A Novel Poly(*p*-phenylene) Containing Alternating Poly(perfluorooctylethyl acrylate-*co*-methyl methacrylate) and Polystyrene Grafts by Combination of Atom Transfer Radical Polymerization and Suzuki Coupling Processes

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ABSTRACT: A poly(*p*-phenylene) (PP), carrying perfectly alternating, well-defined poly(perfluorooctylethyl acrylate-*co*-methyl methacrylate) [P(FEA-*co*-MMA)] and polystyrene (PS) side chain grafts, was synthesized by the combination of atom transfer radical polymerization (ATRP) and Suzuki cross-coupling processes. First, dibromobenzene and diboronic ester functional macromonomers of P(FEA-*co*-MMA) and PS, respectively, were prepared by ATRP. In the second step, PP with lateral alternating P(FEA-*co*-MMA) and PS chains was synthesized by a Suzuki coupling reaction in the presence of Pd(PPh₃)₄ catalyst. The wetting behavior of the polymers was studied by

INTRODUCTION Conjugated polymers have been widely studied for application in devices such as light emitting diodes,^{1,2} field effect transistors,^{3,4} solar cells,^{5,6} solid-state lasers,⁷ chemical and biomolecular sensors.^{8,9} Among them, poly(p-phenylene)s (PPs) have been extensively studied due to the excellent mechanical properties and thermo-oxidative stability. They are some of the potentially most useful polymers for organic conducting materials and organic polymeric ferromagnets because of their extended planar conjugated π system, along with high strength and high heat resistance. Current methodologies for the direct synthesis of various PPs are primarily based upon nickel¹⁰⁻¹⁶ and palladiummediated^{17,18} cross-coupling reactions largely due to their preservation of regiochemistry and nearly quantitative yields. Palladium mediated cross-coupling, known as Suzuki-Miyura coupling reaction,¹⁹ has become a common synthetic way for formation of carbon-carbon bond because of mild reaction conditions, high functional groups tolerance, stability, easy to handling, and low toxicity of organoboron coupling patterns. Although both catalysts have been widely used, nickel has a

measurements of the static contact angle θ of thin films (200–400 nm thickness) using water and *n*-hexadecane as wetting liquids. The obtained fluorinated PP showed high static contact angles with both interrogating liquids, exhibiting simultaneously hydrophobic ($\theta_w = 111^\circ$) and lipophobic ($\theta_h = 67^\circ$) properties. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2012

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growing interest as more available, economical and environmental friendly catalyst.²⁰ Percec et al. have reported several examples using nickel catalyst for the preparation of alternating PPs via the homocoupling of readily available phenol derivatives with high reaction yield.^{21–25}

The solubility problem of PPs in many organic solvents causes limited processability. Therefore, attachment of conformationally mobile alkyl side chains to the backbone has been usually applied strategy for the controlled synthesis of soluble and processable PPs with high molecular weight.^{26–29} Besides, incorporation of fluorinated alkyl groups into PPs significantly increases reaction yield by increasing solubility.³⁰ In addition to a series of functionalized PPs with pendant alkyl groups, the synthesis of PP graft copolymers³¹ by using the macromonomer technique via controlled polymerizations, such as atom transfer radical polymerization (ATRP)^{32–35} or ring opening polymerization (ROP),^{36–40} was reported.

Polymers containing a pendant perfluoroalkyl group have unique properties⁴¹ such as low friction coefficient, low

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surface energy, hydrophobicity, self-organization, chemical inertness, and thermal resistance. They have been explored in the field of electronics due to low dielectric properties and have also attracted much attention as optical materials because of low refractive index and high transmittance.^{42–44} Incorporation of fluorine and perfluorocarbon units into polymers has normally been achieved by polymerizations of fluorine-containing monomers.^{45–50} Alternatively, fluorine atoms can be incorporated into preformed polymers by postmodification through functional groups by using various organic reactions.⁵¹ Recently, many copolymerizations of fluorine-containing (metha)acrylates with nonfluorinated acrylates using controlled polymerization methods, including ATRP,^{48,52–54} have been reported.

The combination of unique characteristics of fluorine and specific properties of conjugated polymers can also lead to the development of new fluorinated conducting polymers^{55,56} exhibiting superior performance because of their enhanced chemical environment stability in addition to their existing intrinsic electronic and optical properties.

