Correlation of Free Radical Copolymerization Behavior and Copolymer Properties with the Strength of $\pi-\pi$ Stacking Interactions between Aromatic Fluorocarbons and Aromatic Hydrocarbons: Copolymerization of Styrene and Fluorinated Styrenes at the Two Extreme Levels of Fluorination

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ABSTRACT: In order to determine if the alternating tendency of styrene with fluorinated styrenes in free radical copolymerizations correlates with the strength and/or extent of $\pi-\pi$ stacking interactions between aromatic fluorocarbons and aromatic hydrocarbons, styrene (St) was copolymerized with 2,3,4,5,6-pentafluorostyrene (PFS) and 4-fluorostyrene (4FS) under a variety of conditions. For the copolymerization of styrene with PFS at 25 °C, $r_{St}r_{FS} = 0.048$ and 0.069 in bulk and toluene, respectively, using *tert*-butylperoxy pivalate as the initiator. For the copolymerization of styrene with PFS at 70 °C using benzoyl peroxide as the initiator, $r_{St}r_{FS} = 0.17$ in bulk and $r_{St}r_{FS} = 0.14$ in toluene. For the copolymerization of styrene with 4FS, $r_{St}r_{FS} = 0.69$ at 25 °C under redox conditions and $r_{St}r_{FS} = 0.62$ at 70 °C in bulk. As confirmed by ^{1}H, ^{13}C, and ^{19}F one-dimensional NMR and ^{1}H−^{13}C heteronuclear single quantum coherence and ^{1}H−^{1}H nuclear Overhauser effect two-dimensional NMR spectroscopy results, St and 4FS tend to form random copolymers whereas the St-PFS copolymers tend to alternate with the alternating tendency increasing with decreasing temperature. The glass-transition temperatures determined by differential scanning calorimetry of the St-PFS copolymers are elevated relative to their mole-average values, whereas those of the corresponding homopolymer blends and the St-4FS copolymers occur at mole-average values. The water and ethylene glycol contact angles of both the St-PFS and St-4FS copolymer films occur at their mole-average values.

Introduction

Aromatic fluorocarbons interact with aromatic hydrocarbons by $\pi-\pi$ stacking via arene−perfluoroarene interactions.[1] In contrast to pure benzene[2] (and pure hexafluorobenzene[3]), which crystallizes primarily by an edge-to-face interaction of the electron-rich π system with an electron-deficient hydrogen atom on another aromatic ring, hexafluorobenzene forms transient 1:1 complexes with aromatic hydrocarbons such as benzene,[4,5] toluene,[5] and *p*-xylene[5] by electrostatic interaction of its electron-deficient aromatic ring with the electron-rich aromatic ring of the hydrocarbon. Benzene and hexafluorobenzene are alternately stacked face-to-face at a distance of 3.7 Å within columns of their 1:1 mixture in both the solid[6] and liquid[7] states. This 1:1 complex of hexafluorobenzene and benzene melts at 24 °C,[4,5] which is higher than the melting point of either benzene (5.5 °C) or hexafluorobenzene (5 °C). Hexafluorobenzene also forms 1:1 complexes with mesitylene[4,5] (mp −45 °C) and 2-methylnaphthalene[4] (mp 35 °C), which are stable enough to crystallize from ether; the complexes have significantly higher melting points (mp 34 and 56 °C, respectively) than their constituents. Similarly, hexafluorobenzene forms a 1:1 complex with 1-methylnaphthalene (mp −22 °C), which melts at a significantly higher temperature (mp 100 °C) than either component.[8]

Such $\pi-\pi$ stacking interactions between aromatic fluorocarbons and aromatic hydrocarbons have been used to engineer crystal structures,[9] orient reactants for polymerization[10] and photodimerization[11] in the solid state, generate one-dimensional ribbon structures,[12] provide physical cross-links,[13] stabilize liquid crystalline phases,[14] influence electronic properties,[15] and enhance the poling efficiency and temporal stability of electrooptic materials.[16] In spite of the ability of these interactions to profoundly affect the supramolecular ordering of a wide variety of materials, the strength of $\pi-\pi$ stacking interactions between aromatic fluorocarbons and aromatic hydrocarbons are quite weak, similar to that of a weak hydrogen bond, as recently determined using heat capacity measurements in *n*-heptane[17] and infrared spectroscopy in liquid krypton.[18] For the combinations studied, the association enthalpy was highest for the 1:1 complex of hexafluorobenzene with 1-methylnaphthalene (−10.8 ± 0.1 kJ/mol).[17] The association enthalpies between hexafluorobenzene and benzene (−9.1 ± 0.9 kJ/mol), toluene (−8.8 ± 0.4 kJ/mol), and naphthalene (−8.7 ± 0.2 kJ/mol) and between pentafluorobenzene and 1-methylnaphthalene (−8.6 ± 0.2 kJ/mol) were the same within experimental error; the association enthalpy of the 1:1 complex of pentafluorobenzene and benzene was significantly lower (−4.4 ± 0.2 kJ/mol).[17]

In addition to the recent microcalorimetry and IR measurements of the strength of $\pi-\pi$ stacking interactions between aromatic fluorocarbons and aromatic hydrocarbons, the ability of these two types of aromatic structures to interact and/or complex has been studied using the excess volumes[19] and excess enthalpies[20] of mixing, vapor pressure measurements,[21] and phase diagrams of their mixtures,[4,5,22] which sometimes show an elevated melting point of the 1:1 complex relative to the melting temperatures of the pure aromatic fluorocarbon and aromatic hydrocarbon. However, these thermodynamic measurements require very careful experimentation and often demanding procedures, such as the IR spectroscopy in liquid krypton described in ref 18.

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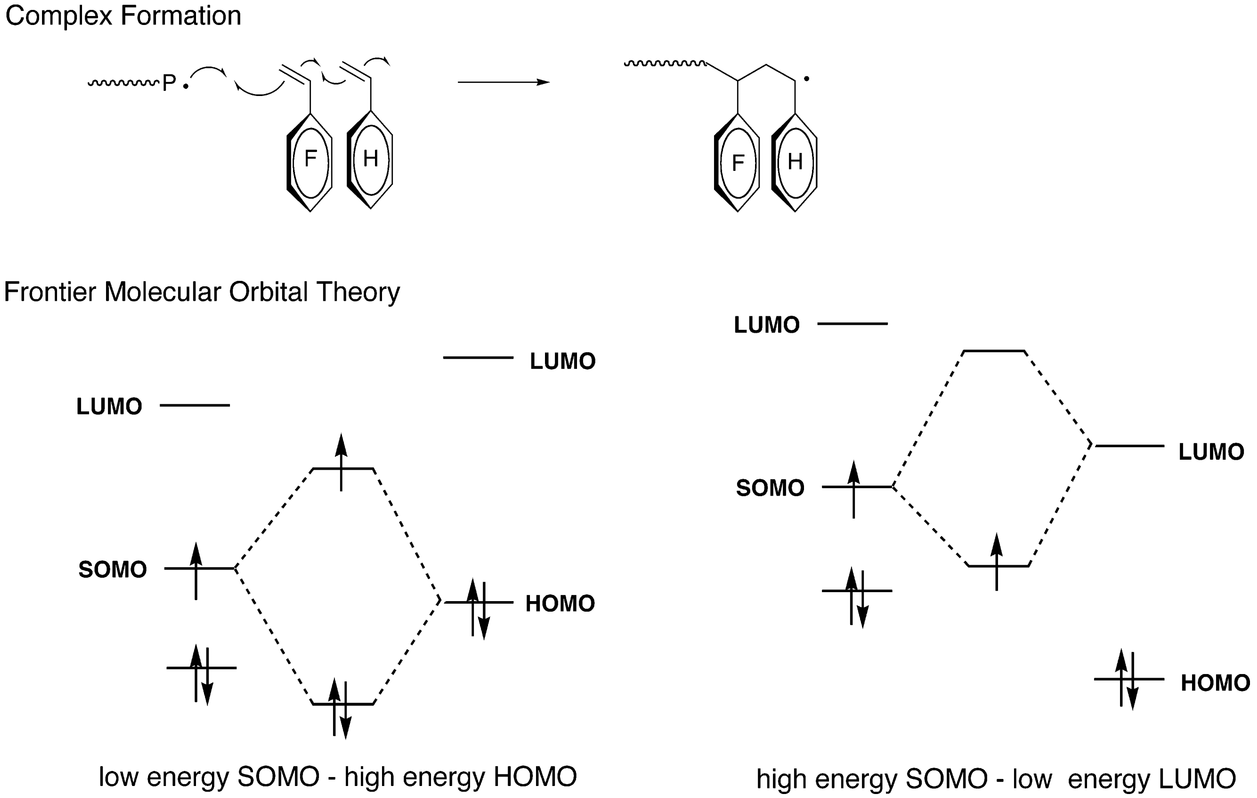
Scheme 1. Two Explanations for Formation of Alternating Copolymers ($r_1 = r_2 = r_1r_2 = 0$) in Free Radical Copolymerizations[a]



[a] LUMO is the lowest unoccupied molecular orbital, HOMO is the highest occupied molecular orbital, and SOMO is the singly occupied molecular orbital.

