



Blends of polystyrene and poly(n-butyl methacrylate) mediated by perfluorocarbon end groups

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Abstract: Structurally well-defined C₄F₉, C₇F₁₅, C₁₀F₂₁ and C₁₃F₂₇ end-functionalized polystyrene (RF-PS) and polybutylmethacrylate (RF-PBMA) were prepared by Atom Transfer Radical Polymerization using RF-tagged initiators. Blends (1/1 wt/wt) of these polymers were studied by differential scanning calorimetry (DSC), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), optical transmittance(OT), electron microscopy (TEM) and optical transmittance (OT). The RF-PS/RF-PBMA blends having molecular weights of 20,000 and C₇F₁₅ or larger end groups, were optically transparent. The AFM micrographs show crater, necklace and other RF mediated morphologies typically at the submicron scale. TEM images of the corresponding blends show assembly of elongated domains with sizes in the micron or nanometer scales depending on MW and RF size. Thus, above about 3 wt percent RF content only microphases (m) are observed while below 1.8 wt percent only macrophases (M) are seen. A semi-quantitative “phase diagram” of the blends shows that lower MWs and longer RF groups improve phase compatibilities.

Key words: Polymer blend, Perfluorocarbon, Self-assembly

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1. Introduction

Polymer blends have been of great interest for many years as these allow the development of materials with properties that combine desirable features of the homopolymer components. Moreover, blend properties can be adjusted easily through compositional variation. However, most polymers do not mix readily and undergo phase separation. This has been shown to be due to negligible increases in the entropies of mixing so that polymer blends tend to be stable if mixing is exothermic [1]. Hence, in the absence of enthalpic bonding between the polymer components, the free energy of mixing is typically positive. Numerous attempts have been made to cope with this problem including the use of compatibilizers such as block [2] and graft copolymers [3], and the introduction of functional groups designed to allow non-covalent inter-polymer bonding using hydrogen bonding, dipole–dipole and π – π interactions [4-7].

It is well known that perfluorocarbons (RFs) have both hydrophobic as well as lipophobic/oleophobic properties. Because of the reduced polarizability of fluorine, the highly electronegative RF groups exhibit relatively weak but size dependent intermolecular interactions that tend to show strong solvophobicity [8-19]. Due to their unique properties that differ greatly from their hydrogenated counterparts, including good chemical and thermal stability, low friction coefficients, biocompatibility, low surface free energies, and non-adhesive properties, fluorinated polymers have received considerable attention [10-23]. For aqueous systems, unusually strong interpolymer hydrophobic association has been shown for polymers with C_8F_{17} pendent groups [22-23]. Fluorophilic association in organic media has been demonstrated for low molecular weight (MW) compounds with high perfluorocarbon contents [15,24-26]. Strong fluorophilic association

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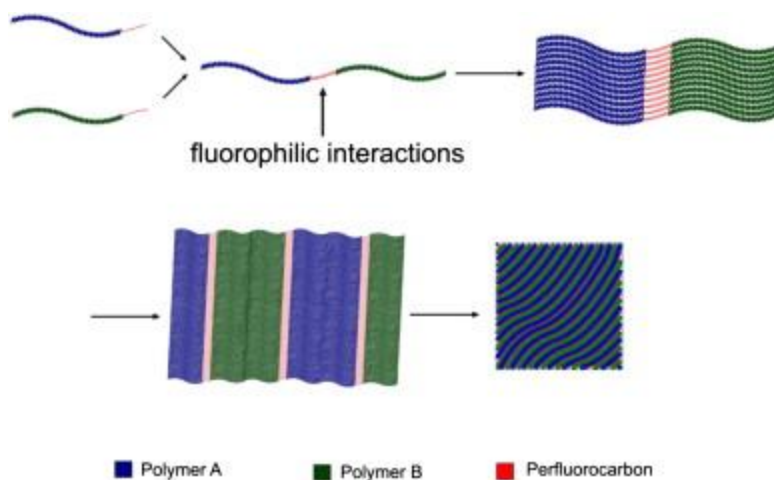
was also demonstrated of polydimethylacrylamide having RF pendent groups attached through polyethyleneglycol (PEG) spacers in organic (dioxane) as well as aqueous media [17-18]. This association was shown to be strongly PEG length dependent. More recently, the simultaneous compartmentalization of hydrocarbon, fluorocarbon and hydrophilic domains has been reported by several groups [27-31]. The importance of self assembly at the surface or in the bulk driven in part by solvophobic and mesogenic interactions of polymer bound RF groups is well established. [32-40]

We have recently reported the formation of 1/1(w/w) compatible blends of C₈F₁₇ end-functionalized polystyrene (RF-PS) and the corresponding poly(n-butylmethacrylate) (RF-PBMA) which appears to have been a first example of binary blends of this type (Scheme 1.) [41] The choice of PS and PBMA as blend polymers is based in part on their moderate incompatibility and their differing glass transition temperatures (T_g's) that allow the use of differential scanning calorimetry (DSC) analysis. The synthesis of such polymers using RF-containing ATRP type initiators is straightforward and has the advantage of placing the RF groups at well-defined terminal positions. Atomic force microscopy (AFM) and transmission electron microscopy (TEM) of 1/1 (w/w) blends of 1,1-dihydroperfluorooctyl end-functionalized PS and PBMA having MWs of about 20,000 indicate the presence of elongated domains with widths (*d*) and lengths (*l*) of less than about 10–20 nm and 200 nm respectively, much smaller than the sizes of the corresponding blend of the unmodified polymers. Homopolymer properties such as T_g's are retained in this blend, consistent with the presence of distinct PS or PBMA domains. These blends were completely transparent above 300 nm in wavelength, unlike that of the unfunctionalized polymers that are opaque. Analogous PS-PBMA

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blends have been reported in which self assembly occurs through end groups capable of forming multiple H-bonds [4-5].



Scheme 1: Schematic drawings of polymer self-assembly promoted by FI.

For conventional binary polymer blends, phase behavior is characterized semi-quantitatively by MW, the Flory-Huggins (F–H) interaction parameter, χ , volume fraction, and other factors. This approach is not strictly valid for the above blends where the RF end- or pendent groups mediate increased compatibility. Computational studies based on modified F–H theory have been reported but these do not necessarily apply to blends of this type (see below) [42-43].

In the following, we describe the synthesis of C₄F₉, C₇F₁₅, C₁₀F₉ and C₁₃F₂₇ end-functionalized PS and -PBMA with MWs between about 7000 and 30,000 (7-30k). We report the characterization of 1/1(w/w) blends of these polymers by AFM, XPS TEM, DSC, X-ray photoelectron spectroscopy (XPS) and optical transmittance (OT). Many of the blends are highly compatible and give highly variable RF size and MW dependent, but thermally stable, morphologies that appear to be unprecedented. Most blends retain the properties (e.g. T_g values) of their polymer components. Generally, domain sizes decrease with increasing RF size and decreasing MWs with miscible blends

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being formed at RF contents above between about 1.8 and 3.0 wt percent. For the case of blends with lower MW's (<15 k) and large end groups (i.e. C₁₃F₂₇) truly homogeneous blends with single T_g's could be obtained. We show generally good consistency between the bulk (TEM, DSC, and OT) and surface properties (AFM and XPS).

2. Experimental

2.1 Materials and reagents

All chemicals were purchased from Aldrich and used as received unless otherwise noted. Copper (I) Bromide (99.999%) was purified by stirring in acetic acid. After filtration, it was washed with 2-propanol and then dried in vacuum. Styrene (S) and n-butyl methacrylate (BMA) were freshly distilled after being stirred over CaH₂ overnight. Fluorinated alcohols for the synthesis of initiators were purchased from SynQuest Labs, Inc. Ligand N-(n-pentyl)-2-pyridylmethanimine (NPMA) was synthesized according to a published procedure [44]. Silica wafers for AFM studies (University Wafer, P/100 Prime Grade) were first sonicated in a detergent solution for 5 min, and then rinsed successively with deionized water and acetone, before being blow-dried.