Herein, we describe synthesis of a novel PP copolymer, consisting of poly(perfluorooctylethyl acrylate-*co*-methyl methacrylate) [P(FEA-*co*-MMA)] and polystyrene (PS) alternating side chain grafts by the Suzuki polycondensation reaction of the respective aryl diboronic acid diester and aryl dihalide macromonomers. It was expected that chemical incompatibility of the fluorocarbon polymer grafts with both hydrocarbon polymer grafts and main chain backbone could result in a microphase separated system. The soluble luminescent polymer could also be processed to form nonwetting low surface tension films.

EXPERIMENTAL

Materials

Perfluorooctyletyl acrylate (FEA, 97% Fluorochem), (MMA, 99%, Aldrich), Styrene (S, 99%, Aldrich) was passed through basic alumina column to remove the inhibitor. 2,5-Dibromotoluene (98%, Aldrich), *N*-bromosuccinimide (NBS, 99%, Merck), *n*-butyl lithium (*n*-BuLi, 2.5*M* solution in hexane, Acros), trimethylborate (\geq 99%, Merck), 1,3-propanediol (\geq 99%, Fluka), NaHCO₃ (Aldrich), Pd(PPh₃)₄ (Merck), benzoyl peroxide (Aldrich), CuBr (98%, Acros), 2,2-bipyridine (bpy, \geq 99% Acros), and silicagel 90 (Fluka, 0.2–0.5 mm) were used as received. CCl₄ was distilled over phosphorus pentoxide, and stored over 4 Å molecular sieves. Hexane was distilled over sodium wire. Tetrahydrofuran (THF) was dried over potassium hydroxide, distilled over sodium wire, and then distilled over benzophenone.

Synthesis of 1,4-Dibromo-2-(bromomethyl)benzene (1)

2,5-Dibromotoluene, (5.0 g, 20 mmol), NBS (3.91 g, 22 mmol), and benzoyl peroxide (0.096 g, 0.40 mmol) were heated under reflux in 20 mL of CCl₄ under nitrogen for 4 h. The reaction mixture was filtered to remove succinimide. Succinimide was washed with a supplementary amount of CCl₄ and finally with a little quantity of CH₂Cl₂. The combined organic solutions were washed several times with

water and than dried over MgSO₄. The solvent was removed by rotary evaporator. The product was purified by passing through a silica gel column using diethyl ether as eluent. Finally, the product was obtained as white crystals after recrystallizing twice from petroleum ether. Yield: 38%, m.p: 89° C. ¹H NMR (CDCI₃): 4.51 (s, 2H, CH₂Br), 7.25 (1H, aromatic), 7.35 (1H, aromatic), 7.58 (1H, aromatic).

IR (cm⁻¹): 3053-2950 (aromatic and aliphatic CH stretching), 1488-1455 (aromatic C=C stretching), 1380, 1270-951 (C—H bending), 885, 876, 815, 719, 616.

Synthesis of Benzene-2-methyl-1,4-bis(boronic acid)

2,5-Dibromotoluene (21.74 g, 87 mmol) was dissolved in 140 mL of *n*-hexane and refluxed for 2 h under nitrogen. The solution was allowed to cool down to room temperature for 30 min. The reaction mixture was then cooled to -78° C, and n-BuLi (96 mL, 238 mmol) was added at that temperature. The solution was stirred for an additional 1 h at -80° C, and then was allowed to reach slowly to room temperature in 3 h. After stirring at room temperature for 12 h, the solution was heated to reflux temperature under nitrogen for 2 h. The solution was cooled down one more time to room temperature for 30 min and then to -78° C, followed by adding trimethylborate (100 mL, 870 mmol). The solution was allowed to warm up to room temperature for 3 h before the reaction was guenched with the addition of 2M HCl. The two phases were separated, and the water phase was extracted with four portions of diethyl ether and then dried over MgSO₄ and evaporated to yield the boronic acid as a white solid, which was used without further purification. Yield: 50%.

¹H NMR (CDCI₃): 2.29 (3H, CH₃), 7.38 (1H, aromatic), 7.56 (1H, aromatic), 7.73 (1H, aromatic) 7.90 (bs, 4H, OH).

IR (cm⁻¹): 3202 (OH stretching of B(OH)₂ as a broad peak overlap with stretching of aromatic CH), 2980 (aliphatic CH), 1488 (aromatic C=C stretching), 1446 (vibration of Ph-B bond), 1388 (stretching of B–O in B(OH)₂), 1321 and 1110 (vibration of the bond B–O and B–OH), 1023, 699.