This paper investigates the free radical copolymerization behavior of styrene (St) with 2,3,4,5,6-pentafluorostyrene (PFS) and 4-fluorostyrene (4FS) as an alternative method for determining the ability of aromatic fluorocarbons to interact with aromatic hydrocarbons, which has the added benefit of generating isolatable new materials that may have some of the desirable properties[23] of typical aliphatic fluoropolymers, such as low surface energy, low refractive index, high optical clarity, and/or high UV, thermal, and chemical stabilities. In particular, the strength of the $\pi-\pi$ stacking interactions between styrenes and fluorinated styrenes may be correlated with their tendency to alternate in free radical copolymerizations. That is, if styrene and the fluorinated styrene form a complex as exemplified in Scheme 1, addition of the two monomers into the growing copolymer should be concerted, thereby generating an alternating copolymer in which the monomer reactivity ratios $r_1 = r_2 = r_1r_2 = 0$ ($r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$; k_{11} and k_{22} are the rate constants of homopropagation; k_{12} and k_{21} are the rate constants of cross-propagation);[24] if styrene and the fluorinated styrene have only weak $\pi-\pi$ stacking interactions or do not interact, their copolymerization behavior should tend toward a random copolymer in which $r_1 = r_2 = r_1r_2 = 1$. Although the tendency of styrene and the fluorinated styrene to alternate should also be consistent with the optimum cross interactions of the frontier molecular orbitals of vinyl monomers substituted with electron-withdrawing (lower energy molecular orbitals) and electron-donating groups (higher energy molecular orbitals) as also shown in Scheme 1,[25] formation of $\pi-\pi$ complexes between comonomer pairs may be detected by a concentration, solvent, and/or temperature dependence of the reactivity ratios[24,26] since copolymerization reactivity ratios (or at least their products[27]) are generally independent of these variables in the absence of complexation or specific interactions involving monomer(s).[28] This paper therefore compares the copolymerization behavior of styrene with fluorinated styrenes at the two extreme levels of fluorination in bulk at different temperatures and in the presence of a solvent.

Experimental Section

Materials. *tert*-Butylperoxy pivalate (Pfaltz and Bauer, 75% solution in mineral spirits), 2,6-di-*tert*-butyl-*p*-cresol (butylated hydroxytoluene, BHT, Aldrich ≥99.8%), dimethylaniline (Aldrich, 99%), [1,3-(diphenylphosphino)propane]nickel(II) chloride ($NiCl_2$(dppp), Strem, 99%), and 1-bromo-4-fluorobenzene (Aldrich, 99%) were used as received. Benzoyl peroxide (BPO, Acros, 85%) was recrystallized from a solution of chloroform and methanol (25:75 v/v) below 25 °C and stored in a freezer at <-10 °C. Magnesium turnings (Acros, 98%) were ground with a mortar and pestle and heated overnight (15 h) in vacuo at temperatures between 100 and 140 °C. 2,3,4,5,6-Pentafluorostyrene (Acros or Oakwood, 97%) and styrene (Aldrich, 98%) were passed through short columns of basic activated alumina (Aldrich, 150 μm mesh size, 58 Å pore size) to remove inhibitor immediately before each (co)polymerization. Vinyl bromide (Aldrich, 95%) was dried by passing it through a drying tube containing calcium chloride and phosphorus pentoxide. Reagent-grade diethyl ether was dried by distillation from purple sodium benzophenone ketyl under N_2. Diglyme (Acros, 99%) was distilled from CaH_2 in vacuo. Synthesis of the poly(2,3,4,5,6-pentafluorostyrene) (PPFS) used for thermal analysis and contact angle measurements was described previously.[29] All other reagents and solvents were commercially available and used as received.

Techniques. All reactions were performed under a N_2 atmosphere using a Schlenk line or a Vacuum Atmospheres drybox unless noted otherwise. Elemental analysis was performed on a PE 2400 Series II CHNS/O Analyzer. Qualitative ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra (δ, ppm) were recorded on a Mercury 300 spectrometer. All ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$, and the resonances were measured relative to residual solvent resonances and referenced to tetramethylsilane. In copolymerizations of PFS and styrene, the monomer conversions were determined by ^{1}H NMR spectroscopy with *n*-butyl acetate as the internal standard from the intensities of the PFS HC*H*= resonance at 6.1 (d) and the styrene HC*H*= resonance at 5.25 ppm (d), relative to that of the CH_2O$_2$C resonance of *n*-butyl acetate at 4.1 ppm (t). The St-PFS copolymer compositions were calculated by determining the area per styrene proton from the sum of its aromatic resonances at 6.6 and 7.1 ppm (broad s), and the area per PFS proton by subtracting the contribution of the three styrene protons from the overlapping styrene and PFS alkyl resonances at 1.3−2.8 ppm; the contribution from the water in the solvent was also subtracted. The mol % yield of the recovered St-PFS polymer was determined from the weight of the recovered copolymer and its composition using eq 1.

$$\% \text{ yield} = \frac{\text{wt of copolymer}}{\left(\text{initial wt of FS} \times \dfrac{\%\text{ FS in copolymer}}{100}\right) + \left(\text{initial wt of St} \times \dfrac{\%\text{ St in copolymer}}{100}\right)} \times 100 \quad (1)$$

In copolymerizations of 4FS and styrene, the monomer conversions were determined by ^{1}H NMR spectroscopy with diglyme as the internal standard from the intensities of the 4FS C*H*= resonance at 5.7 (d) and the styrene C*H*= resonance at 5.9 ppm (d), relative to that of the $-$CH_3 resonance of diglyme at 3.4 ppm (s). The St-4FS copolymer compositions were calculated by determining the area per styrene proton from the aromatic resonance at 7.1 ppm (br s), and the area per 4FS proton by subtracting the contribution of the two styrene protons from the overlapping styrene and 4FS aromatic resonances at 6.1−6.8 ppm. The mol % yield of the recovered St-PFS polymer was determined from the weight of the recovered copolymer and its composition as above using eq 1.

^{19}F NMR (282 MHz) spectra were recorded on either a Mercury 300 or a Gemini 300 spectrometer in either *n*-butyl acetate (using either acetone-d_6 or dimethyl sulfoxide-d_6 to lock the signal) or $CDCl_3$ and referenced to trifluoroacetic acid. Quantitative ^{13}C (97 MHz) NMR spectra were recorded on an INOVA 400 spectrometer in 10 mm probe tubes with 250−300 mg of polymer in 3−4 mL of $CDCl_3$. Gradient heteronuclear single quantum coherence (HSQC) spectra were recorded on an INOVA 400 spectrometer, and nuclear Overhauser effect spectra (NOESY) were recorded on a Unity-INOVA 750 spectrometer.

Molecular weights relative to linear polystyrene were determined by gel permeation chromatography (GPC) from calibration curves of log M_n vs elution volume at 35 °C using tetrahydrofuran (THF) distilled from $LiAlH_4$ as the solvent (1.0 mL/min), a set of 50, 100, 500, and 10^4 Å and linear ($50-10^4$ Å) Styragel 5 μm columns, a Waters 486 tunable UV/vis detector set at 254 nm, and a Waters 410 differential refractometer. A Perkin-Elmer Pyris 1 differential scanning calorimeter was used to determine the glass-transition temperatures (T_gs), which were read as the middle of the change in heat capacity. All heating and cooling rates were 10 °C/min. Transition temperatures were calibrated using indium and zinc or benzophenone standards.

Water contact angles were determined using a Rame Hart NRL-100 contact angle goniometer equipped with an environmental chamber and a tilting base mounted on a vibrationless table (Newport Co.). A 10 μL droplet of deionized water was placed on the surface of a film, and the static contact angle was measured 30 s later. Each reported value is the average of four independent measurements. The sample films were made by spin coating or depositing five drops of a solution of copolymer in toluene ($\leq$2% w/w) on a silicon wafer, evaporating the solvent in air, and drying the film in vacuo at 75 °C for 1 h.

Synthesis of 4-Fluorostyrene. 4FS was synthesized in 31−61% yield as in the following example. A solution of 1-bromo-4-fluorobenzene (50 g, 0.29 mol) in dry diethyl ether (90 mL) was added dropwise over 4 h to a mixture of magnesium (8.0 g, 0.33 mol) and a catalytic amount of iodine, and the reaction mixture was stirred at reflux for 17 h. After cooling to room temperature, the resulting solution was degassed by four freeze−pump−thaw cycles, decanted into the glass sleeve of a Parr reactor in the drybox, and $NiCl_2$(dppp) (0.21 g, 0.39 mmol) and dry diethyl ether (60 mL used to rinse the reaction flask) were added. After removing the assembled Parr reactor from the drybox and purging it with N_2 for approximately 5 min, vinyl bromide (42 g, 0.39 mol) was condensed into the reactor at ≤ -50 °C. The solution was stirred at room temperature for 12.5 h. After purging the solution with N_2 for 1 h and exposing it to air for 2.5 h to remove residual vinyl bromide, it was poured into diethyl ether (300 mL), and aq HCl (10% v/v, 100 mL) was added dropwise over 30 min. The organic layer was separated, washed twice with satd aq $NaHCO_3$ (50 mL) and twice with water (50 mL), and dried over $MgSO_4$. After filtering, BHT was added, the solvent was distilled from the filtrate, and then 21 g (61%) of 4FS was collected as a colorless liquid by trap-to-trap vacuum distillation. ^{1}H NMR: 5.21 (d, HCH_{trans}=), 5.65 (d, HCH_{cis}=), 6.67 (dd, C*H*=), 7.00 (dd, two aromatic H ortho to F), 7.37 (d, two aromatic H meta to F). ^{13}C NMR: 113.4 (CH_2=), 115.5 (two aromatic C3), 128.0 (two aromatic C2), 134.0 (aromatic C1), 135.9 (*C*H), 161.1 and 164.4 (*C*−F).