2.1.1 Initiator synthesis

ATRP initiators with the structure 1H,1H,2H,2H-perfluoroalkyl-2-bromoisobutyrate (PFDHI) were prepared via esterification of RFCH₂CH₂OH with 2-bromoisobutyryl bromide. [44] and [45] In a typical procedure 1H,1H,2H,2H-perfluorodecanol (2 g, 4.3 mmol) and 4-(dimethylamino)-pyridine (24.4 mg, 0.2 mmol) were suspended in anhydrous toluene (10 mL). The mixture was heated and

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stirred until the fluorinated alcohol dissolved. Triethylamine (0.767 mL, 5.5 mmol) and 2-bromoisobutyryl bromide (0.68 mL, 5.5 mmol) were added slowly and the suspension was stirred at room temperature for 8 h. The suspension was filtered and toluene was removed by rotary evaporation. The waxy solids were dissolved in dichloromethane and washed extensively with saturated NaHCO₃ and distilled water. The product was dried over MgSO₄ and dichloromethane was removed by rotary evaporation to leave a pale yellow gelatinous solid. Yield = 71%, ¹H NMR (CDCl₃) δ (ppm from TMS) = 4.45 (t, 2H, *J* = 6.03 Hz), 2.49 (tt, 2H, *J*₁ = 6.03 Hz, *J*₂ = 18.1 Hz), 1.90 (s, 6H); ¹³C NMR (CDCl₃) δ (ppm from TMS) 171.6, 121–107 (heavily split CF signals), 58, 55, 30.5 (t), 30.7; ¹⁹F NMR (CDCl₃) δ (ppm from TMS) –81.4(3F, CF₃), –114.1(2F, CF₂), –122.3(4F, 2 × CF₂), –122.5(2F, CF₂), –123.3(2F, CF₂), –124.2(2F, CF₂), –126.7(2F, CF₂).

2.21H,1H,2H,2H-perfluorohexyl-2-bromoisobutyrate

Colorless liquid. ¹H NMR (CDCl₃, 298 K, 300 MHz) δ (ppm from TMS) = 4.45 (t, 2H, *J* = 6.03 Hz), 2.49 (tt, 2H, *J*₁ = 6.03 Hz, *J*₂ = 18.1 Hz), 1.90 (s, 6H); ¹⁹F NMR (CDCl₃, 298 K, 282.2 MHz) δ (ppm from TMS) –81.5 (3F, CF₃), –115.2 (2F, CF₂), –124.9 (2F, CF₂), –126.5 (2F, CF₂).

2.31 H,1H-perfluorooctyl-2-bromoisobutyrate

Colorless liquid. ¹H NMR (CDCl₃, 298 K, 300 MHz) δ (ppm from TMS) = 4.45 (s, 2H), 1.90 (s, 6H); ¹⁹F NMR (CDCl₃, 298 K, 282.2 MHz) δ (ppm from TMS) –81.5(3F, CF₃), –114.2(2F, CF₂), –122.3(2F, CF₂), –122.5(2F, CF₂), –123.3(2F, CF₂), –124.2(2F, CF₂), –126.7(2F, CF₂).

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2.41 H,1H,2H,2H-perfluorododecyl-2-bromoisobutyrate

White powder. ^1H NMR (CDCl_3 , 298 K, 300 MHz) δ (ppm from TMS) = 4.45 (t, 2H, $J = 6.03$ Hz), 2.49 (tt, 2H, $J_1 = 6.03$ Hz, $J_2 = 18.1$ Hz), 1.90 (s, 6H); ^{19}F NMR (CDCl_3 , 298 K, 282.2 MHz) δ (ppm from TMS) -81.5 (3F, CF_3), -120.2 (2F, CF_2), -122.5 (6F, $2 \times \text{CF}_2$), -122.7 (4F, $2 \times \text{CF}_2$), -123.5 (2F, CF_2), -124.0 (2F, CF_2), -126.9 (2F, CF_2).

2.5 1H,1H-perfluorotetradecyl-2-bromoisobutyrate

White powder. ^1H NMR (CDCl_3 , 298 K, 300 MHz) δ (ppm from TMS) = 4.45 (s, 2H), 1.90 (s, 6H); ^{19}F NMR (CDCl_3 , 298 K, 282.2 MHz) δ (ppm from TMS) -81.5 (3F, CF_3), -120.1 (2F, CF_2), -122.4 (12F, $6 \times \text{CF}_2$), -122.7 (4F, $2 \times \text{CF}_2$), -123.5 (2F, CF_2), -124.0 (2F, CF_2), -126.9 (2F, CF_2).

2.6 RF-end-functionalized PS and PBMA

These were prepared by ATRP using [Initiator]:[CuBr]:[Ligand] ratios of 1:1:2. Most samples were synthesized using 2,2'-bipyridyl (BPy) as a ligand. No significant difference in the polymerization rate or product yield was detected, when BPy was replaced with N-(n-pentyl)-2-pyridylmethanimine (NPMA). In a typical example, a 25 mL Schlenk flask was charged with 52.2 mg (0.364 mmol) CuBr and then degassed and refilled with argon three times. Varying amounts of distilled monomer and 113.58 mg of BPy (0.728 mmol) (or 128.3 mg of NPMA) were added to the flask. The system was then evacuated and refilled with argon three times. Then 10 mL pre-deoxygenated toluene was injected and the solution was stirred for 10 min to form the Cu(I)-Ligand complex. The flask was then immersed in an oil bath at 110 °C and the polymerization was initiated by the injection of

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200 mg (0.364 mmol) of the undiluted initiators. After 8 h, the reaction mixture was opened to air and cooled down to room temperature, diluted with THF and passed through a neutral activated aluminum oxide column to remove the copper catalysts. The polymer was then precipitated in a large excess of methanol, characterized by SEC and dried in a vacuum oven at 25 °C to a constant mass. Monomer conversions are typically less than quantitative in order to preserve acceptable MW distributions [46-47].

2.6.1 Sample preparation

AFM thin film samples were prepared by spin coating a filtered (0.5 µm Teflon filter) toluene PS/PBMA blend solution of a certain concentration (depending on the desired thickness of the film) onto cleaned silica wafers (about 0.5 × 0.5 in. square), 4500 rpm for 60 s followed by annealing at 120 °C for 3 h in vacuum ($\sim 10^{-5}$ Torr).

Samples for optical studies were prepared by drop casting 2 g/L toluene solutions of the 1/1 (wt/wt) polymer blends onto cleaned cover glass. The thickness of the films was assumed to be the same (about 2 µm) as that on silica wafers prepared in the same fashion (measured by ellipsometry). The XPS samples were prepared by spin coating 2 wt % toluene 1/1 (w/w) solutions onto cleaned silica wafers (0.5 × 0.5 in.) at 3000 rpm for 60 s, followed by annealing for 24 h at 120 °C. The resulting films had a thickness of approximately 100 nm, determined by ellipsometry. TEM samples of less than 120 nm in thickness were obtained by one of the following methods: (a) solution-casting of 0.1wt % toluene solutions of the 1/1 (w/w) blend onto carbon-coated copper grids. (b) ultramicrotomy of a bulk blend solid sample sandwiched between two blocks of cured epoxy resin. (c) spin-coating of a 1wt percent toluene blend solution onto freshly cleaved sodium chloride crystal

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surface, that is subsequently dissolved in water allowing the resulting polymer film to be collected on copper grids. Heavy element staining was performed by exposing thin specimens to vapor of a 0.5% RuO₄ water solution (Electron Microscopy Sciences). Samples for DSC measurements were prepared by allowing toluene solutions of the polymer blends 5 wt% 1/1 (wt/wt) to evaporate. The remaining solid was dried in a vacuum oven at 120 °C for 24 h weighed, transferred to aluminum pans covered with lids and crimped. The T_g's were measured in the second heating ramp at 10 °C per minute.

2.7 Characterization

Size Exclusion Chromatography (SEC) was performed on a HPLC system (consisting of a Waters 510 HPLC pump, a Waters UK6 injector, Polymer Laboratories PLgel, 5 μm MIXED-C column × 2, a 410 RI detector and a 484 UV absorbance detector), at ambient temperature, using THF (EMD, HPLC grade) as the elution solvent with a flow rate of 1 ml/min. Polystyrene or poly methyl methacrylate standards were used for calibration. Proton and ¹³C NMR spectra were recorded on a FT-NMR (Bruker model AM-300 MHz). Fluorine-19 NMR spectra were recorded on a FT-NMR (Varian Mercury 400 MHz). Polymer blend thin films were prepared with a P-6712 spin coater (Specialty Coating Systems). Film thickness was assumed to be the same for samples prepared in identical conditions and was measured by ellipsometry (Gaertner L116SF). Glass transition temperature measurements were carried out with DSC instruments (Shimadzu DSC 50 and TA Instruments MDSC Q2000) with a heating rate 20 °C/min and 10 °C/min, respectively and then cooled down to -40 °C at maximum cooling rate. T_g was measured in the second heating ramp of 20 °C/min. AFM images were recorded (Nanoscope III, Digital Instruments) using tapping mode

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with Si tips (Tap300, Budget Sensor, 300 kHz, 40 N/m). XPS studies of films having a thickness of about 100 nm deposited on silicon wafers were carried out on a Kratos Ultra X-ray photoelectron spectrometer.