Synthesis of Benzene-2-methyl-1,4-bis(boronic acid) 1,3-propanediol Diester

1,3-Propanediol (10.5 mL, 146 mmol) and 10.85 g benzene-2-methyl-1,4-bis(boronic acid) were refluxed in dry benzene (200 mL) for 6 h under nitrogen using a Dean-Stark trap. The reaction mixture was washed several times with water and then dried over MgSO₄. The solvent was removed in vacuo to afford a light yellow solid that was recrystallized from hexane. Yield: 18%. m.p.: 116°C.

¹H NMR (CDCI₃): 1.99–2.08 (t, 4H, 0–CH₂–*CH*₂–CH₂–O), 4.13–4.17 (t, 8H, 0–*CH*₂–*CH*₂–*CH*₂–O), 2.37 (s, 3H, CH₃), 7.50 (s, 1H, aromatic), 7.65 and 7.68 (2H, aromatic).

IR (cm⁻¹): 3053–3019 (aromatic CH stretching), 2955–2926 (aliphatic —CH stretching), 1483 (aromatic C=C stretching), 1421 (vibration of Ph-B bond), 1392, 1372 (B=O in B(OCH₂)₂), 1297, 1198, 1157, 1128, 1113 (C=O stretching), 1033, 1005, 925, 903, 724, 688.

Synthesis of Benzene-2-bromomethyl-1,4-bis(boronic acid) propanediol Diester (2)

Benzene-2-bromomethyl-1,4-bis(boronic acid) propanediol diester was synthesized according to a modified literature procedure.⁵⁷ Benzene-2-methyl-1,4-bis(boronic acid) propanediol diester (1.79 g, 6.9 mmol), NBS (1.48 g, 8.3 mmol), and benzoyl peroxide (0.033 g, 0.14 mmol) were heated at reflux in 15 mL of CCl₄ under nitrogen for 24 h. The reaction mixture was filtered to remove succinimide and washed with little amount of CCl₄ and CH₂Cl₂. The combined organic solutions were washed several times with water and then dried over MgSO₄. The solvent was removed by rotary evaporator. The product was purified by passing through a silica gel column using diethyl ether as eluent. Finally, the product was obtained as white crystals after recrystallizing twice from diethyl ether. Yield: 30%.

¹H NMR (CDCI₃): 2.02–2.10 (m, 4H, 0–CH₂–CH₂–CH₂–O), 4.12–4.20 (m, 8H, 0–*CH*₂–CH₂–*CH*₂–O), 4.89 (s, 2H, –*CH*₂–Br), 7.51 (bs, 1H aromatic), 7.64 (1H aromatic), 7.73 (1H aromatic).

IR (cm⁻¹): 3064 (aromatic CH stretching), 2956–2895 (aliphatic CH stretching), 1481(aromatic C=C stretching), 1425 (vibration of Ph-B bond), 1393 (vibration of B-O), 1313–1150 (stretching of C=O linkages), 1097, 1023, 928, 822, 798, 724, 687, 653.

Preparation of Polystyrene Macromonomer by ATRP

A Schlenk tube was charged with CuBr (0.039 g, 0.28 mmol), bipyridine (0.13 g, 0.83 mmol), benzene-2-bromomethyl-1,4-bis(boronic acid) propanediol diester as initiator (0.090 g, 0.28 mmol), and styrene (2.48 g, 23.82 mmol). Three freeze-pump-thaw cycles were performed and the polymerization was let to proceed under stirring at 110°C for 50 min. After the given time, the mixture was diluted with THF and passed through a neutral alumina column to remove copper complex following by rotary evaporation of THF. The polymer was precipitated in methanol and the solid was collected after filtration and dried at room temperature in a vacuum overnight (32%, $M_{n, NMR} = 8250$, $M_{n, GPC} = 9150$, $M_w/M_n = 1.40$).

¹H NMR (CDCI₃): 1.17–2.26 (aliphatic of PS, O–CH₂ –*CH*₂–CH₂–O, Ar–*CH*₂), 4.13 (O–*CH*₂–CH₂–*CH*₂–O), 4.47 (Ph*CH*-Br), 6.47–6.57 (aromatic of PS), 7.04–7.46 (aromatic of PS).

IR (cm⁻¹): 3059–3026 (aromatic CH stretching), 2924–2849 (aliphatic CH stretching), 1944–1601 (out-of-plane C—H deformation), 1583, 1493, 1452 (aromatic C=C stretching), 1370, 1262, 1181, 1154, 1070, 1027, 907, 840, 802, 756.

