

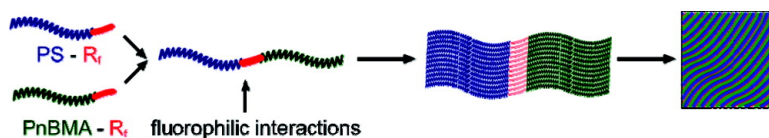
Communication

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## Block Copolymer-like Self-Assembly of Fluorocarbon End-Functionalized Polystyrene and Polybutylmethacrylate

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Polymer blending is a potentially effective method to design materials with desirable combinations of homopolymer properties. However, most polymer pairs are immiscible and separate into macrophases. One solution to this problem is to add compatibilizers such as the corresponding block or graft copolymers.<sup>1</sup> An alternative approach is to endow the homopolymers with functionalities allowing attractive enthalpic interpolymer interactions such as hydrogen bonding,<sup>2</sup> acid–base,<sup>3</sup> charge-transfer,<sup>4</sup> ion-dipole,<sup>5</sup> donor–acceptor adducts,<sup>6</sup> and transitional metal complexes<sup>7</sup> to stabilize the interfaces between immiscible phases.

It has been shown that perfluorocarbon chains exhibit hydrophobic or fluorophilic/solvophobic interactions.<sup>8–15</sup> We reasoned that such interactions could facilitate the phase behavior of polymer blends through the self-assembly of perfluorocarbon ( $R_F$ ) groups.

Here, we report that 1/1 (w/w) blending of 1,1-dihydro-perfluorooctyl (HPFO) end-capped polystyrene (HPFO-PS) and the corresponding HPFO end-capped polybutylmethacrylate (HPFO-PBMA) gives rise to the formation of block copolymer-like lamellar structures as shown by transmission electron microscopy (TEM) and several other characterization methods.

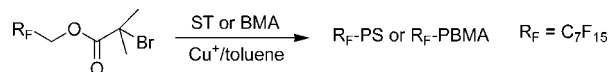
Relatively narrow molecular weight (MW) distribution HPFO end-capped polymers were synthesized by a 1,1-dihydro-perfluorooctyl-2-bromoisobutyrate initiated atom transfer radical polymerization (ATRP) (Scheme 1) and were characterized by size exclusion chromatography (SEC) and <sup>1</sup>H, <sup>19</sup>F NMR.<sup>16</sup> The corresponding nonfunctionalized polymers of comparable molecular weights and polydispersities were prepared similarly by ATRP (Table 1).

Thin films of the 1/1 (w/w) blends of HPFO-PS/HPFO-PBMA and conventional PS/PBMA were cast from their toluene solutions onto glass surfaces and subsequently dried and annealed in vacuo for 24 h at 423 K, well above the glass transition temperatures ( $T_g$ ) of PS and PBMA (373 and 293 K, respectively). As illustrated in Figure 1a,b, the film of the 1/1 (w/w) blended HPFO end-functionalized polymers was essentially transparent above 340 nm, while that of the corresponding homopolymers was opaque below 1000 nm.

The  $T_g$ 's of the HPFO-PS/HPFO-PBMA 1/1 blend measured by DSC are 371 and 301 K, respectively, indicating retention of the PS and PBMA domains. The gap between the two  $T_g$ 's is slightly smaller than that for the conventional PS/PBMA blend, consistent with improved miscibility as shown for many block copolymers with multiphase morphologies.<sup>18</sup> The domain retention and the transparency of films of the 1/1 blends above 340 nm (Figure 1b) suggests the formation of much smaller nanosized domains (see below).

It is interesting to note that, for the case of PS and PBMA functionalized with multiple hydrogen-bonding pendent groups, Zimmerman and co-workers have shown PS-PBMA blending at

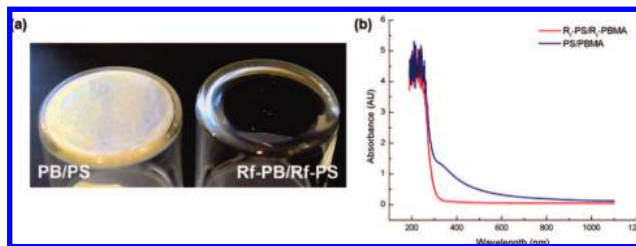
**Scheme 1.** Synthesis of Perfluorocarbon End-Functionalized Polystyrene and Polybutylmethacrylate