Statistical AFM data analysis (Root Mean Square Roughness and Mean Grain Area calculations) was performed using software package Gwyddion (gwyddion.net). TEM images were obtained at 100 or 200 kV (JEOL JEM-1011 or FEI Tecnai G2).

3. Results

3.1 Synthesis of RF-PS and RF-PBMA

The choice of the two polymer blend components was motivated in part by the commercial importance of PS and the convenient ATRP polymerization methods of styrene and methacrylates that allows a convenient incorporation of a perfluorocarbon end group. PBMA was chosen given its much lower T_g value (293 K) compared to that of PS (273 K) that made it possible to distinguish the PS and PBMA domains and plausibly their domain compositions by DSC.

Relatively narrow molecular weight (MW) distribution RF end-capped polymers (PS or PBMA) were synthesized by atom transfer radical polymerization (ATRP) according to published procedures [44-45] and were characterized by size exclusion chromatography (SEC) and ^1H and ^{19}F NMR. The MW distributions were relatively narrow with PDIs between 1.36 and 1.05 and most being between 1.1 and 1.2. There is good correspondence (within about 10–15%) of calculated and SEC number average molecular weights (Table 1).

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Blends ^c	PS M_n ($\times 10^{-3}$) (PDI)	PBMA M_n ($\times 10^{-3}$) (PDI)
F4-7k	7.2 (1.15)	6.8 (1.19)
F4-10k	9.7 (1.18)	11.2 (1.23)
F4-15k	17.1 (1.18)	16.5 (1.20)
F7-15k	15.6 (1.16)	15.9 (1.29)
F7-20k	20.5 (1.21)	21.4 (1.10)
F7-25k	23.7 (1.25)	26.1 (1.08)
F7-30k	31.8 (1.3)	28.0 (1.1)
F10-15k	14.5 (1.05)	17.1 (1.14)
F10-20k	19.7 (1.06)	20.8 (1.13)
F10-25k	26.1 (1.15)	23.0 (1.30)
F10-30k	30.5 (1.15)	28.4 (1.35)
F13-13k	13.1 (1.05)	13.5 (1.12)
F13-20k	21.4 (1.08)	20.1 (1.26)
F13-25k	23.1 (1.11)	27.6 (1.36)
F13-30k	29.8 (1.10)	32.4 (1.32)

Table 1: SEC characterization of RF-End-Functionalized PS and PBMA.^{a,b}

^a SEC results of precipitated polymer samples using PS standards.

^b All polymerizations in toluene at 90 °C [Initiator]:[CuBr]:[Ligand] = 1:1:2 with Bpy as ligand.

^c The last number represents calculated M_n .

Polymer blends were formed by mixing equal polymer masses of RF-functionalized PS and PBMA in toluene followed by evaporation and further treatment as discussed in the Experimental section.

The 1/1 (wt/wt) blends are composed of the RF- PS and RF-PBMA polymers of approximate same number average MW (M_n) listed side by side in Table 1. The codes in the “Blends” column denote

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the number of the perfluorocarbon atoms in the RF group (C_4F_9 , C_7F_{15} , $C_{10}F_{21}$, $C_{13}F_{27}$) followed by the calculated M_n values of the PS and PBMA components in units of 1000 g/mole and their MW distributions. For instance F4-15k indicates a 1/1 blend of the C_4F_9 -end-capped PS ($M_n = 17.1$ k, PDI = 1.18) and the corresponding functionalized PBMA ($M_n = 16.5$ k, PDI = 1.20) polymers with calculated MWs of 15 k.

3.2 AFM studies

The AFMs of the blends are highly RF size- and MW dependent in that the calculated statistical root mean square roughness (RMSR) and mean grain area (MGA) tend to increase with decreasing RF lengths and increasing MW (Fig. 1 and Fig. S1). For instance, the F4-7k blend shows a smooth surface with height differences (HDs) of less than 3.5 nm and a RMSR of 0.65 nm (Fig. 1). In contrast, the AFMs of the F4-15k blend and that of F4-10k (AFM not shown) indicate a macrophase-separated morphology, with some domains exceeding 5 μm (Fig. 1, Table 2). These morphologies still differ with that of the corresponding blends of the unfunctionalized PS and PBMA in that all showed irregularly shaped μm -sized domains [41].

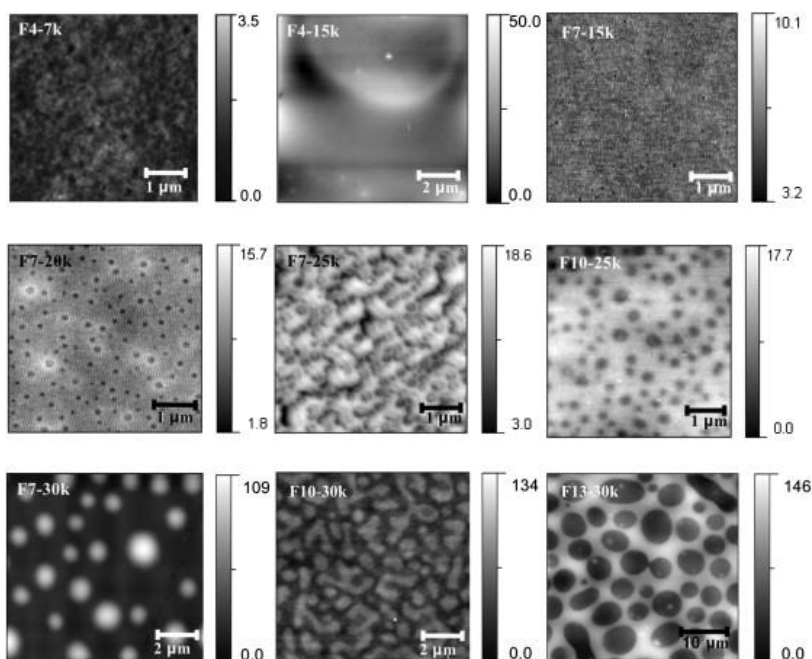


Figure 1: AFM images of F4-7k, F4-15k, F7-15k, F7-20k, F7-25k, F7-30, and F10-30k and F13-30k (height scale bars in nm).

PS-PBMA blend	RMSR (nm) ^a	MGA ^b ($\times 10^{-3} \text{nm}^2$)	PS-PBMA blend	RMSR (nm) ^a	MGA ^b ($\times 10^{-3} \text{nm}^2$)
F4-7k	0.65	– ^c	F10-20k	1.3	4.2
F4-10k	23.8	680	F10-25k	2.1	18.7
F7-15k	1.0	1.6	F10-30k	18.5	340
F7-20k	1.8	2.7	F13-13k	0.6	– ^c
F7-25k	2.7	40	F13-20k	0.7	– ^c
F7-30k	19.6	730	F13-25k	0.8	– ^c
F10-15k	0.7	2.0	F13-30K	22.4	5300

Table 2: Statistical coefficients for AFMs of F7, F10 and F13 blends.

^a Root mean square roughness.

^b Mean grain area; grain refers to the sizes of the round-shaped domains.

^c No features were observed.

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In comparison with the F4-10 and F4-15k blends, the F7-blends at comparable MWs show much smoother surfaces with well defined micro-domains such as pinholes or depressions the size of which increases with MW (Fig. 1, Table 2). For instance, compared with the F4-15k blend the AFM of the F7-15k blend shows a smooth surface having RMSR of about 1 nm and widely dispersed small (<50 nm) pinholes (Fig. S2, Table 2).