Homopolymerization of Styrene. Polystyrene (PSt) was synthesized for thermal analysis and comparison to the St-PFS copolymers by first degassing a solution of BPO (70 mg, 0.29 mmol) in styrene (3.0 g, 29 mmol) in a round-bottom glass reactor (7 mL) sealed to a glass tube by four freeze−pump−thaw cycles. The tube was then flame-sealed under vacuum. After stirring in an oil bath at 70 °C for 25 min, the polymerization was quenched by immersing the flask into ice water before breaking the tube. The polymerization mixture was diluted with THF (approximately 5 mL), precipitated in methanol (25 mL), collected, and dried in-vacuo at room temperature to yield 0.35 g (11%) of PSt as a white powder; $M_n = 2.12 \times 10^4$, pdi = 1.89.

PSt (3% yield) was synthesized for comparison of its thermal behavior to that of the St-4FS copolymers using the same procedure except that a different batch of BPO was used and the polymerization time was 30 min; $M_n = 4.93 \times 10^4$, pdi = 1.90.

The PSt (84% yield) used in the blends with P4FS was also synthesized by the same procedure except that a different batch of BPO was used and the polymerization time was 24 h; $M_n = 3.53 \times 10^4$, pdi = 1.85.

Homopolymerization of 4-Fluorostyrene. Poly(4-fluorostyrene) (P4FS, 2% yield) was synthesized from 4FS (1.2 g, 10 mmol) for thermal analysis and comparison to the St-4FS copolymers using the same procedure as in the homopolymerization of styrene except that 0.3 mol % initiator (BPO) was used, the polymerization time was 45 min, and the polymerization was quenched by immersing the flask into liquid N_2 before breaking the tube; $M_n = 5.27 \times 10^4$, pdi = 1.47.

The P4FS (71% yield) used in the blends with PSt was synthesized by the same procedure except that a different batch of BPO was used and the polymerization time was 70 h; $M_n = 8.63 \times 10^4$, pdi = 2.86.

Copolymerization of Styrene and 2,3,4,5,6-Pentafluorostyrene in Bulk at 70 °C. The copolymerizations were performed using comonomer feed compositions of 5−90 mol % styrene and 95−10 mol % PFS as in the following example. After removing a small aliquot for ^{1}H NMR measurement of the monomer/internal standard (*n*-butyl acetate) ratio, a solution of styrene (0.16 g, 1.5 mmol), PFS (0.29 g, 1.5 mmol), BPO (7.3 mg, 30 μmol), and *n*-butyl acetate (5.8 mg, 50 μmol) in a round-bottom reactor (7 mL) sealed to a glass tube was degassed by four freeze−pump−thaw cycles, and then the glass tube was flame-sealed under vacuum. After stirring in an oil bath at 70 °C for 25 min, the copolymerization was quenched by immersing the flask into ice water before breaking the tube. A small aliquot was taken for ^{1}H NMR analysis of the monomer conversions (10 mol % of both). The copolymerization solution was diluted with THF (1 mL) and then precipitated in methanol (15 mL). After storing for 20 h at room temperature, the precipitate was collected in a fritted glass filter and dried in vacuo at room temperature to yield 13 mg (6 mol %) of a white electrostatic solid; $M_n = 4.71 \times 10^4$, pdi = 2.30; 57 mol % styrene, 43 mol % PFS.

Copolymerization of Styrene and 2,3,4,5,6-Pentafluorostyrene in Bulk at Room Temperature. The room-temperature bulk copolymerizations of styrene and PFS were performed as above except that *tert*-butylperoxy pivalate was used as the initiator instead of BPO, the comonomers and internal standard were cooled in an ice bath prior to addition of the initiator, the copolymerization time was 2.5 h, and the precipitated copolymers were stored at <5 °C for 20 h before collecting the precipitate.

Copolymerization of Styrene and 2,3,4,5,6-Pentafluorostyrene in Toluene at 70 °C. The copolymerizations in toluene at 70 °C were performed as in the bulk copolymerizations at 70 °C except that toluene was used as the internal standard, the copolymerization time was 35 min, the copolymerizations were quenched by immersing the flask into liquid N_2 before breaking the tube, and the precipitate generated in methanol was collected almost immediately.

Copolymerization of Styrene and 2,3,4,5,6-Pentafluorostyrene in Toluene at Room Temperature. The room-temperature solution copolymerizations of styrene and PFS were performed as in the bulk copolymerizations at 70 °C except that *tert*-butylperoxy pivalate was used as the initiator instead of BPO, the comonomers and internal standard were cooled in an ice bath prior to addition of the initiator, and the copolymerization time was 3 h.

Copolymerization of Styrene and 2,3,4,5,6-Pentafluorostyrene at Room Temperature under Redox Conditions. The copolymerizations were performed using comonomer feed compositions of 40−90 mol % styrene and 60−10 mol % PFS as in the following example. After removing a small aliquot for ^{1}H NMR measurement of the monomer/internal standard (diglyme) ratios, a solution of styrene (1.9 g, 18 mmol), PFS (0.39 g, 2.0 mmol), BPO (5.8 mg, 24 μmol), and *N*,*N*-dimethylaniline in diglyme (0.67 M, 39 mg, 29 μmol) in a round-bottom reactor (7 mL) sealed to a glass tube was degassed by five freeze−pump−thaw cycles, and then the glass tube was flame-sealed under vacuum. After stirring in an oil bath at 25 °C for 2.5 h, the copolymerization was quenched by immersing the flask into liquid N_2 before breaking the tube. A small aliquot was taken for ^{1}H NMR analysis of the monomer conversions (<1 mol % of both). The copolymerization solution was precipitated in methanol (25 mL), collected in a fritted glass filter, and dried in vacuo at room temperature to yield 37 mg (2 mol %) of a white electrostatic solid; $M_n = 7.10 \times 10^4$, pdi = 2.16; 78 mol % styrene, 22 mol % PFS. 5.8 mg, 24 μmol

Copolymerization of Styrene and 4-Fluorostyrene at 70 °C. The copolymerizations with 4FS at 70 °C were performed as in the bulk St-PFS copolymerizations at 70 °C except that diglyme was used as the internal standard, 0.3 mol % initiator (BPO) was used, the copolymerization time was 30 min, the copolymerizations were quenched by immersing the flask into liquid N_2 before breaking the tube, and the precipitate generated in methanol was collected almost immediately.

Copolymerization of Styrene and 4-Fluorostyrene at Room Temperature. The room-temperature copolymerizations of styrene and 4FS were performed as in the St-PFS copolymerizations at room temperature under redox conditions.

Preparation of Polymer Blends. Blends of PSt and PPFS were prepared as in the following example for an equimolar blend. Polystyrene (20 mg, $M_n = 2.12 \times 10^4$, pdi = 1.89, 0.19 mmol repeat units) and PPFS (37 mg, $M_n = 4.85 \times 10^4$, pdi = 1.68, 0.19 mmol repeat units) were dissolved in THF (5.8 mL) and stirred for 26 h. The solvent was evaporated at atmospheric pressure, and the blend was dried in vacuo to constant weight (two 24 h cycles) to yield 41 mg (87% yield) of the blend.

Blends of PSt and P4FS were prepared as in the following example. Polystyrene (90 mg, $M_n = 3.53 \times 10^4$, pdi = 1.85, 0.86 mmol repeat units) and P4FS (10 mg, $M_n = 8.63 \times 10^4$, pdi = 2.86, 0.082 mmol repeat units) were dissolved in $CDCl_3$ (1.5 mL). The next day the blend was precipitated in methanol (25 mL), collected in a fritted glass filter, and dried in vacuo at ~60 °C to yield 91 mg (90%) of a blend with 87 mol % PSt and 13 mol % P4FS.

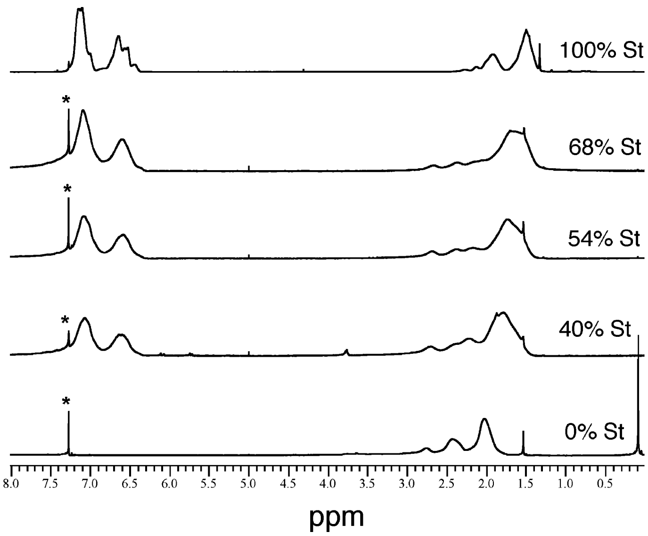
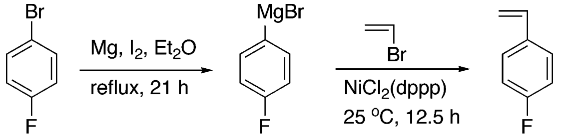


Figure 1. ^{1}H NMR spectra of poly(2,3,4,5,6-pentafluorostyrene), P(St-*co*-PFS) with 40, 54, and 68 mol % St, and polystyrene synthesized by radical (co)polymerization of 2,3,4,5,6-pentafluorostyrene (PFS) and/or styrene (St) in bulk at 70 °C for 25 min using 1 mol % benzoyl peroxide as the initiator; asterisk (*) = $CHCl_3$.