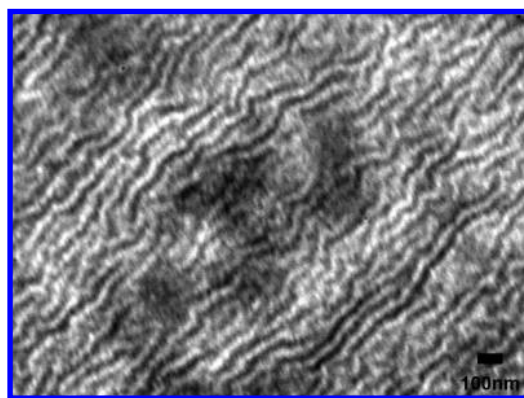
**Table 1.** Physical Properties of Polymer Blend Components

polymer	$M_n \times 10^{-3a}$	PDI	surface tension (dyn/cm) <sup>b</sup>	glass transition $T_g$ (K)
$R_F$ -PS	20.5	1.21		373
$R_F$ -PBMA	21.4	1.10		293
PS	17.9	1.12	40.7	373
PBMA	18.3	1.26	31.2	293

<sup>a</sup> SEC value calibrated against PS standard samples. <sup>b</sup> See ref 17



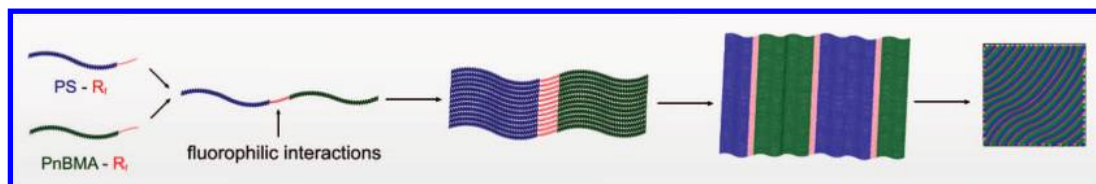
**Figure 1.** (a) Photograph of (1/1, w/w)  $R_F$ -PS and  $R_F$ -PBMA and PS/PBMA blend films prepared by slow solvent evaporation from toluene solution. (b) Absorbance profiles of the films measured by UV/vis.



**Figure 2.** TEM images of a 1/1 (w/w) blend of HPFO-PS and HPFO-PBMA. PS domains are dark as being stained by  $RuO_4$ .

the molecular level.<sup>2</sup> Thus, in that case, separate glass transition temperatures were not seen.

Unlike the blends of the unmodified PS and PBMA that show a typical two-phase disordered morphology on the micrometer scale, transmission electron microscopy (TEM) images of the blend of the HPFO end-capped polymers show lamellae having lengths between 0.4 and 1.0  $\mu$ m and widths of 30–40 nm (Figure 2).

**Scheme 2.** Proposed Fluorophilic Association of HPFO-PA and HPFO-PBMA

Remarkably, the dramatic changes we see are due to very small fractions of the  $R_F$  groups ( $\sim 2$  wt %). The lamellae are not all evenly aligned with the cross-section plane so that the longer range order is limited. For instance, PS-PBMA block copolymer shows much greater long-range ordering ( $> 10 \mu\text{m}$ ).<sup>19</sup> The lamellar widths are consistent with the absorbance data and roughly agree with the length scales one would expect from the self-assembly mediated through the formation of perfluorocarbon micellar structures at the blend interfaces as illustrated in Scheme 2.

Likewise, in contrast to films of conventional PS/PBMA blends that show not discernible order, the surface topography obtained by tapping mode atomic force microscopy (AFM) of the above 1/1 HPFO-PS/HPFO-PBMA blend in some cases shows more or less evenly distributed circular domains having central “craters” of about 20 nm in depth and about 100 nm in diameter and would seem to be consistent with the TEM data (Supporting Information, Figures S1).

Recent theoretical work has addressed the self-assembly of binary (A/B) polymer melts.<sup>20,21</sup> For instance, Feng et al. calculate the phase diagrams due to self-assembly of such a blend formed through a reversible enthalpy-driven association of A and B polymers.<sup>20</sup> In this case, the Flory interaction parameter,  $\chi$ , is included as one of the key parameters. Although our results appear to be consistent with that theory, it may not be fully applicable to our case as the interfacial interaction of the two polymer domains (Scheme 2) is mediated by the presence of  $R_F$  micelles, and this should affect enthalpy and hence  $\chi$ .

In order to obtain a more comprehensive picture of the phase behaviors of the above  $R_F$  polymer blends at greater length scales, an investigation using small-angle X-ray and/or neutron scattering is clearly needed and is currently underway. Furthermore, the effects on phase behavior of the homopolymer sizes and structures (interaction parameters), perfluorocarbon lengths, temperature, and other variables are essential to explore this type of polymer self-assembly. Preliminary data on other polymer blends having  $R_F$  end groups show similar results, indicating that our results extrapolate to analogous systems.