Distances between closest craters vary between 300 and 500 nm. Geometric fitting of the placements of the craters failed to reveal clear ordering. Compared to the F7-20k blend, the MGA values of the F7-25k blend are 16 times larger. In this case, larger (~200 nm) craters appear to be linked, indicating the onset of intermediate domain sizes of up to ~500 nm and greater crater depths of 10–15 nm (Fig. 1, Table 2). Upon increasing the MW further (F7-30k blend), the AFM is clearly of a macrophase type and shows elevated large (0.5–1.5 μm) round domains and RMSR of about 80 nm with RMSR and MGA values that are similar to that seen for the F4-15k and F4-10k blends (Fig. 1). The above changes in RMSR and MGA with increasing MW and RF size are also present for the F10 and F13 series. Compared to the F7-15k and F7-20k blends (RMSR of 1.6 and 2.7 nm respectively), the AFMs of the F10-15k and F10-20k blends on the whole show slightly smoother surfaces with RMSR values of 0.7 and 1.3 nm but comparable MGA values (Table 2, Fig. 1). Compared with the F7-20k blend, the AFM of the F10-25k blend shows a somewhat similar AFM but with larger (150–350 nm) crater-like structures, and its RMSR and MGA values are somewhat smaller than the F7-25k blend, consistent with the above trends. This is also the case for the F10-30k blend that has similar RMSR but a smaller MGA (3.4. 105 nm²) than the F10-30k blend that, unlike the F10-25k and F10-20k blends, shows sea-island like, angular and elevated 0.5–2 μm -sized

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structures with widths on the order of 200–300 nm (Fig. 1). These MW related changes are intriguing given the moderately narrow MW distributions that overlap significantly.

Following the above trends, the AFM morphology of the F13-13k, F13-20k and F13-25k blends, compared to the F7- or F10 blends, show smoother surfaces and very small surface domains (≤ 50 nm) and height differences on the order of 4–6 nm. (Fig. S1, Table 2). Surprisingly, the F13-30k blend shows a much rougher (MGA/RMSR values of 5.3×10^6 nm² and 22.4 nm respectively) surface morphology with surface domains in the order of 1–3 μ m and height differences of about 150 nm (Fig. 1 and Fig. S1, compared with the other F13 blends and even with the F7-30 and F10-30k blends (Table 2).

The above observations indicate some correlation of RF content with surface morphologies. Thus, above 2.5 RF wt percent the AFM morphologies are sub-micron, whereas at or below about 1.8 wt percent they are macrophase-separated. However, the correlation is only partial, as shown in Table 2. In contrast with the blend morphologies, the RF–PS and RF-PBMA homopolymer films showed surfaces without any noticeable features such as pinholes or other distinct features (Discussion).

3.3 Blend composition

The effect of polymer blend composition on AFM, shown in Fig. 2 indicates surface displays of the minor and major component of the F10-25k PS/PBMA (3/1) and (1/3) blends having overall contents of 75 wt percent C₁₀F₂₁-PS and 75 wt percent C₁₀F₂₁-PBMA respectively (Fig. 2). This is consistent with PBMA being appreciably more surface active than PS ($\gamma = 31.2$ and 40.7 dyn/cm respectively at 20 °C) [48]. However, the surface tension of the RF groups is much smaller (15–23 dyn/cm) [49].

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This conclusion is expected to apply to all of the AFMs discussed previously. Thus, the blend surfaces should be enriched in RF and PBMA content (see below).

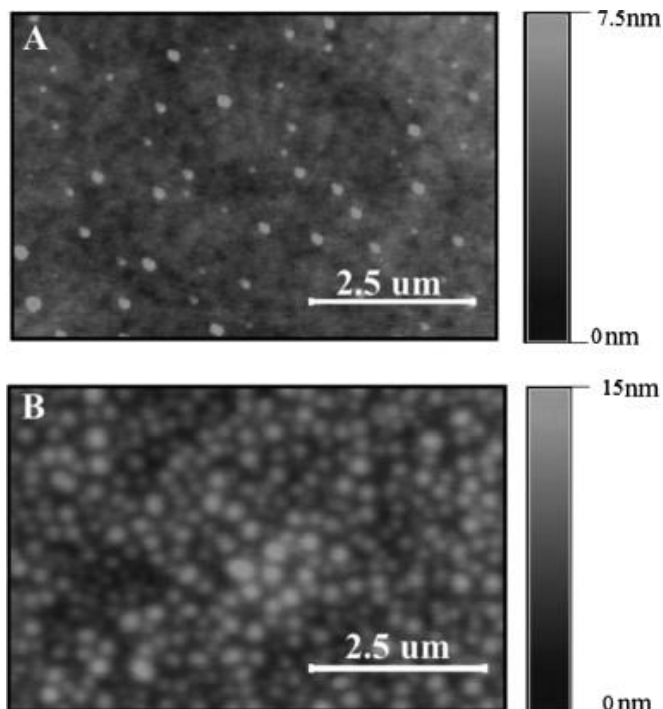


Figure 2: The effects of polymer blend composition on AFM topography. A) F10-PS-25k/F10-PBMA-25k 1/3 (wt/wt) blend; B) F10-PS-25k/F10-PBMA 1/3(wt/wt) blend.

3.4 X-ray photoelectron spectroscopy

XPS studies were carried out on films of the F7-15k PS/PBMA blend having a thickness of about 100 nm deposited on silicon wafers using a Kratos Ultra X-ray photoelectron spectrometer. At a take-off angle of 5°, the fluorine-content exceeds the calculated value by a factor of about six, indicating a significant surface enrichment of the RF groups (Table 3). This value decreases significantly at 85° but is still elevated, indicating a high perfluorocarbon content in the top layer, consistent with expectations [50-53]. The oxygen values are also larger in the top layers, indicating

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a greater content of PBMA relative to PS, consistent with the lower surface energy of PBMA relative to PS.

Atom %						Bulk (%)
Take off angles:	90°	45°	30°	15°	5°	
Carbon	75.2	76.8	77.6	77.0	78.8	89.2
Oxygen	22.9 ^b	20.9 ^b	20.2 ^b	20.2 ^b	12.4	9.37
Fluorine	1.87	2.21	2.23	2.80	8.71	1.40

Table 3: XPS studies of Films of RF –End-functionalized PS and -PBMA.^a

^a Substrate: silica wafer, sample thickness ~ 100 nm. See Experimental Section for details.

^b Artifact resulting from the silicon wafer.

3.5 TEM measurements

The TEM images of the above blends show great variability in morphology with RF length and MW and indicate qualitatively similar trends seen for the AFMs (Fig. 1 and Fig. 3).

As seen in the AFMs, in general the sizes of the polymer micro-dispersions increase with decreasing RF size and increasing MW. Thus, the TEM image of the F4-7k blend appears to be highly homogeneous and shows randomly oriented elongated domains with about 1 nm sized widths and variable lengths of up to 7 nm (Fig. 3). Thin films (~1 μ) of this blend are optically transparent. However, the thin film of the F4-10k blend is optically translucent and the TEM is consistent with this, having domain sizes in the order of 0.5–1.5 μm (Fig. 4).

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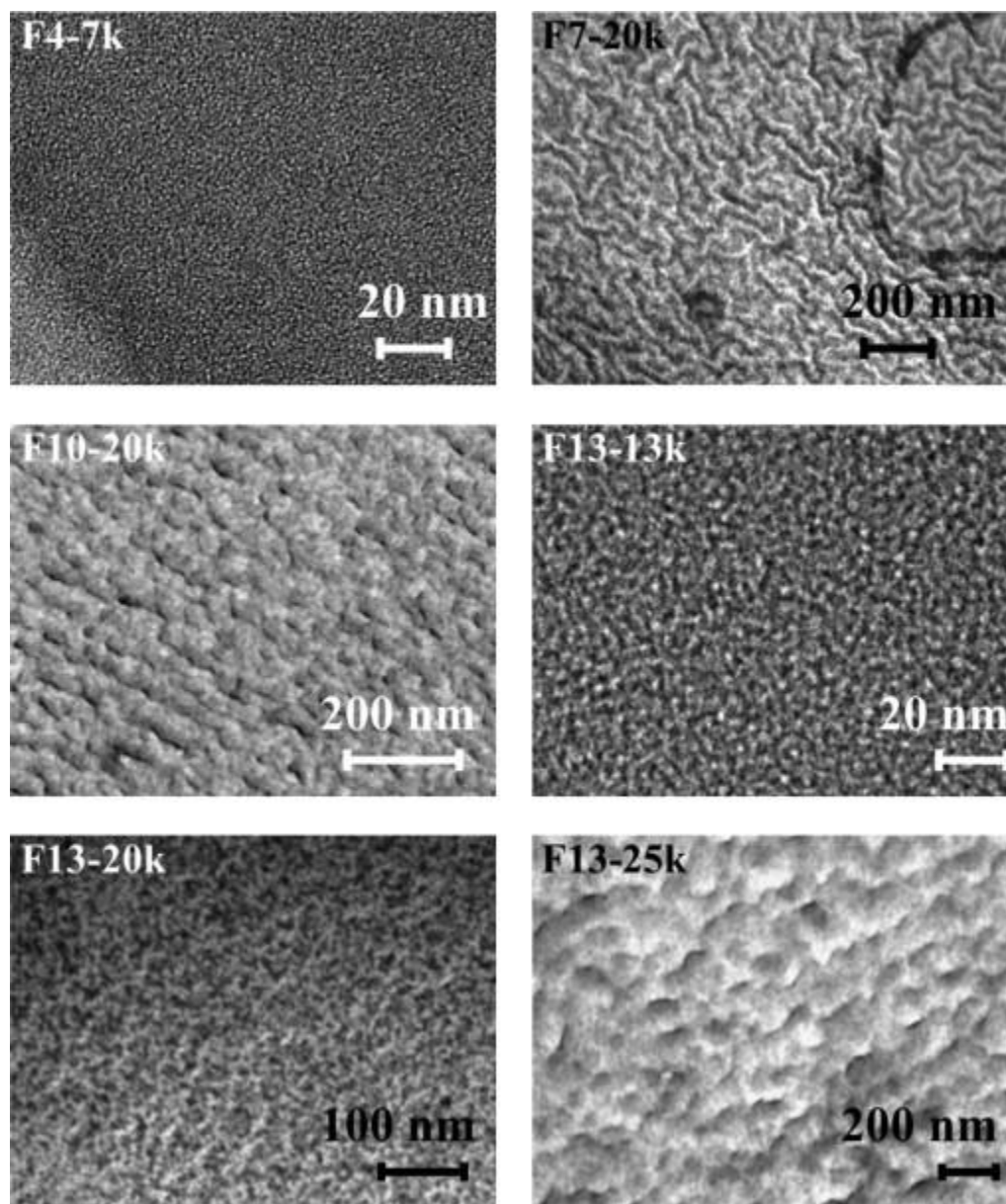