Scheme 2. Synthesis of 4-Fluorostyrene[a]



[a] dppp = 1,3-(diphenylphosphino)propane.

Results and Discussion

Synthesis of 4-Fluorostyrene. Although 4-fluorostyrene is commercially available, we synthesized it much more economically by a nickel-catalyzed Kumada[30] coupling of the Grignard reagent of 1-bromo-4-fluorobenzene with vinyl bromide using $NiCl_2$(dppp) as the catalyst (Scheme 2).

Free Radical Copolymerization Reactivity Ratios. In order to determine the viability of this copolymerization approach for qualitatively measuring the strength of $\pi-\pi$ stacking interactions between aromatic hydrocarbons and aromatic fluorocarbons, we investigated the copolymerization of styrene with fluorinated styrenes at the two extreme levels of aromatic fluorination: 2,3,4,5,6-pentafluorostyrene and 4-fluorostyrene. We first used BPO as the initiator at 70 °C because it is an efficient initiator for PFS,[29] in contrast to azobisisobutyronitrile. For bulk copolymerizations at 70 °C in reactors that were flame-sealed under vacuum, 25 and 30 min was a sufficient amount of time to recover a minimum amount of isolatable St-PFS and St-4FS copolymers, respectively, yet maintain comonomer conversions at ≤10 mol % in order to minimize compositional drift. (Copolymerization of an equimolar mixture of PFS and St at 70 °C for 2 h resulted in 60% monomer conversions.) Both monomer conversions and copolymer compositions were determined by ^{1}H NMR spectroscopy and are listed in Tables S1 and S2 of the Supporting Information for the St-PFS and St-4FS copolymerizations, respectively.

Figure 1 compares the ^{1}H NMR spectra of three of the St-PFS copolymers with those of PSt and PPFS. The alkyl resonances of PPFS[29] are similar to those of free-radically synthesized PSt[31] but shifted downfield by approximately 0.5 ppm, with the CH_2 resonance of PPFS at 2.0 ppm vs 1.5 ppm for PSt, the mr + rr C*H* resonance of PPFS at 2.4 ppm vs 1.9 ppm for PSt, and the mm C*H* resonance of PPFS at 2.75 ppm

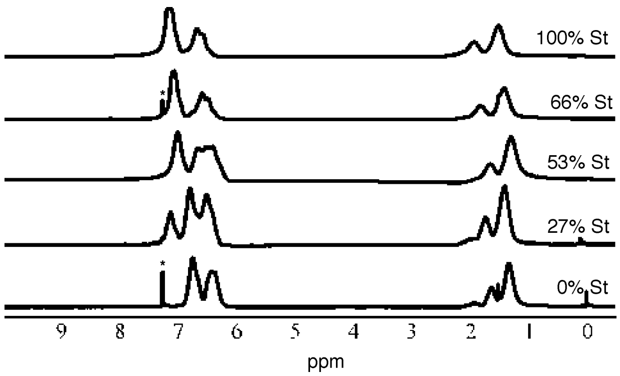


Figure 2. ^{1}H NMR spectra of poly(4-fluorostyrene), P(St-*co*-4FS) with 27, 53, and 66 mol % St, and polystyrene synthesized by radical (co)-polymerization of 4-fluorostyrene (4FS) and/or styrene (St) in bulk at 70 °C for 30 min using 3 mol % benzoyl peroxide as the initiator; asterisk (*) = $CHCl_3$.

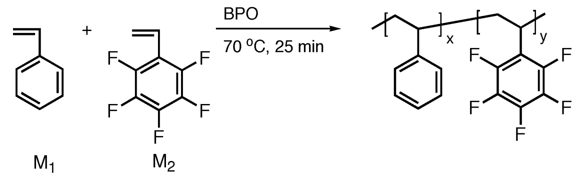
vs a downfield shoulder on the 1.9 ppm resonance for PSt. We determined the styrene content of the St-PFS copolymers from the sum of the integrals of the aromatic resonances at 6.6 and 7.1 ppm, and the PFS content from the integral of the resonances in the alkyl region at 1.3−2.8 ppm after subtracting the contribution of the styrene units from the alkyl region. Many of the St-PFS copolymer compositions determined by ^{1}H NMR spectroscopy were confirmed by elemental analysis (Table S3), as also listed in Table S1.

Figure 2 compares the ^{1}H NMR spectra of three of the St-4FS copolymers with those of PSt and P4FS. The alkyl resonances of P4FS[32] are similar to those of free-radically synthesized PSt[31] but shifted upfield by approximately 0.2 ppm, with the CH_2 resonance of P4FS at 1.3 vs 1.5 ppm for PSt, and the mr + rr CH resonance of P4FS at 1.6 vs 1.9 ppm for PSt. Since the resonance at 7.1 ppm due to the meta and para protons on the aromatic rings of the styrene units is resolved, we determined the styrene content of the St-4FS copolymers from its integral, and the 4FS content from the integral of the aromatic resonances at 6.1−6.8 ppm after subtracting the contribution of the styrene units.

We calculated the monomer reactivity ratios from the copolymer compositions at low comonomer conversions using the Fineman−Ross,[33] Kelen−Tüdos,[34] and nonlinear least-squares[35] methods. The Fineman−Ross equation ($G = r_1F - r_2$) is a rearranged version of the terminal copolymerization equation[36] in which both G ($G = [x(y - 1)]/y$) and F ($F = x^2/y$) are functions of the feed ($[M_1]$, $[M_2]$, $x = [M_1]/[M_2]$) and copolymer compositions ($d[M_1]$, $d[M_2]$, $y = d[M_1]/d[M_2]$).[33] The reactivity ratios calculated from the slope and intercept of the Fineman-Ross plot presented in Figure 3 for the St-PFS copolymerization in bulk at 70 °C are $r_1 = r_{St} = 0.72$ and $r_2 = r_{PFS} = 0.34$ ($r_1r_2 = 0.24$), respectively.

The Kelen−Tüdos equation ($\eta = [r_1 + (r_2/\alpha)]\zeta - (r_2/\alpha)$, in which $\eta = G/(\alpha + F)$ and $\zeta = F/(\alpha + F)$) modifies the Fineman−Ross equation with an arbitrary constant α (typically $\alpha = (F_HF_L)^{1/2}$ in which F_H and F_L are the highest and lowest values of F, respectively) to distribute the data points evenly over the range of the abscissa.[34] The reactivity ratios calculated from the intercepts at $\zeta = 1$ and 0, respectively, of the Kelen−Tüdos plot presented in Figure 3 are $r_1 = r_{St} = 0.64$ and $r_2 = r_{PFS} = 0.27$ ($r_1r_2 = 0.17$). (The calculated parameters for both equations are listed in Table S4 of the Supporting Information.)

In contrast to the Fineman−Ross and Kelen−Tüdos linearization methods, the nonlinear least-squares method uses an iterative procedure to find the pair of reactivity ratios that best fits the experimentally observed copolymer composition as a function of comonomer feed according to the instantaneous copolymerization equation of the terminal model by minimizing the sum of the squares of the differences in the observed and calculated copolymer compositions.[35] It is considered the most statistically correct method for determining reactivity ratios at low conversion.[37] We used the Kelen−Tüdos reactivity ratios as starting values for minimizing the nonlinear least-squares errors in the Mayo−Lewis copolymer composition plots. The reactivity ratios that best fit the Mayo−Lewis plot in Figure 3 for the St-PFS copolymerization in bulk at 70 °C are $r_1 = r_{St} = 0.62$ and $r_2 = r_{PFS} = 0.28$ ($r_1r_2 = 0.17$).



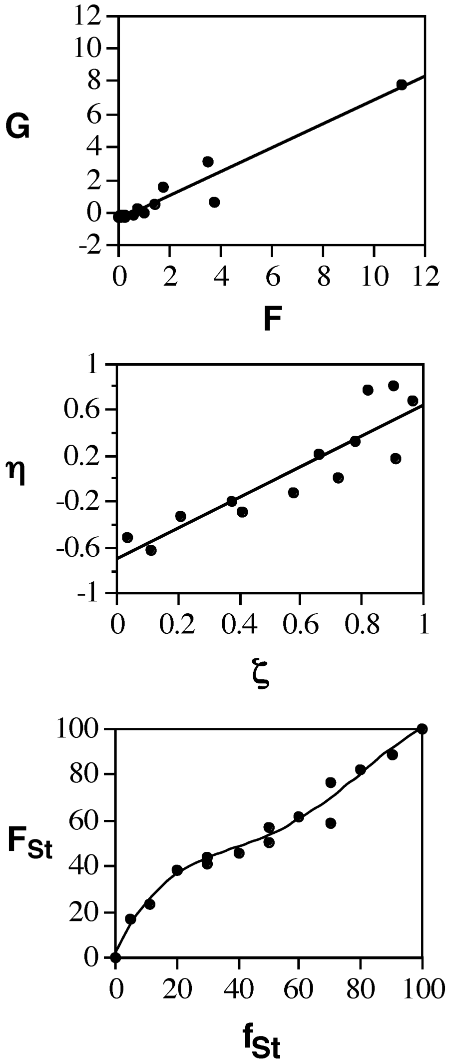


Figure 3. Fineman−Ross (top; $y = 0.717x - 0.345$), Kelen−Tüdos (middle; $y = 1.34x - 0.702$), and Mayo−Lewis (bottom) plots used to determine the monomer reactivity ratios in the radical copolymerization (25 min) of styrene (M_1) and 2,3,4,5,6-pentafluorostyrene (M_2) in bulk at 70 °C using 1 mol % benzoyl peroxide (BPO) as the initiator; f_{St} and F_{St} are the mole fraction of styrene in comomomer feed and copolymer, respectively.