In conclusion, the formation is described of optically transparent PS/PBMA blends due to the presence of relatively small perfluorocarbon end groups. The TEM images show a morphology that resembles that of the corresponding PS-PBMA block copolymers, but the lamellar ordering is less pronounced.

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**Supporting Information Available:** Synthesis and AFM, TEM characterization details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) Utracki, L. A. *Polymer Blends Handbook*; Kluwer Academic: Boston, 2002.
- (2) (a) Park, T.; Zimmerman, S. C. *J. Am. Chem. Soc.* **2006**, *128*, 11582–11590. (b) Park, T.; Zimmerman, S. C.; Nakashima, S. *J. Am. Chem. Soc.* **2005**, *127*, 6520–6521.
- (3) (a) Feng, Y.; Weiss, R. A.; Han, C. C. *Macromolecules* **1996**, *29*, 3925–3930. (b) Goh, S. H.; Lee, S. Y.; Dai, J.; Tan, K. L. *Polymer* **1996**, *37*, 5305–5308.
- (4) Piton, M. C.; Natansohn, A. *Macromolecules* **1995**, *28*, 1605–1608.
- (5) Kim, J.; Kim, S. S.; Kim, K. H.; Jin, Y. H.; Hong, S. M.; Hwang, S. S.; Cho, B.; Shin, D. Y.; Im, S. S. *Polymer* **2004**, *45*, 3527–3533.
- (6) Cowie, J. M. G.; Demaude, A. *Polym. Adv. Technol.* **1994**, *5*, 178–183.
- (7) Das, P. K.; Lee, J.; Belliore, L. A. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 677–688.
- (8) Percec, V.; Dulcey, A. E.; Balagurusamy, V. S. K.; Miura, Y.; Smidrak, J.; Peterca, M.; Nummelin, S.; Edlund, U.; Hudson, S. D.; Heiney, P. A.; Duan, H.; Magonov, S. N.; Vinogradov, S. A. *Nature* **2004**, *430*, 764–768, and references therein.
- (9) (a) Zhang, H.; Pan, J.; Hogen-Esch, T. E. *Macromolecules* **1998**, *31*, 2815. (b) Zhang, Y.-X.; Da, A.-H.; Butler, G. B.; Hogen-Esch, T. E. *J. Polym. Sci., Polym. Lett.* **1990**, *28*, 213.
- (10) Hillmyer, M. A.; Lodge, T. P. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1.
- (11) Gladysz, J. A.; Curran, D. P.; Horváth, I. T. *Handbook of Fluorous Chemistry*; Wiley-VCH: Weinheim, Germany, 2004.
- (12) Zhang, G.; Marie, P.; Maaloum, M.; Muller, P.; Benoit, N.; Krafft, M. P. *J. Am. Chem. Soc.* **2005**, *127*, 10412–10419.
- (13) (a) Horváth, I. T.; Rábai, J. *Science* **1994**, *266*, 72–75. (b) Horváth, I. T. *Acc. Chem. Rev.* **1998**, *31*, 641–650.
- (14) Sato, S.; Iida, J.; Suzuki, K.; Kawano, M.; Ozeki, T.; Fujita, M. *Science* **2006**, *313*, 1273–1276.
- (15) (a) Da, J.; Hogen-Esch, T. E. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *42*, 360–373. (b) Da, J.; Hogen-Esch, T. E. *Macromolecules* **2003**, *36*, 9559–9563.
- (16) (a) Perrier, S.; Jackson, S. G.; Haddleton, D. M.; Ameduri, B.; Boutevin, B. *Macromolecules* **2003**, *36*, 9042–9049. (b) Perrier, S.; Jackson, S. G.; Haddleton, D. M.; Ameduri, B.; Boutevin, B. *Tetrahedron* **2002**, *58*, 4053–4059.
- (17) Brandrup, J.; Immergut, E. H.; Grulke, E. A. *Polymer Handbook*, 4th ed.; John Wiley & Sons: New York, 1999.
- (18) Wunderlich, B. *Thermal Analysis of Polymeric Materials*; Springer: New York, 2005.
- (19) Arnold, M.; Hofmann, S.; Weidisch, R.; Michler, G.; Neubauer, A.; Poser, S. *Macromol. Chem. Phys.* **1998**, *199*, 31–38.
- (20) Feng, E. H.; Lee, W. B.; Fredrickson, G. H. *Macromolecules* **2007**, *40*, 693–702.
- (21) (a) Anthamatten, M. *J. Polym. Sci., Part B: Polym. Phys.* **2007**, *45*, 3285–3299. (b) Lee, W. B.; Elliott, R.; Katsov, K.; Fredrickson, G. H. *Macromolecules* **2007**, *40*, 8445–8454.

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