Figure 3: TEM images of 1/1 (w/w) F4-7k, F7-20k, F10-20k, F13-13k, F13-20k, F13-25k blends.

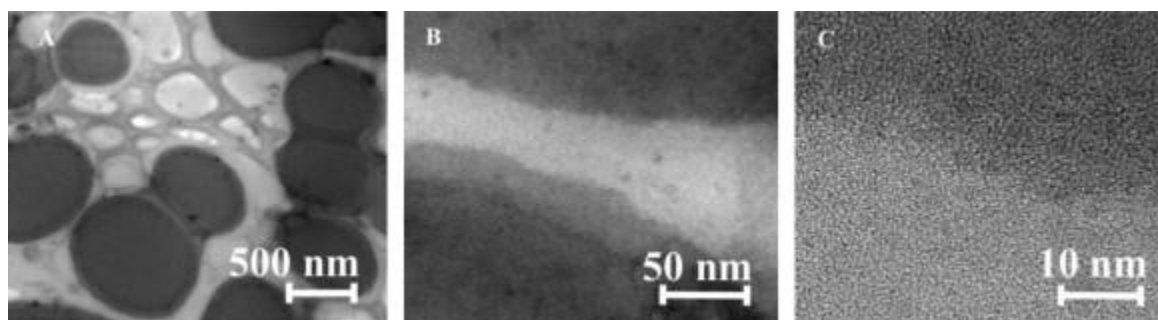


Figure 4: TEM images of the 1/1 (w/w) F4-10k (A) polymer blend and magnified at the PS-PBMA interface (B, C).

Therefore, the C₄F₇ end group is sufficient to raise the critical MW, the boundary MW where micro- to macro-phase separation occurs, from 4 k [54] to at least 7 k. This should be reflected in its DSC and optical properties (below). However, the interfacial area of F4-10k viewed at higher magnification reveals a micro-morphology of the PS- and PBMA-rich domains that show nm-sized domains and are qualitatively quite similar to that of the homogeneous F4-7k blend (Fig. 4).

In addition, distinct small (≤ 1 nm) dark dots are clearly visible in the PS rich dark grey domains and even in the light-grey PBMA-rich domain (Discussion). The F4-15k blend is optically opaque and hence presumably macrophase separated as also suggested by its AFM (Fig. 1).

In contrast, the TEM image of the F7-15k blend (Fig. 3) shows only low-contrast, submicron (< 50 nm) phases. The corresponding AFM also shows relatively small surface domains. However, as seen for the AFM, the TEM morphology of the F7-20k blend (Fig. 3) shows relatively well-defined PS and PBMA elongated domains but with widths and lengths of 25–40 nm and 0.4–1.0 μm respectively with some very limited directional persistence that superficially resembles a block copolymer TEM [55] but appears to lack directional order at any length scale. Unlike the case of the F4-10k blend, there is no clear evidence of sub-nm-sized areas in either the PS or PBMA domains. However, small spherical dark domains (≤ 7 nm) are seen that may be associated with the PS domains and may

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indicate PS micelles with a large RF content [56,57]. Like the F7-20k, the F10-20k blend appears to indicate a submicron morphology but surprisingly shows wider (30–80 nm) and elongated (40–200 nm) but randomly placed PS- and PBMA segmented domains with some longer range orientation (Fig. 3).

Unlike the F7-20k blend the F7-25k blend is no longer microphase-separated and shows scattered PBMA macro-domains (0.5–2.5 μm) but interestingly no PS macro domains (Discussion) (Fig. 5). The domain sizes indicate that this blend is near the macro-microphase boundary. In addition much smaller elongated, 30–60 nm wide, dark grey PS- rich but PBMA-depleted, micro-domains are visible. The TEM image of the F10-25k blend also shows PBMA macro-domains, but compared with the F7-25k blend, these are smaller (long axes of 200–500 nm) and, show dark fringes (Fig. 5). As seen for the F7-25k blend, no PS macro-domains are visible. In addition “striped” microphases in which darker 40 nm wide PS rich elongated domains are visible that are suspended in a light grey, presumably PBMA-depleted phase. In contrast, the TEM image of the F7-30k blend shows only macrophases as may be expected on the basis of the low RF content. This is also observed for the corresponding AFMs (Fig. 1).

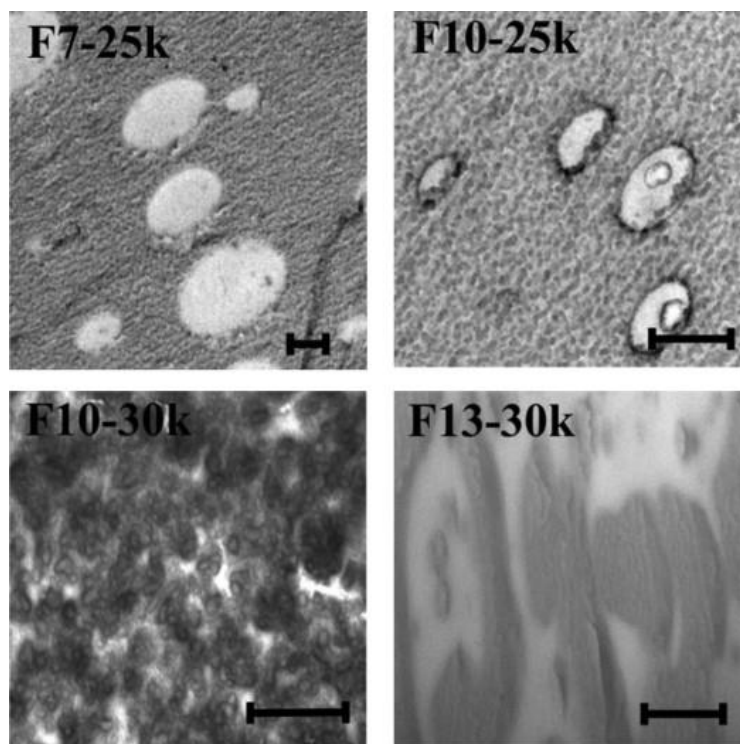


Figure 5: TEM images of the F7-25k, F10-25k, F10-30k and F13-30k blends.
Scale bar 500 nm.

The TEM image of the F10-30k blend in contrast with the F10-25k blend, now shows a population of smaller (30–80 nm) ellipsoidal, dark-fringed PS micellar structures that are associated into larger highly disordered clusters embedded in a lighter PBMA phase in which no fine structures could be seen (Fig. 5). Given the seemingly large influence of the MW on the blend morphologies, it is possible that the differences with the F10-25k blend may correlate with smaller MWs of the PBMA component (Table 1). This would have to be checked with blends with more closely matched MW and narrower MW distributions (see below).