Figure 4 presents the corresponding plots for the St-4FS copolymerization at 70 °C; the calculated parameters for the Fineman−Ross and Kelen−Tüdos plots are listed in Table S5

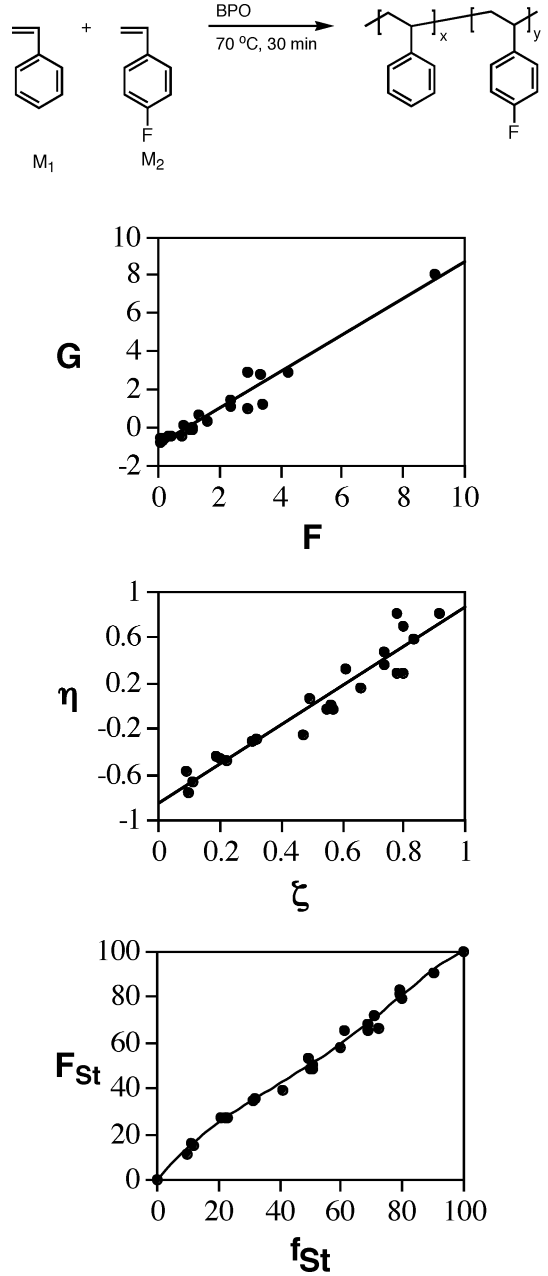


Figure 4. Fineman–Ross (top; $y = 0.961x - 0.853$), Kelen–Tüdos (middle; $y = 1.71x - 0.845$), and Mayo–Lewis (bottom) plots used to determine the monomer reactivity ratios in the radical copolymerization (30 min) of styrene (M_1) and 4-fluorostyrene (M_2) in bulk at 70 °C using 3 mol % benzoyl peroxide (BPO) as the initiator; f_{St} and F_{St} are the mole fraction of styrene in comomomer feed and copolymer, respectively.

of the Supporting Information. In this case, $r_1 = r_{St} = 0.96$ and $r_2 = r_{4FS} = 0.85$ ($r_1r_2 = 0.82$) according to the Fineman–Ross plot, $r_1 = r_{St} = 0.86$ and $r_2 = r_{4FS} = 0.72$ ($r_1r_2 = 0.62$) according to the Kelen–Tüdos plot, and $r_1 = r_{St} = 0.84$ and $r_2 = r_{4FS} = 0.74$ ($r_1r_2 = 0.62$) according to the nonlinear least-squares fit of the Mayo–Lewis plot. The products of the reactivity ratios of 4FS and styrene approach 1 at 70 °C and therefore confirm that the comonomer pair with the minimum level of fluorination approaches a random distribution of comonomer units; these values are the reverse of those cited in the literature.[38] In contrast, the products of the reactivity ratios of styrene and PFS approach zero at 70 °C and therefore confirm that the comonomer pair with the maximum level of fluorination tends to alternate. These results are therefore consistent with PFS and styrene forming $\pi-\pi$ complexes during the copolymerization, in contrast to 4FS and styrene. Nevertheless, as mentioned in the Introduction, the correlation between the tendency to alternate in radical copolymerizations and the known ability of aromatic fluorocarbons to interact with aromatic hydrocarbons by $\pi-\pi$ stacking interactions may be fortuitous and simply the result of the optimum cross interactions of the frontier molecular orbitals of PFS and styrene (Scheme 1).

Table 1. Comonomer Reactivity Ratios (r_{St}, r_{FS}) and Their Products Determined by the Nonlinear Least-Squares Curve-Fitting Method in the Radical Copolymerizations of Styrene (St) with 2,3,4,5,6-Pentafluorostyrene (PFS) and 4-Fluorostyrene (4FS)

	reactivity ratios		
conditions	r_{St}	r_{FS}	$r_{St}r_{FS}$
	St-PFS		
70 °C, bulk	0.62	0.28	0.17
70 °C, toluene	0.47	0.30	0.14
60 °C, bulk[a]	0.43	0.22	0.095
25 °C, bulk	0.22	0.22	0.048
25 °C, toluene	0.30	0.23	0.069
	St-4FS		
70 °C, bulk	0.84	0.74	0.62
25 °C, redox	1.0	0.69	0.69

[a] From ref 39 using azobisisobutyronitrile as the initiator and the Fineman–Ross method of calculation.

In order to try to determine if $\pi-\pi$ complexation influences the St-PFS copolymerization, we investigated the effect of temperature on the St-PFS and St-4FS copolymerizations and the effect of dilution on the St-PFS copolymerization. Table 1 summarizes the nonlinear least-squares reactivity ratios of the St-PFS and St-4FS copolymerizations under different copolymerization conditions using the Mayo–Lewis plots presented in Figures 3, 4, S1 and S2 and the data summarized in Tables S1 and S2 of the Supporting Information; Table S6 summarizes the Kelen–Tüdos reactivity ratios that were used for the starting values for the nonlinear least-squares calculations, and the data used for the Kelen–Tüdos plots (Figures 3, 4, S1, and S2) are summarized in Tables S4 and S5 of the Supporting Information. Table 1 also includes the reactivity ratios reported in the literature for the free radical copolymerization of PFS and styrene at 60 °C using AIBN as the initiator.[39] In bulk, PFS has little tendency to homopropagate ($r_{FS} \approx 0.24$) at 25, 60, or 70 °C, in contrast to styrene whose tendency to homopropagate increases with increasing temperature ($r_{St} = 0.22-0.62$). The consistency of these trends indicates that the difference in the products of the reactivity ratios of PFS and styrene reported in Table 1 is not due to experimental error and that the product of the reactivity ratios varies with temperature. This implies that the strength and/or extent of the $\pi-\pi$ stacking interactions between styrene and PFS decrease with increasing temperature. In contrast, the individual reactivity ratios of styrene and 4FS reported in Table 1 are similar at 25 and 70 °C, and the products of the reactivity ratios therefore do not vary with temperature; the copolymerizations of 4FS and styrene at 25 °C were performed using a redox system[40] of approximately equimolar BPO and *N,N*-dimethylaniline.[41]

The trend in the effect of dilution on the St-PFS copolymerizations is less consistent than that with temperature. Although toluene is an aromatic hydrocarbon that should compete with styrene for $\pi-\pi$ complexation with PFS, r_{PFS} is only slightly higher in the presence of toluene than in bulk at 70 °C, whereas r_{St} is slightly lower in toluene than in bulk, with the product of the two reactivity ratios being similar at 70 °C. At 25 °C, r_{PFS} is the same in bulk and in the presence of toluene, whereas r_{St} is greater in toluene than in bulk with the product of the reactivity ratios being slightly higher in toluene than in bulk.

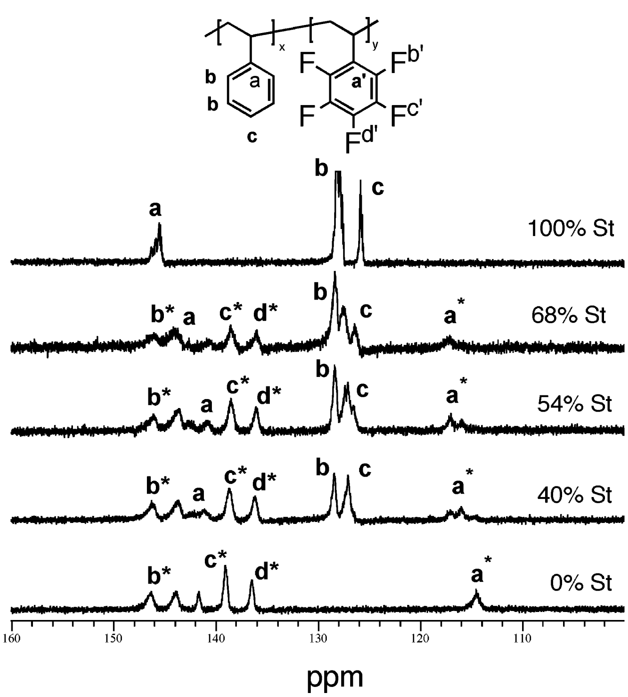


Figure 5. ^{13}C NMR spectra in the aromatic region of poly(2,3,4,5,6-pentafluorostyrene), P(St-*co*-PFS) with 40, 54 and 68 mol % St, and polystyrene synthesized by radical (co)polymerization of 2,3,4,5,6-pentafluorostyrene (PFS) and/or styrene (St) in bulk at 70 °C for 25 min using 1 mol % benzoyl peroxide as the initiator.