Preparation of Poly(perfluorooctylethyl acrylate-*co*-methyl methacrylate) [P(FEA-*co*-MMA)] Macromonomer by ATRP

CuBr (0.037 g, 0.26 mmol), bipyridine (0.081 g 0.52 mmol), 1,4-dibromo-2-(bromomethyl)benzene as initiator (0.087 g, 0.26 mmol), (perfluorooctylethyl acrylate (2.53 mL, 8.01mmol), methyl methacrylate (MMA) (2 mL, 18.70 mmol) and toluene (5 mL) were introduced in a Schlenk tube, and

the reaction mixture was degassed by three freeze-pumpthaw cycles and left in vacuo. The tube was placed at 90°C in an oil bath and stirred for 90 min. Then the mixture was diluted with THF, and passed through an alumina column to remove the copper catalyst. Precipitation of the polymer was performed in a 10-fold volume of heptane. The solid was then collected after filtration (16%, $M_{\rm n, NMR} = 21,640$, $M_{\rm n, GPC} = 18,200$, $M_{\rm w}/M_{\rm n} = 1.49$).

¹H NMR (CDCI₃): 0.8–2.2 (backbone protons), 2.47 (COO– $CH_2-CH_2-CF_2$), 3.57 (COO CH_3), 4.26 (bs, COO– $CH_2-CH_2-CF_2$), 6.92–7.33 (aromatic protons).

IR (cm⁻¹): 2997, 2943 (aromatic and aliphatic CH stretching), 1727 (C=O stretching), 1477, 1450, 1435, (aromatic C=C stretching), 1236–1144 (C–F vibration), 653 (CF₂ wagging).

Synthesis of Poly(p-phenylene) by Suzuki Polycondensation Reaction

A round-bottom-flask equipped with a condenser, a septum nitrogen inlet-outlet, and magnetic stirrer, was charged with 20 mL 1*M* of NaHCO₃ and 30 mL THF. The solvents were previously degassed by bubbling nitrogen over a period of 30 min. The mixture was refluxed under nitrogen for 3 h. A 20 mL three neck round-bottom-flask equipped in the same way as the previous one was charged under inert atmosphere with PS macromonomer (0.10 g, 0.012 mmol), P(FEA-co-MMA) macromonomer (0.26 g, 0.012 mmol) and Pd(PPh₃)₄ (1.0 mg, 8.64 \times 10^{-4} mmol). Three milliliter of the mixture of solvents was introduced with a syringe through the septum. The reaction was maintained under vigorous stirring and with the exclusion of oxygen and light at reflux. After 48 h, supplementary amount (5 mL) of solvent mixture was added through the septum and stirred additional for 24 h. The polymer was obtained by precipitation in methanol (44%, $M_{\rm n, GPC} = 36,000, M_{\rm w}/M_{\rm n} = 2.46$).

¹H NMR (CDCI₃): 0.82–1.80 [aliphatic of PS and P(FEA-*co*-MMA)], 2.47 [C(0)0–CH₂– CH_2 –CF₂ of P(FEA-*co*-MMA)], 3.57 [CO0*CH*₃ of P(FEA-*co*-MMA), 4.26 (COO– CH_2 of P(FEA-*co*-MMA)], 7.20–6.56 (aromatic of PS and PP).

IR (cm⁻¹): 3019, 2918, 2849 (aromatic and aliphatic CH stretching), 1731 (C=0 stretching), 1600, 1488–1435, (aromatic C=C stretching), 1236–1146 (C-F vibration), 699 (CF₂ wagging).

¹⁹F NMR (CDCl₃/CF₃COOH): δ (ppm) = -6 (3F, CF₃), -38 (2F, CF₂CH₂), -45 to -48 (10F, CF₂), -51 (2F, CF₂CF₃).

Characterization

¹H NMR spectra of 5–10% (w/w) solutions in CDCl₃ with Si(CH₃)₄ as an internal standard were recorded at room temperature at 250 MHz on a Bruker DPX 250 spectrometer. ¹⁹F NMR spectra were recorded with a Varian Gemini VRX300 spectrometer on CDCl₃ using CF₃COOH as an internal standard. Gel permeation chromatography (GPC) measurements were obtained from a Viscotek GPCmax Autosampler system consisting of a pump, a Viscotek UV detector and Viscotek a differential refractive index (RI) detector. Three ViscoGEL