As expected, the presence of the very large $C_{13}F_{27}$ end groups in the F13-13k and F13-20k blends gives rise to much smaller domains than seen for the F7- and F10- blends (Fig. 3). As also observed for the AFMs, the difference between the F7 and F10- domains is rather small compared with the

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F13 blends. The morphology of the F13-13k blend superficially resembles that of the F4-7k blend having similarly sized (0.5–2.0 nm) but irregularly shaped domains. Low contrast darker- (PS-rich) lighter-grey (PBMA-rich) domains are visible suggesting some degree of phase mixing (Discussion). The presence of black small (≤ 1 nm) sized “dots” seemingly superimposed on the PS-rich domains is noted, some of which are clustered (Discussion).

Compared with the F7-20k and F10-20k blends, the F13-20k blend shows the more easily observed disordered and elongated PBMA domains having lengths and widths on the order of ~ 10 – 20 nm and 2 – 5 nm respectively that are at least one order of magnitude smaller than those seen for the F7-20k (20 – 40 nm) and F10-20k (50 – 100 nm) blends (Fig. 3). The PS rich domains appear to have similar small sizes and shapes. This is consistent with the F13-20k blend being completely optically transparent above 300 nm. The decrease in domain sizes is remarkable and indicates the formation of more stable RF micelles, as may be expected on the basis of the formation of liquid crystalline (LC) domains for these large RF groups. However, the F13-25k blend (Fig. 3) shows a different TEM morphology in which PS-rich and PBMA-rich domains appear aggregated into light and dark irregularly-shaped larger (~ 200 – 800 nm) domains, the size of which is difficult to gauge. The optical transmittance of this blend is high ($\sim 90\%$) but largely wavelength independent. In addition, thin (~ 10 nm wide) filament-like black domains with lengths of 100 – 300 nm are seen that seem to be present at the PS/PBMA interfaces of the lighter (PBMA) and darker (PS) domains (Discussion).

In contrast, the F13-30k blend shows a completely different and disordered morphology with micron-sized, irregularly shaped areas corresponding to dark- and light-gray PS- and PBMA-rich domains, suggesting significant phase mixing (see below) (Fig. 5). The dramatic difference compared with the F13-25k blend is remarkable, indicating again the importance of MW and hence

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plausibly of MW distribution in blend morphology. This is also seen in the AFMs showing very large (2–10 μ) ellipsoidal surface domains (Fig. 1).

The TEM morphology data is summarized in a RF-size vs. MW plot, in which the various blends are characterized with blue and orange indicating macro- (≥ 500 nm) and micro- (≤ 500 nm) domain sizes respectively (Fig. 6). The line separating macro- from micro-phase is drawn through the F10-25k blend where the domain sizes are on the order of ~ 500 nm. The large decrease in miscibility of the three RF types of blends due to increases near 30 k is dramatic (Discussion).

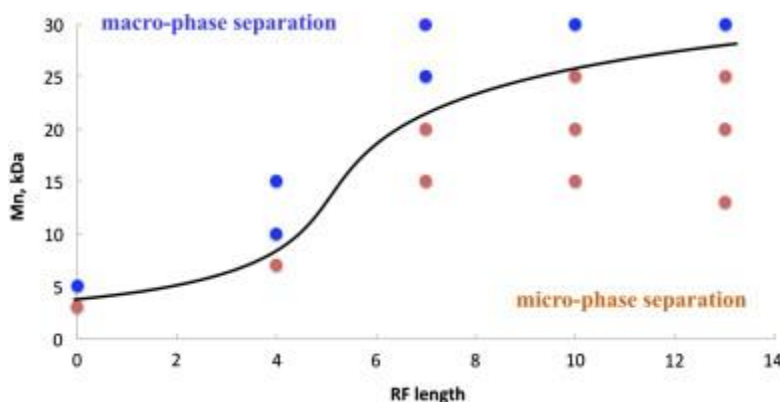


Figure 6: “Phase Diagram” of RF end-functionalized PS-PBMA blends. Blue and orange dots denote inhomogeneous and homogeneous blends respectively (line is intended to guide the eyes). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.6 Small angle X-ray scattering (SAXS)

A F-20k blend with a relatively well-defined morphology was analyzed by SAXS. NO clear refraction patterns were observed indicating a lack of order on relatively small length scales. This could have been predicted as there is no discernible order in any of the TEMs (Discussion).

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3.7 Optical properties

The optical transmittance of films is a convenient method to qualitatively assess polymer blend miscibility [58]. Three different transmittance patterns are seen for the functionalized blends (Fig. 7). The first (F4-7k, F7-15k, F7-20k, F10-20k, F10-25k, F13-13k, F13-20k), shows a virtual complete transmittance ($\geq 97\%$) above 350 nm with some (F4-7k, F7-15k, F7-20k, F10-20k, F13-20k) showing nearly complete transmittance ($\geq 99\%$) above 300 nm, consistent with the TEM data that indicate the presence of domain sizes well below the optical wavelengths.

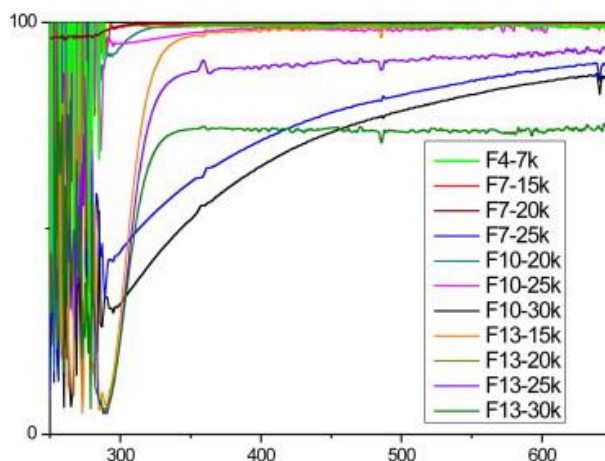


Figure 7: Transmittance Spectra of F7E, F10E and F13E blend films of about 2 μm thickness prepared by drop casting a toluene solution of polymer blends 50/50 (wt%) on cover glass.

The second pattern (F7-25k, F10-30k) indicates a strongly wavelength dependent transmittance ranging from around 90% at 600 nm to 50–60% at 350 nm. Again this appears to be consistent with the TEM data that show domain sizes in the optical wavelength scale.

The third transmittance type (F13-25k and F13-30k blends) on the other hand, is reduced but largely wavelength independent (transmittances of 90–93% and 75% respectively) consistent with the presence of domains that are large compared to the optical wavelengths. This is clearly illustrated

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for the F13-30k blend where the domain sizes are in μ scale. In that case the considerable phase mixing is consistent with very similar PS/PBMA compositions mediated by strong association of the C13F27 groups. For several blends that were close to macro/microphase transitions, no clear changes in opacities were seen after 24 h upon heating up to 150–180 °C (F7-25k and F10-25k). This is consistent with the phase separation not being strongly entropy driven.

3.8 Differential scanning calorimetry

As shown in Table 5, DSC measurements in most cases show two T_g 's corresponding to the two polymers. Single T_g 's were observed only for the F4-7k and F13-13k blends (315.0 K and 326.0 K) and were close to the calculated values of 316 K and 329 K respectively. For the F7- and F10- blends the T_g 's of the RF-PBMA increased significantly with the differences from the homopolymers (ΔT_g) being about 6–8 °C) compared to slight decreases (0–2 °C) in the T_g 's of the RF-PS. This appears to be consistent with a greater solubility of the RF-PS in RF-PBMA than that of RF-PBMA into the RF-PS domains seen earlier by TEM (Discussion). Large ΔT_g values for both RF-PS and RF-PBMA were seen for the F13 blends, consistent with appreciable phase mixing due to stronger interactions of the C13F27 groups (Discussion).

4. Discussion

The analysis of blends of RF-functionalized PS and PBMA is complex compared to the case of blends of the unfunctionalized polymers and the corresponding diblock copolymers. Thus, in addition to the independent variables such as MWs, RF sizes and blend compositions, this includes the partial, and presumably MW dependent, solubilization of RF-PS into the RF-PBMA domains

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and vice versa in a few cases, as suggested by the DSC and TEM data (Table 5). To our knowledge, no RF mediated polymer blend of this or any other type has been studied systematically. The thermal and solvent annealing of all blend samples prior to analysis ensures that the results represent thermodynamically stable states (Experimental section). Thus the above results are repeatable and reproducible.

We start with a summary of the effects of MW and RF lengths on the bulk properties as expressed by DSCs, TEMs, optical transmittance data and the correlation of these data with the AFMs. This is followed by a discussion of the nature of the fluorophilic interactions. Finally, we discuss some peculiar AFM surface features of some of the blends.