NMR Characterization of the Copolymers. Although we used ^{1}H NMR spectroscopy primarily to determine the copolymer compositions, even the ^{1}H NMR spectra of the St-PFS copolymers containing 40%, 54%, and 68% styrene units presented in Figure 1 have unique resonances compared to those of the two homopolymers. These unique resonances are presumably due to the heterodyads of the predominantly alternating comonomer sequences. In particular, the CH_2 resonances (farthest upfield) are positioned between those of the two homopolymers and shift more upfield the higher the styrene content. The aromatic resonances of the copolymers appear at the same positions as those of PSt, although they lack the fine structure exhibited by the homopolymer. In contrast, the alkyl resonances of PSt, P4FS, and their copolymers overlap, as shown by the ^{1}H NMR spectra presented in Figure 2, although the intensities of the resonance at 1.7 ppm are lower than expected based on weighted additions of the spectra of the two homopolymers. The aromatic resonances of the St-4FS copolymers appear as a sum of those of the two homopolymers, albeit with a very slight downfield shift toward the aromatic resonances of polystyrene as the styrene content increases.

Figure 5 shows the aromatic region of the quantitative ^{13}C NMR spectra of the same five St-PFS samples presented in Figure 1. The full ^{13}C NMR spectra are presented in Figure S3 of the Supporting Information; the alkyl regions of the spectra are similar to that of the homopolymer of the more abundant monomer, although the methine resonances are broader in the copolymers. (The compositions determined from the ^{13}C NMR spectra agree very well with those determined by ^{1}H NMR spectroscopy.) All of the aromatic resonances are influenced by the alternating tendency of the sequence distribution in the St-PFS copolymers. In particular, the resonances due to the ipso carbons (*a*) on the styrene units shift upfield, while those of the corresponding carbons (*a′*) on the PFS units shift downfield and either split or appear as more than one resonance. There is also a new resonance appearing between those of the *b* and *c* resonances of the styrene units. In contrast, the ^{13}C NMR spectra of the St-4FS copolymers seem to be simply a sum of the spectra of the two homopolymers (Figure 6).

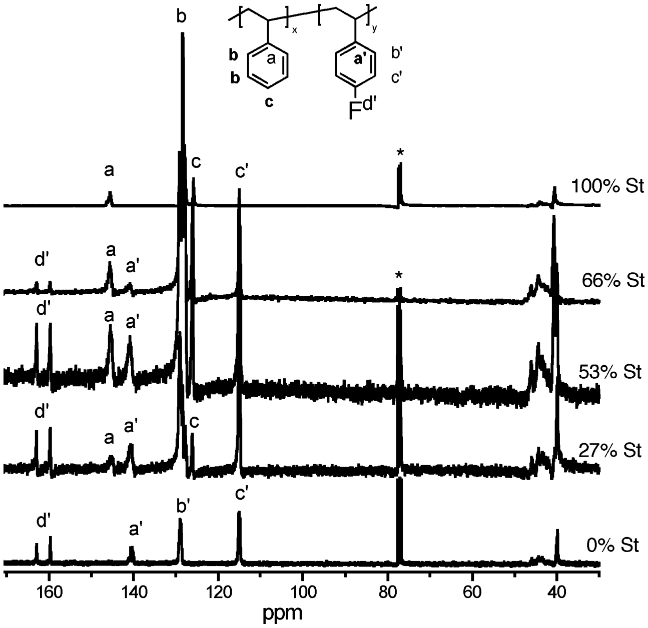


Figure 6. ^{13}C NMR spectra of poly(4-fluorostyrene), P(St-*co*-4FS) with 27, 53 and 66 mol % St, and polystyrene synthesized by radical (co)polymerization of 4-fluorostyrene (4FS) and/or styrene (St) in bulk at 70 °C for 30 min using 3 mol % benzoyl peroxide as the initiator; asterisk (*) = $CHCl_3$.

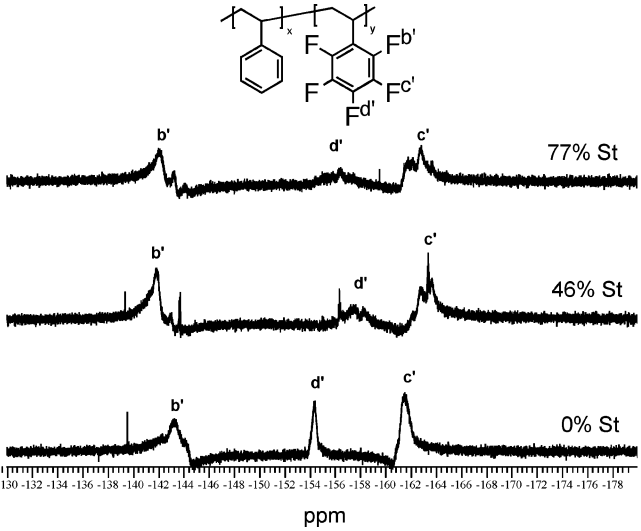


Figure 7. ^{19}F NMR spectra of poly(2,3,4,5,6-pentafluorostyrene) and P(St-*co*-PFS) with 46 and 77 mol % St synthesized by radical (co)polymerization of 2,3,4,5,6-pentafluorostyrene (PFS) and/or styrene (St) in bulk at 70 °C for 25 min using 1 mol % benzoyl peroxide as the initiator.

The ^{19}F NMR resonances of the PFS-St copolymers are also shifted relative to those of the PPFS homopolymer (Figure 7) and appear as split or multiple resonances rather than singlets as with the homopolymer. In contrast, the ^{19}F NMR spectra of the St-P4S copolymers are nearly identical to that of the P4FS homopolymer (Figure 8). The ^{19}F NMR resonance of the P4S-St copolymers shift very slightly upfield (0.8 ppm for the copolymer containing 66 mol % styrene) with increasing styrene content relative to that of the P4FS homopolymer and is slightly broader for the copolymers.

The one-dimensional ^{1}H, ^{13}C, and ^{19}F NMR results therefore confirm that the sequence distributions of the two types of

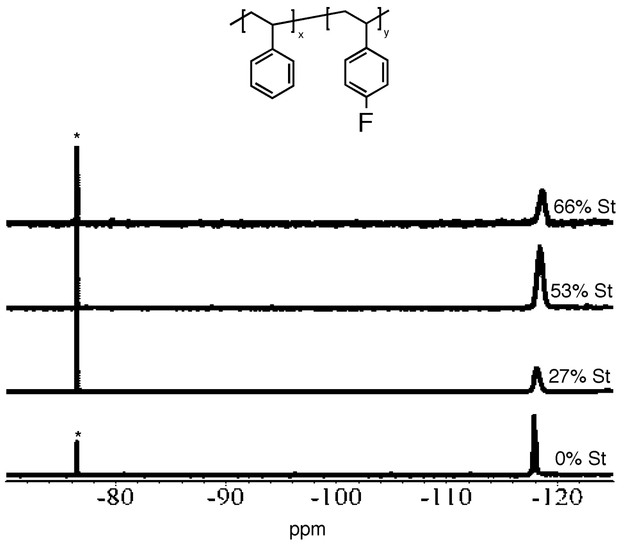


Figure 8. ^{19}F NMR spectra of poly(4-fluorostyrene) and P(St-*co*-4FS) with 27, 53 and 66 mol % St synthesized by radical (co)polymerization of 4-fluorostyrene (4FS) and/or styrene (St) in bulk at 70 °C for 30 min using 3 mol % benzoyl peroxide as the initiator; asterisk (*) = trifluoroacetic acid.

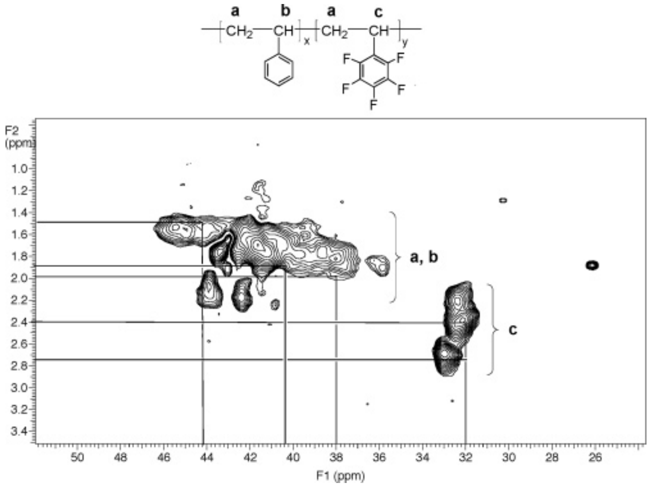


Figure 9. Expanded region of the ^{1}H(F2)$-^{13}$C(F1) gradient heteronuclear single quantum coherence spectrum of poly(styrene-*co*-2,3,4,5,6-pentafluorostyrene) composed of 54 mol % styrene produced by radical copolymerization of styrene and 2,3,4,5,6-pentafluorostyrene for 25 min in bulk at 70 °C using benzoyl peroxide (1 mol %) as the initiator.