GPC columns (G2000H_{HR}, G3000H_{HR}, and G4000H_{HR}), (7.8 mm internal diameter, 300 mm length) were used in series. The effective molecular weight ranges were 456-42,800, 1050-107,000, and 10,200-2,890,000, respectively. THF was used as an eluent at flow rate of 1.0 mL min⁻¹ at 30°C. Both detectors were calibrated with PS standards having narrow molecular weight distribution. Data were analyzed using Viscotek OmniSEC Omni-01 software. Molecular weights were calculated with the aid of PP standards. FTIR spectra were recorded on a Perkin-Elmer FTIR Spectrum One B spectrometer. UV spectra were recorded on a Shimadzu UV-1601 spectrometer for 4.84 $\times~10^{-5}$ mol L^{-1} polymer solutions in CH₂Cl₂ Fluorescence measurements were carried out using a Hitachi F-4500 fluorescence spectrophotometer and the excitation and emission spectra of PP were recorded in CH₂Cl₂ at room temperature. Emission spectrum was obtained with a maximum at 351 nm, which was determined from scanning emission spectrum of sample in the spectral range of 270-500 nm by fixing excitation wavelength at 260 nm. Differential scanning calorimetry (DSC) was performed on Perkin-Elmer Diamond DSC calibrated with indium. Glass transition temperatures were measured, after a first heating (from 0 to 200°C) and cooling (from 200 to 0°C) cycle. Thermograms were recorded during the second heating cycle (from 0 to 200°C) at 10°C/min under nitrogen flow and the glass transition temperature (T_g) was determined at the midpoint between upper and lower intersection of the baseline with the tangent to the transition step. Static contact angle measurements were carried out with a FTA200 Camtel goniometer using water and *n*-hexadecane of the highest purity commercially available (>99%) as interrogating liquids. Polymer films were prepared by spin-coating 3 wt% polymer solutions in CHCl₃ on glass slides followed by annealing for 12 h in a vacuum oven at 120°C.

RESULTS AND DISCUSSION

The synthesis of PP with well-defined macromolecular side chains by macromonomer technique has been previously reported by our group.^{32,57} The Suzuki coupling of aryl halides and aryl boronic acid containing macromonomers not only improves solubility and processability of PP but also conveniently combines the physico-chemical properties of different polymers, which can be prepared by controlled radical polymerization techniques. The overall strategy, as presented in Scheme 1, is based on the preparation of dual functional compounds having suitable sites for the initiation of both ATRP and Suzuki coupling processes. 1,4-Dibromo-2-(bromomethyl)benzene (1) was synthesized through bromination of the methyl group of commercially available 2,5dibromotoluene with N-bromosuccinimide (NBS). Benzene-2bromomethyl-1,4-bis(boronic acid) propanediol diester (2) was synthesized starting from the same compound by a three step reaction, which included boronic acid formation and its reaction with 1,3-propanediol followed by the bromination with NBS of the benzene-2-methyl-1,4-bis(boronic acid) 1,3-propanediol diester.³⁵ The FTIR analysis of the boronic acid compound indicates that the OH stretching of



SCHEME 1 Synthesis of aryl dihalide (1) and aryl diboronic acid (2) initiators.

-B(OH)2 group gives a broad peak at \sim 3202 cm⁻¹, which overlaps with aromatic CH stretching. The vibration of phenyl boronic acid linkage Ph-B gives a strong peak at 1446 cm^{-1} . The absorption bands at 1321 and 1110 cm^{-1} are assigned to the vibrations of the bonds B-O and B-OH. After the esterification reaction, OH stretching of boronic acid at 3202 cm^{-1} completely disappeared, while the vibrations of Ph-B and stretching of B-O were still observed at 1421 and 1392 cm⁻¹, respectively. The structures of intermediates were also confirmed by ¹H NMR analysis. The peak at 7.90 ppm corresponding to boronic acid protons completely disappeared after the ester formation. The spectrum of bis(boronic acid) propanediol diester showed that methylene protons linked to oxygen and methylene protons in the middle of the ester structure resonance at 4.17 and 2.08 ppm, respectively. Bromination of methyl group of benzene-2methyl-1,4-bis(boronic acid) propanediol diester was clearly evidenced by the shifting of the peak corresponding to the methyl protons from 2.37 to 4.89 ppm.

The subsequent step in the process was the preparation of macromonomers for the final Suzuki coupling reaction. Thus, dual-functional initiators, 1 and 2 were used in the ATRP of the respective monomers. In principle, both initiators can be used for the preparation of fluorinated and nonfluorinated segmented macromonomers. For our convenience, we selected initiator 1 for the preparation of the macromonomer with fluorinated segment because of its structural simplicity.