4.1 Morphologies. Effects of MW, RF-size and content

In this exploratory study we have focused on the blends that are close to the micro-macro phase boundary (Fig. 6). As indicated above, we define micro- and macrophase morphologies as having average domain sizes smaller and larger than about 500 nm respectively. The RF-PS/RF-PBMA blends form, in part, by the reduction of the PS-PBMA interfacial energies mediated by the RF end groups as represented in Scheme 1.

As indicated above, miscibilities increase with increasing RF content and size and decreasing MW (Table 4). Thus, above about 3 wt percent RF content, only microphases (m) are observed while below 1.8 wt percent only macrophases (M) are seen. For a given RF group, all blends show increases in MGAs and TEM domain size with MWs. This is seen for the F10 and F13 series as shown in Fig. 6 and Table 4. Also for a blend with a given MW, domain size decreases are observed with larger RF end groups (Fig. 6). For instance, the F4-15k blend shows macrophases (M) while

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microphases (m) are seen for the F7-15k blend the size of which decreases further for the F13-15k blend (Table 4). In some cases these changes are relatively modest, for instance, for the F7-25 and F10-25k blends. In others, the effects are more dramatic, for instance, in comparing the F13-20k with the F7-20k and F10-20k blends that have similarly sized domains. This may be due, in part, to liquid crystalline interactions due to the large C13F27 groups that may not be present for the F7 and F10 blends. For instance, the melting points for C7F16, C10F22, and C13F28 are reported as about -81, 37 and 102 °C [39, 59].

Blend	RF-content ^c	Blend	RF-content ^c	Blend	RF-content ^b	Blend	RF-content ^c
F4-7k (h)	3.1%	F7-15k (m) ^b	2.3%	F10-15k (m)	3.3%	F13-13k (h)	5.0%
F4-10k (Mm)	2.1%	F7-20k (m)	1.8%	F10-20k (m)	2.6%	F13-20k (m)	3.2%
F4-15k (M)	1.3%	F7-25k (Mm)	1.5%	F10-25k (m)	2.1%	F13-25k (m)	2.6%

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		F7-30k (M)	1.2%	F10-30k (Mm)	1.8%	F13-30k (M)	2.1%
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Table 4: Dependence of AFM/TEM morphology on MW and RF content of RF-PS/RF-PBMA blends.^{a,c}

^a *h*: homogeneous blend; *m*: microphase separated blend ($d < 500$ nm); *M*: macrophase separated ($d > 500$ nm). *Mm*: macro–micro phase separated.

^b *Highlighted cells indicate polymer blends with identical or almost identical perfluorocarbon content.*

^c *Calculated RF weight percent.*

However, RF content is not the only factor that influences morphology. For instance, the TEM domain sizes of the F7-20k blend (1.8 wt% RF) are smaller than those of the F10-25k, F13-25k and F13-30k blends having larger RF contents (Table 4). Also, the F4-7k blend is homogeneous, while this is not the case for the F10-15k blend having a higher RF content. The F10-20k blend shows micro domains, while this is not the case for F13-25k blend with a higher RF content (Table 4). The TEMs of the F7-, F10- and F13- compatible blends in most cases show elongated microphases, as illustrated in the F7-20k F10-20k and F13-20k blends. It is plausible that these structures are formed by stacking of micellar aggregates illustrated in Scheme 1.

The AFMs, on the whole, show good qualitative consistency with the TEM data (Table 2 and Table 4). For instance, the TEMs and AFMs of F4-7k, F7-15k, F7-20k, F10-15k, F10-20k, F13-13k and F13-20k all indicate small MGAs ($\leq 4.2 \cdot 10^3$ nm²) and TEM domains (Table 2, Fig. 1 and Fig. 3). Furthermore, the AFM data, like the TEM morphologies, show length scales that change in similar ways with blend MW and RF size (Fig. 1 and Fig. 2). Even in blends, the miscibilities of which deviate from correlation of TEM morphologies, this correlation appears to be reflected in the AFM data. Like the TEM of the F4-10k (M) blend, its AFM also indicates large domains (MGA of 6.8×10^5 nm²) compared with more miscible blends. The F13-30k blend with the largest TEM domains also shows the largest MGAs ($53 \cdot 10^5$ nm²), followed by much smaller values

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($7.3 \cdot 10^5$, $6.8 \cdot 10^5$ and $3.4 \cdot 10^5$ nm²) for the F7-30k, F4-10k and F10-30k blends, respectively (Table 2), roughly in line with the TEM domain sizes. Also the MGAs for the F7-20k and F7-25k blends are 2.7×10^3 and $40\text{--}10^3$ nm² and an increase of almost 15 fold. This is reflected in the TEM domains sizes that increase from less than 100 nm for the F7-20k to between 0.5 and 2.0 μ for the F7-25k blend. Similar changes are seen for the MGAs and TEM domains sizes of the F10-20k, F10-25k and F10-30 k blends (Table 2 and Fig. 3 and Fig. 5).

The DSC and optical data show good agreement with the TEMs. For instance, the F4-7k and F13-13k blends show a single T_g value, confirming homogeneous (h) blends (Table 5). The F7-15k, F7-20k, F10-20k, F13-20k and similar blends, show dual T_g values, but should be considered to be compatible in the sense that the TEM domains sizes are on the nm scale (<300 nm), consistent with their near quantitative optical transmittances (Fig. 7). It has been noted that the occurrence of two T_g values is not inconsistent with effective polymer blending [60].

Blend	T_g (K) ^b	ΔT_g (K) ^c	Blend	T_g (K) ^b	ΔT_g (K)
F4-7k	315	–	F10-25k	300, 373	7/0
F4-10k ^d	300, 351	7/–10	F10-30k	300, 373	7/0
F7-15k	300, 371	7/–2	F13–13k	326	–
F7-20k	301, 371	8/–2	F13–20k	302, 364	9/–9
F7-25k	300, 373	7/0	F13–25k	301, 368	8/–5

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F10-20k	299, 371	6/-2	F13-30K	301, 366	8/-7
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Table 5: Glass Transition Temperatures of F4, F7, F10 and F13 blends.^a

^a For DSC methods see Exp. Section.

^b T_g values for PBMA and PS respectively.

^c T_g differences with the corresponding PBMA and PS 20 k homopolymers ($T_g = 293$ and 373 K respectively).

^d The T_g (361 K) of PS 10 k is based on data in Ref. [60]. The T_g of PBMA 10 k (274 K) is based on data in Ref. [61].

There is also a general correlation between morphologies of the M and Mm type blends and their optical transmittances. For instance, the large TEM domain sizes ($>1-2 \mu$) seen for the F13-30k blend are consistent with its reduced ($OT \approx 75\%$) and wavelength independent OT, whereas that of the F10-30k and F7-25k blends are highly wave length dependent (Fig. 7), indicating the presence of domains sizes on the approximate order of optical wavelengths (Fig. 5). On the other hand, films of the F10-25k blend are nearly optically clear above 400 nm, again consistent with the TEM data. The TEM morphology of the F13-25k blend with light and dark domains adjacent to filament-like structures appear to have a predominantly microphase (m) morphology (Fig. 3). However, this blend is only partially transparent and largely wavelength independent (OT values of 88 and 92% at 350 and 600 nm), consistent with the presence of sparse but larger ($\geq 1\mu$) domains that can be seen in the TEM (Fig. 3). Almost complete disorder is seen in the TEMs of all RF-PBMA/RF-PS blends. Hence, the lack of SAXS diffraction patterns is not surprising.