copolymers are different, which according to the reactivity ratios are primarily alternating in the St-PFS copolymers and primarily random in the St-4FS copolymers. The alternating tendency of the St-PFS copolymers is further supported by two-dimensional NMR analysis. Figure 9 presents a gradient ^{1}H$-^{13}$C HSQC spectrum, which identifies directly bonded protons and carbons, of the St-PFS copolymer with almost equimolar amounts of styrene and PFS. It includes only the copolymer backbone region of the spectrum, which provides information about the sequence distribution of the styrene and PFS units, and does not include the aromatic region, which corresponds only to C$-$H bonds within the styrene aromatic rings. According to the ^{13}C NMR spectra of PSt and PPFS in Figure S3, the styrene resonances are at 40.4 (CH) and 44.2 ppm (CH$_2$), and the PFS resonances are at 32.0 (CH) and 38.0 ppm (CH$_2$) in the homopolymers. According to the ^{1}H NMR spectra of PSt and PPFS in Figure 1, the styrene resonances are at 1.5 (CH_2) and 1.9 ppm (mr + rr CH, including a downfield shoulder for mm CH), and the PFS resonances at 2.0 (CH_2), 2.4 (mr + rr CH), and 2.75 ppm (mm CH) in the homopolymers. Therefore, the HSQC spectrum of PSt homopolymer or a copolymer with longer sequences of styrene homodyads would have cross-peaks at the intersections of 1.5 and 44.2 (CH_2) and 1.9 and 40.4 ppm (CH). The HSQC spectrum of PPFS homopolymer or a copolymer with longer sequences of PFS homodyads would have cross-peaks at the intersections of 2.0 and 38.0 (CH_2), 2.4 and 32.0 (mr + rr CH), and 2.75 and 32.0 ppm (mm CH). The lack of cross-peaks at these five positions in the HSQC spectrum of the St-PFS copolymer confirms that long sequences of either homodyad are not present in the St-PFS copolymers. Instead, the cross-peaks are shifted, evidently due to the alternating tendency of the two comonomer units.

Figure 10 presents the ^{1}H$-^1$H NOESY spectrum of the same St-PFS copolymer containing almost equimolar amounts of styrene and PFS. This spectrum identifies nonbonded protons that are located within 5 Å of each other with the intensity of the cross-peaks being inversely proportional to the sixth power of the distance between the two nuclei; the diagonal corresponds to the 1-dimensional ^{1}H NMR spectrum, and the areas above and below the diagonal containing the cross-peaks of through-space correlations are symmetric. The three cross-peaks at the intersections of 1.8/2.2, and 1.75/2.5 and 1.8/2.75 ppm correspond to CH_2-CH protons on the backbone and are therefore consistent with CH_2Ar$_F-$CHPh and CH_2Ph$-$CHAr$_F$ heterodyads, respectively. Two cross-peaks also appear at the intersection of 6.6 and 1.75, and 6.6 and 1.6 ppm involving the ortho aromatic protons on styrene and the alkyl protons on the backbone of the copolymer. The similarity of the intensities of the two cross-peaks indicates that the two types of interactions occur with similar frequency and/or that they do not involve one Ar$H-$CH_2 and one Ar$H-$CH interaction. The only other option is that both cross-peaks involve Ar$H-$CH_2 interactions, evidently involving Ar$H-$CH_2Ph correlations within a single styrene repeat unit (6.6/1.6 ppm cross-peak) and Ar$H-$CH_2-Ar$_F$ correlations within a heterodyad (6.6/1.75 ppm cross-peak). The slightly higher intensity of the upfield cross-peak (b') at 6.6/1.6 ppm relative to the downfield cross-peak at 6.6/1.75 ppm (b) is also consistent with the somewhat greater tendency of styrene to homopropagate ($r_{\mathrm{St}} = 0.62$) compared to PFS ($r_{\mathrm{PFS}} = 0.28$) at 70 °C. Therefore, the two-dimensional NMR results are also consistent with the sequence distribution of the St-PFS copolymers being primarily alternating.

Thermal Properties of the Copolymers. One copolymer property that may be influenced by interactions between the two types of repeat units is the glass-transition temperature.[42] Figures 11 and 12 plot the T_gs of the St-PFS and St-4FS copolymers, respectively, as a function of copolymer composition. All of the copolymers exhibit a single glass transition. Since the glass-transition temperature of a copolymer varies with both composition and molecular weight, the difficulty with such plots is choosing the correct homopolymers for comparison. We found that the most reasonable results are obtained using homopolymers produced under exactly the same conditions as the copolymers, including polymerizing for approximately the same amount of time and using initiator that has been similarly aged. The number-average degrees of polymerization and polydispersities of each sample are listed in Tables 2 and 3. Since the St-PFS and St-4FS copolymerizations were performed at different times and for slightly different amounts of time, the molecular weights of the two homopolystyrenes are different. With one exception, the polydispersities of the St-PFS copolymers (pdi = 2.0$-$2.6) are slightly higher than the St-4FS copolymers (pdi = 1.6$-$2.0).

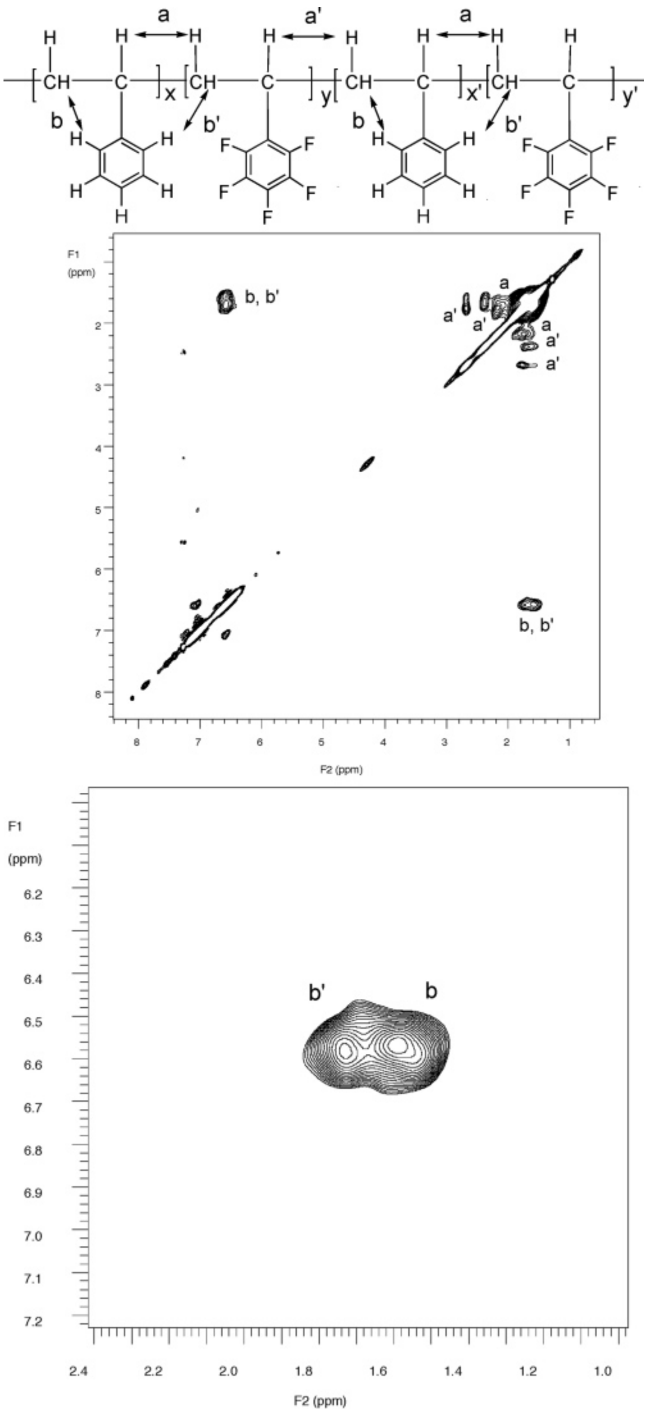


Figure 10. Full and expanded region of the nuclear Overhauser effect spectroscopy spectrum of poly(styrene-*co*-2,3,4,5,6-pentafluorostyrene) with 54 mol % styrene produced by radical copolymerization of styrene and 2,3,4,5,6-pentafluorostyrene for 25 min in bulk at 70 °C using benzoyl peroxide (1 mol %) as the initiator.

The glass-transition temperatures of the St-PFS copolymers (Figure 11) increase with increasing PFS content. With the exception of the copolymers containing small amounts of PFS, the T_gs are elevated relative to the mole-average glass-transition temperatures of the two corresponding homopolymers. This is consistent with stiffening of the copolymer backbone by intramolecular $\pi-\pi$ stacking interactions between alternating aromatic hydrocarbon and aromatic fluorocarbon rings. It is not due to increasing molecular weight with increasing PFS content; for example, the copolymer (21 mol % St) with the highest positive deviation of the glass transition has the lowest molecular weight. Figure 11 also plots the T_gs of blends of the PPFS and PSt homopolymers as a function of composition. Although there are enough intermolecular $\pi-\pi$ stacking interactions for the two homopolymers to be miscible, they are not strong enough or frequent enough to elevate the T_g relative to the mole-average values.

