *Macromolecules* **1995**, *28*, 1999.
(12) Lee, Y.; Char, K. *Macromolecules* **1994**, *27*, 2603.
(13) Ide, F.; Hasegawa, A. *J. Polym. Sci.* **1974**, *18*, 963.
(14) Takenaka, K.; Hirao, A.; Nakahama, S. *Macromol. Chem. Phys.* **1995**, *196*, 1687.
(15) Dickstein, W. H.; Lillya, C. P. *Macromolecules* **1989**, *22*, 3882.
(16) Ueda, K.; Hirao, A.; Nakahama, S. *Macromolecules* **1990**, *23*, 939.
(17) Blends were made at 180 °C for 20 min in the MiniMAX mixer (Custom Scientific Instruments, Cedar Knolls, NJ). It is a cup-and-rotor type mixer with a 13 mm diameter. In all blends 90 mg of the liquid polydiene was first placed in the preheated cup; then 210 mg of polystyrene powder was added. The rotor was immediately lowered and turned at a speed of 280 rpm, providing a maximum shear rate of 80 s^{-1} at the outside of the cup. Periodically, the mixer was opened and a sample (~20 mg) was removed with tweezers and quenched in liquid nitrogen. A nitrogen blanket was kept on the mixer at all times to avoid degradation of the polydienes which contained 0.1−0.2 wt % Irganox 1010 as an antioxidant. Degradation was seen in GPC if either the nitrogen or antioxidant was omitted.
(18) All of the polymers were synthesized by anionic polymerization. The polydispersity (M_w/M_n) of all the polymers was less than 1.05. The polydienes contained 90−95% 1,4-addition.
(19) Padwa, A. R.; Sasaki, Y.; Wolske, K. A.; Macosko, C. W. *J. Polym. Sci., Polym. Chem. Ed.* **1995**, *33*, 2165. Chu, N.-J.; Huang, J.-W. *Polym. J.* **1990**, *22*, 725.
(20) Samples for transmission electron microscopy were microtomed to ~50 nm at −90 °C and then stained using OsO_4. TEM was performed using a JEOL JEM-1210 operated at 120 kV.
(21) Winey, K. I.; Thomas, E. L.; Fetters L. J. *Macromolecules* **1992**, *25*, 2645.
(22) Antonietti, M.; Coutandin, J.; Grütter, R.; Sillescu, H. *Macromolecules* **1984**, *17*, 798. Green, P. F.; Palmstrøm, C. J.; Mayer, J. W.; Kramer, E. J. *Macromolecules* **1985**, *18*, 501.
(23) Nam, K. H.; Cho, J. C.; Jo, W. H. *Polym. J.* **1995**, *27*, 904.
(24) Estimated from lamellar spacing of similarly sized pure PS−PI diblock. Khandpur, A. K.; Förster, S.; Bates, F. S.; Hamley, I. W.; Ryan, A. J.; Bras, W.; Almdal, K.; Mortensen, K. *Macromolecules* **1995**, *28*, 8796.
(25) Tadmor, Z.; Gogos, C. G. *Principles of Polymer Processing*; Wiley: New York, 1979; p 221.
(26) O'Shaughnessy, B.; Sawhney, U. *Phys. Rev. Lett.* **1996**, *76*, 3444.
(27) Koppi, K. A.; Tirrell, M.; Bates, F. S.; Almdal, K.; Colby, R. H. *J. Phys. II* **1992**, *2*, 1941. Patel, S. S.; Larson, R. G.; Winey, K. I.; Watanabe, H. *Macromolecules* **1995**, *28*, 4313. Gupta, V. K.; Krishnamoorti, R.; Chen, Z-R.; Kornfield, J. A.; Smith, S. D.; Satkowski, M. M.; Grothaus, J. T. *Macromolecules* **1996**, *29*, 875.
(28) Kressler, J. Personal communication, University of Freiburg. Kramer, E. J. Personal communication, Cornell University. Lu, S. Unpublished results, University of Minnesota.
(29) Levitt, L.; Pearson, S. D.; Macosko, C. W. *Polym. Eng. Sci.* **1996**, *36*, 1647.

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