4.2 Domain composition

Although the F4-10k blend shows TEM macro (M) domains, closer inspection suggests the presence of PS- and PBMA-rich nm sized (<10 nm) micro-phases within each of the micron sized PBMA- and PS-rich domains (Fig. 3). This is consistent with DSC data that show positive ΔT_g ($+7$ °C) and Jingguo Shen, Victoria A. Piunova, Steven Nutt and Thieo E. Hogen-Esch, "Blends of Polystyrene and Poly (n-Butyl Methacrylate) Mediated by Perfluorocarbon End Groups" *Polymer* **21** 5790-5800 (2013) DOI<<http://dx.doi.org/10.1016/j.polymer.2013.08.059>>.



negative ΔT_g 's values ($-10\text{ }^\circ\text{C}$) values for PBMA and PS respectively (Table 5). The miscibilities of the RF functionalized polymers should be even greater than the unfunctionalized polymers. Phase mixing for the F7- and F10- blends is also suggested by the DSC data but this effect seems more pronounced for the PBMA domains with ΔT_g values between $+6$ and $+8^\circ$ but much smaller ΔT_g 's for the PS domains ($\Delta T_g = 0$ to $-2\text{ }^\circ\text{C}$) indicating contamination of RF-PS in the RF-PBMA domains but little or no RF-PBMA content in the RF-PS domains (Table 5). The contamination of PBMA domains with the PS is not clearly seen in the TEMs of the F7 and F10 blends but, upon magnification, some fine structures suggesting the presence of some PS in the PBMA domains is seen in the F7-25k and F10-25k blends (Fig. 5). For the F13 blends, large ΔT_g values are seen indicating partial but significant phase mixing for both phases plausibly due to the stronger association of the larger $C_{13}F_{27}$ groups. This is clearly illustrated by the low contrast TEMs of the F13-30k and other F13 blends, where the DSC indicates appreciable phase mixing in both phases. Interestingly, PBMA but no PS-macro-phases are seen in the F7-25k and F10-25k blends (Fig. 6) The reverse appears to be the case for the F10-30k blend where 12–50 nm sized PS ellipsoidal domains are visible that are fused into irregularly shaped PS clusters along with smaller, poorly defined, PBMA domains that show relatively good TEM contrast (Fig. 6). The striking change in morphology seen for the F10-25k and F10-30k blends with a small increase in MW is remarkable. As pointed out above, these issues may be addressed by the synthesis of blends of even narrower MW distribution polymers.

The partitioning of the RF-PS into the RF-PBMA domains for the F7-25k and F10-25k blends is expected to be MW-dependent. For instance, the MW of the RF-PS in the PBMA-rich domains should be lower than the RF-PS MW of the microphases. Likewise, the MW of the RF-PBMA in

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the RF-PBMA domains is expected to be larger than the RF-PBMA in the remaining micro domains. This issue may be clarified by effects on the TEMs of addition of small quantities of high or low MW polymers of well-defined narrow distribution blends of this type.

4.3 Perfluorocarbon domains

As indicated above, the RF weight fraction is a major, but not the only, factor in the morphologies and length scales of the PS and PBMA surface and bulk domains. The effectiveness of RF end groups in RF-PS/RF-PBMA blending is remarkable and consistent with the formation of RF domains much smaller than the polymer domains as illustrated in Scheme 1. At low RF length (F4 and F7 blends) the effects are likely caused by “solvophobic” effects of the RF groups due to the much lower cohesive energy density values of aliphatic perfluorocarbons ($\delta = 11.3\text{--}12.7 \text{ MPa}^{1/2}$) compared to both PS and PBMA ($\delta = 17.5$ and $17.9 \text{ MPa}^{1/2}$) [61]. As indicated above, for the longer $\text{C}_{13}\text{F}_{27}$ groups, the formation of LC domains would be plausible [36, 62-64]. For instance, the melting point of $\text{C}_{13}\text{F}_{27}$ can be estimated as about $100 \text{ }^\circ\text{C}$.⁷⁰

Due to the low RF contents, the presence of the RF domains is not readily detected by AFM, DSC or other methods. However, its presence could be inferred from the tiny dark dots along with the low contrast light and grey areas seen in the TEMs of high RF content blends, such as F4-7k, F13-13k and F13-20k that are not readily explained in other ways. Furthermore, these are especially prominent in high RF content blends. Similar dark presumably RF-rich round domains are also seen in the TEM of the F7-20k blend (Fig. 3) where they occur predominantly in the PS domains. The presence of dark, filament-like structures at the interfaces between PS- and PBMA rich domains of the F13-25k blend (Fig. 3) may be another example as is, perhaps, the occurrence of dark fringes

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seen on the PBMA domains in the TEMs of the F10-25k and the PS micellar-like domains of the F10-30k blends (Fig. 6) [27]. Alternative possibilities such as selective staining of benzene rich areas due to pi stacking or polymer density fluctuations, seem insufficient, as these do not explain these ubiquitous TEM contrasts where their presence is most plausible. As pointed out earlier, the AFMs of the component RF- homopolymers or 1:1 (w/w) blends of the unfunctionalized polymers above a MW of about 4000 do not show any of the features seen in the compatibilized RF- blends. Given the consistency of the AFM and TEM data, this is probably also the case for unfunctionalized PS/PBMA blends.

4.4 AFM morphologies

Besides the factors that influence the TEM data, the AFM micrographs are also influenced by air-polymer and substrate-polymer interfacial energies and may not always reflect the bulk morphology in particularly in ultra thin films. For instance, the protrusions and the surprisingly well-defined, micron-sized angular features in the F10-30k blend seem consistent with PS domains partially “coated” with a lower surface energy RF-PBMA (Fig. 2).

The presence of circular depressions (“pin holes” or “craters”) is also noted for the F7-15k, F7-20k, F7-25k blends. Crater sizes increase with MW, as seen for F7-15k (~6 nm), F7-20k (50–150 nm) and F10-25k (150–300 nm) blends (Fig. 1 and Fig. 3), as do the MGAs, again reflecting roughly the trend in the TEM domain sizes (above). Given the low T_g of PBMA relative to that of PS, these relatively well-defined AFM features may represent PS-domains with RF-rich surfaces (Table 4). These structures are as yet unclear, but qualitatively similar features have been seen for hydrocarbon-fluorocarbon micelles [65,66].

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For the AFM of the F7-25 blend, the cavity distribution is no longer random but shows a connectivity that may correlate with the formation of larger PBMA domains seen in the TEM. Hence, the relatively well-defined AFM images for the F7-20k, F7-25k, F10-25k blends may represent PS cavities.

The reason(s) for the peculiar changes in AFM morphology with MW and RF size are likely even more complex than the TEMs, being influenced by the different surface tensions of PS (41 dyn/cm) and PBMA (31 dyn/cm) and by the much more surface active (15–17 dyne/cm) RF groups. The RF groups should also disproportionately populate the surfaces compared to PBMA and PS, as shown by the XPS data. The type of deployment of the RF groups in the AFMs is not clear at present. However, the surface active RF groups are not large and numerous enough to provide complete surface coverage. As pointed out above, PBMA, due to its lower surface tension, may be expected to “coat” the harder PS domains, in agreement with results of the XPS data (Table 4) and earlier studies [67-69]. This is consistent with the morphology of the F10-25k blend, where the presence of much more numerous and larger PBMA-rich protrusions are shown for the 1/3 vs. the 3/1 F10-PS-25k/F10-PBMA blend (Fig. 2). The sizes of these domains are on the order of 150–300 nm, similar to that seen in the TEMs.

The above blends demonstrate properties that differ fundamentally from both conventional PS/PBMA blends and PS-*b*-PBMA block-copolymers. It has been shown that the micro-phase separated PS-*b*-PBMA diblock copolymers undergo order-to-disorder transitions at elevated temperatures followed by entropy driven microphase reformation upon further heating [68,69]. On the other hand, conventional PS/PBMA blends only show macro- to micro-phase separation as the

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blends are heated above the critical temperature, T_c , which is close to the decomposition temperature, T_d of PS.

We acknowledge the limitations of our interpretation of the AFM and TEM data. Both are microscopic imaging methods that sample small volumes and could have yielded atypical localized morphologies. However, the AFM and TEM data were both repeatable and reproducible. Nevertheless, the “micro-macro phase diagram” (Fig. 6) should be considered as semi-quantitative. A more detailed relationship between the AFM and TEM data requires additional investigation. The application of these design principles to other types polymer blends is in progress.

5. Conclusions

We report a new type of polymer blend mediated by perfluoroalkyl end groups appended to isobaric PS and PBMA (RF-PS/RF-PBMA) with average MWs between 7 and 30k. As indicated by TEM, AFM, DSC, XPS and optical transmittance (OT), the blends form by the reduction of the PS-PBMA interfacial energies and phase separation of the RF domains mediated by the RF end groups. The miscibility of the blends as judged from the TEM and AFM domain sizes typically decreases with decreasing MW and increasing RF size. Thus, miscible blends with TEM domains sizes below about 500 nm are formed at RF contents of about 3 wt % or greater, while partially- or immiscible blends form below 1.8 wt %. The TEM domains are generally elongated and irregularly shaped with no long-range order. As shown by DSC, for F7- and F10-25k blends, the solubility of PBMA in the PS domains is much greater than *vice versa*. For the case of the F13 blends, the PS/PBMA blend miscibilities are roughly comparable. The OTs generally correspond well with the TEM and AFM data.

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The feasibility of miscible binary polymer blends from RF end-functionalized components, at least in principle, is far reaching and the number of feasible binary blends is large. This aspect is being explored.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.polymer.2013.08.059>.

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