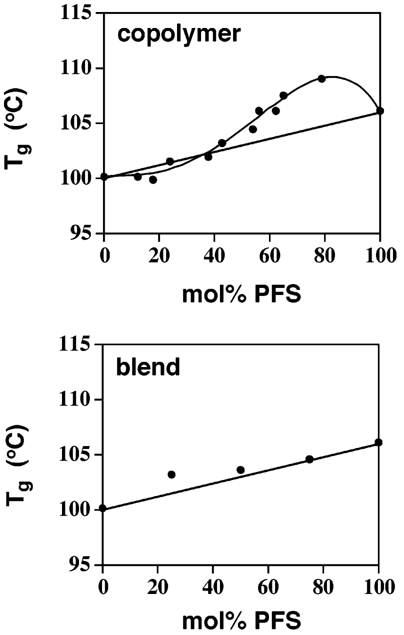


Figure 11. Comparison of the glass-transition temperatures of poly(styrene-*co*-2,3,4,5,6-pentafluorostyrene) copolymers (top) produced by radical copolymerization of styrene and 2,3,4,5,6-pentafluorostyrene (PFS) for 25 min in bulk at 70 °C using benzoyl peroxide (1 mol %) as the initiator and blends of the corresponding homopolymers (bottom) as a function of composition.

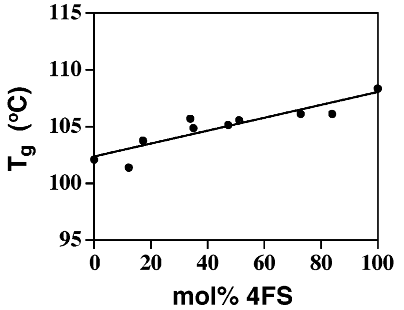


Figure 12. Glass-transition temperatures of poly(styrene-*co*-4-fluorostyrene) copolymers produced by radical copolymerization of styrene and 4-fluorostyrene (4FS) for 30 min in bulk at 70 °C using benzoyl peroxide (3 mol %) as the initiator as a function of composition.

In contrast to the St-PFS copolymers, the glass-transition temperatures of the St-4FS copolymers (Figure 12) are represented by their mole-average values, which is consistent with both the random distribution of comonomer units and weak or no $\pi-\pi$ stacking interactions between the two types of aromatic rings. Also in contrast to the blends of PSt and PPFS, the blends of PSt and P4FS are immiscible (Table S7) as reported previously.[43] This further demonstrates that the $\pi-\pi$ stacking interactions between the two types of aromatic rings are weak or nonexistent.

Surface Properties of the Copolymers. As discussed in the Introduction, the fluorinated copolymers may have one or more of the desirable properties typical of polymers based on aliphatic fluorocarbons, including low surface energies, which can be measured indirectly using water contact angles (θ_c).[44] Figure 13 plots the water contact angles summarized in Table S8 for toluene-cast films of the St-PFS and St-4FS copolymers. The

Table 2. Molecular Weight and Thermal Characterization of the Copolymers Produced by Radical Copolymerization of Styrene (St) and 2,3,4,5,6-Pentafluorostyrene for 25 min in Bulk at 70 °C Using Benzoyl Peroxide (1 mol %) as the Initiator[a]

mol% St in comonomer feed	mol% St in copolymer	GPC $M_n \times 10^{-4}$	GPC DP_n	GPC pdi	T_g (°C)
100	100	2.12	204	1.89	100.1
90	88	5.70	517	2.17	100.1
80	82	3.92	345	2.40	99.8
70	76	4.32	369	2.04	101.4
60	62	3.74	296	2.05	101.9
50	57	4.71	362	2.30	103.1
40	46	6.92	500	2.13	104.4
30	44	5.20	370	2.40	106.0
20	38	6.40	440	2.23	106.1
10	35	4.70	316	2.60	107.5
5	21	4.40	260	2.61	108.9
0	0	4.85	250	1.68	106.0

[a] Number-average molecular weights (M_n), number-average degrees of polymerization (DP_n), and polydispersities (pdi = M_w/M_n) measured by gel permeation chromatography (GPC) in tetrahydrofuran relative to linear polystyrene using the mean of the refractive index and UV detectors; glass-transition temperature (T_g) determined by differential scanning calorimetry as the mean of values from the second and third heating scans at 10 °C/min; copolymer composition determined by ^{1}H NMR analysis of the copolymer after removing unreacted monomers by precipitating the copolymer.

Table 3. Molecular Weight and Thermal Characterization of the Copolymers Produced by Radical Copolymerization of Styrene (St) and 4-Fluorostyrene for 30 min in Bulk at 70 °C Using Benzoyl Peroxide (3 mol %) as the Initiator[a]

mol% St in comonomer feed	mol% St in copolymer	GPC $M_n \times 10^{-4}$	GPC DP_n	GPC pdi	T_g (°C)
100	100	4.93	473	1.90	102.0
90	88	5.02	474	1.62	101.3
79	83	4.30	403	3.10	103.7
72	66	4.55	415	1.87	105.6
69	65	3.79	345	1.97	104.8
49	53	3.53	316	1.79	105.1
51	49	4.22	375	1.94	105.5
23	27	2.70	231	1.68	106.0
11	16	3.78	318	1.63	106.0
0	0	5.27	432	1.47	108.3

[a] Number-average molecular weights (M_n), number-average degrees of polymerization (DP_n), and polydispersities (pdi = M_w/M_n) measured by gel permeation chromatography (GPC) in tetrahydrofuran relative to linear polystyrene using the mean of the refractive index and UV detectors; glass-transition temperature (T_g) determined by differential scanning calorimetry as the mean of values from the second and third heating scans at 10 °C/min; copolymer composition determined by ^{1}H NMR analysis of the copolymer after removing unreacted monomers by precipitating the copolymer.

water contact angles of the St-PFS copolymers are higher than those of the St-4FS copolymers due to the greater hydrophobicity of the PFS units. In both cases, the water contact angles increase linearly with increasing amount of the fluorinated comonomer. However, there is little difference between the water contact angles of polystyrene and the fluorinated polystyrene. We therefore measured ethylene glycol contact angles of the St-PFS copolymers since ethylene glycol contact angles are more dependent on chemical composition. Figure 13 confirms that the contact angles of the copolymers are linear functions of the molar copolymer compositions.

Conclusions

The monomer reactivity ratios from free radical copolymerizations of styrene and 2,3,4,5,6-pentafluorostyrene indicate that this comonomer pair tends to alternate, whereas the copolymerization of styrene with 4-fluorostyrene tends to form a random copolymer. The ^{1}H, ^{13}C, and ^{19}F and two-dimensional NMR results confirm that the sequence distributions of the two types of copolymers are different. Although formation of $\pi-\pi$ complexes apparently contributes to the alternating tendency of styrene and PFS as detected by a slight variation of the monomer reactivity ratios with temperature, the lack of a diluent and/or solvent effect on the reactivity ratios indicates that the contribution of $\pi-\pi$ complexation is small and that the tendency to alternate is primarily due to the influence of the aromatic rings on the frontier molecular orbitals of the vinyl groups. Regardless of the reason for formation of an alternating copolymer, the tendency of styrene and fluorinated styrenes to alternate in free radical copolymerizations *correlates* with the strength and/or extent of their $\pi-\pi$ stacking interactions when considering the two extreme levels of fluorination using 2,3,4,5,6-pentafluorostyrene and 4-fluorostyrene. In addition, the elevation of the glass-transition temperatures of the St-PFS copolymers relative to their mole-average values and the miscibility of the corresponding homopolymer blends also demonstrate that the two types of aromatic rings form strong $\pi-\pi$ stacking interactions compared to those of the St-4FS copolymers, which have glass transitions at the mole-average temperatures and immiscible homopolymer blends. Therefore, the free radical copolymerization behavior and thermal behavior of the resulting copolymers and blends of fluorinated and nonfluorinated styrene derivatives can be used to qualitatively evaluate the strength and/or extent of $\pi-\pi$ stacking interactions between aromatic fluorocarbons and aromatic hydrocarbons. In contrast, the water and ethylene glycol contact angles of the copolymers are linear functions of the molar copolymer composition regardless of the strength and/or extent of $\pi-\pi$ stacking interactions.

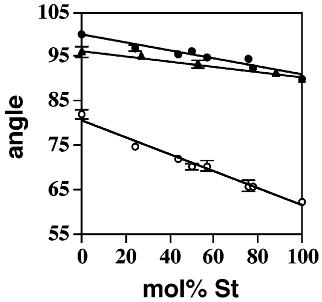


Figure 13. Comparison of the mean water (solid symbols) and ethylene glycol (open symbols) contact angles of poly(styrene-*co*-2,3,4,5,6-pentafluorostyrene) copolymers (circles) and poly(styrene-*co*-4-fluorostyrene) copolymers (triangles) as cast from toluene on a silica surface and dried for 1 h at 75 °C; error bars represent the standard deviations from four replications per sample. The copolymers were produced by radical copolymerization in bulk at 70 °C using benzoyl peroxide (1−3 mol %) as the initiator as a function of composition.

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Supporting Information Available: Tabulated copolymer compositions, copolymerization results, and data used to determine copolymer reactivity ratios by the Fineman–Ross, Kelen–Tüdos, and nonlinear least-squares methods from the St-PFS and St-4FS copolymerizations; tabulated reactivity ratios determined by the Kelen–Tüdos method and used as the starting values for minimizing the nonlinear least-squares errors in the copolymer compositions as a function of comonomer feed composition for the St-PFS and St-4FS copolymerizations; tabulated glass-transition temperatures of PSt-P4FS blends; tabulated water and ethylene glycol contact angle measurements of St-PFS and St-4FS copolymers; additional Kelen–Tüdos and Mayo–Lewis plots for the St-PFS copolymerizations; additional Fineman–Ross, Kelen–Tüdos, and Mayo–Lewis plots for the St-4FS copolymerizations; and full ^{13}C NMR spectra of St-PFS copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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