Experimentally, P(FEA-*co*-MMA) was synthesized as a macromonomer via ATRP using compound (1) as an initiator (Scheme 2). Perfluorooctylethyl acrylate (FEA) was deliberately copolymerized with MMA so as to overcome problems associated with solubility of the fluoropolymer. Copolymer structure and composition were investigated using ¹H NMR spectroscopy. The small peaks at 6.92 and 7.33 ppm clearly indicate the presence of aromatic protons belonging to the 1,4-dibromo-2-(bromomethyl)benzene initiator [Fig. 1(b)]. The signals at 4.26 and 2.47 ppm were attributed to methylene protons of FEA units. The characteristic methyl protons of MMA segment were also noted at 3.57 ppm. The mole fractions of FEA and MMA were calculated from the ratio of



SCHEME 2 Synthesis of poly(perfluorooctylethyl acrylate-*co*-methyl methacrylate) [P(FEA-*co*-MMA)] macromonomer by ATRP.

the peak areas around 4.26 and 3.57 ppm, corresponding to the two methylene protons of FEA and the methyl protons of MMA, respectively. FEA was copolymerized with MMA 30/70



FIGURE 1 (a) ¹H NMR spectra of poly(*p*-phenylene) (PP), (b) poly(perfluorooctylethyl acrylate-*co*-methyl methacrylate) [P(FEA-*co*-MMA)] macromonomer, (c) and polystyrene (PS) macromonomer.

TABLE 1 Synthesis of Poly(*p*-phenylene) (PP) with Alternating Polystyrene (PS) and Poly(perfluorooctylethyl acrylate-*co*-methyl methacrylate) [P(FEA-*co*-MMA)] Side Chains by Suzuki Polycondensation

Polymers	Conversion (%) ^a	<i>M</i> _{nNMR} ^b (g/mol)	<i>M</i> _{nGPC} ^c (g/mol)	$M_{\rm w}/M_{\rm n}^{\rm c}$
P(FEA- <i>co</i> -MMA) ^d	16	21,640	18,200	1.49
PS ^e	32	8,250	9,150	1.40
PP ^f	44	_ ^g	36,000	2.46
P(FEA- <i>co</i> -MMA) ^d PS ^e PP ^f	16 32 44	21,640 8,250 _ ^g	18,200 9,150 36,000	1.49 1.40 2.46

^a Determined gravimetrically.

^b Determined by using the ratio between aromatic protons of initiators and methylene protons of FEA and aromatic protons of PS, respectively.

^c Determined by GPC based on polystyrene standards.

 $^{\rm d}$ Polymerization conditions; $[M]_0/[{\rm CuBr}]_0/[L]_0=103/1/2$ at 90°C in Toluene for 90 min. Bipyridine used as ligand. Copolymer composition, FEA/MMA: 30/70 in feed and FEA/MMA: 23/77 in copolymer. Copolymer composition calculated by using $^1{\rm H}$ NMR spectrum.

 $^{\rm e}$ Polymerization conditions; Bulk, $[M]_0/[{\rm CuBr}]_0/[L]_0=86/1/3$ at 110°C. Bipyridine used as a ligand.

 $^{\rm f}$ Suzuki polycondensation was performed using Pd(0) catalyst at 90°C for 5 days.

^g Not calculated by using ¹H NMR spectrum.

mol % feed ratio and copolymer composition was calculated as FEA/MMA: 23/77, which is enough to have sufficient amount of perfluorooctyl group while maintaining solubility of polymer chain. The number average molecular weight of P(FEA-*co*-MMA) was calculated from ¹H NMR spectrum using the ratio between aromatic protons of initiators and methylene protons of FEA units. As can be seen in Table 1, there is a clear correlation between M_{nNMR} and M_{nGPC} , even though the polymer exhibits relatively broad polydispersity.

The ATRP of styrene using compound (2) as an initiator provided the second precursor polymer preserving two boronic ester functionalities, useful for Suzuki coupling in combination with P(FEA-*co*-MMA) based macromonomer (Scheme 3). Also in this case, there is a good agreement between the molecular weight values obtained by GPC measurement and calculated from ¹H NMR spectrum (Table 1). Furthermore, ¹H NMR spectrum shows the presence of boronic ester structure at the chain end as specified by the peak at 4.13 ppm corresponding to methylene protons of boronic ester structures [Fig. 1(c)]. As can be seen in Table 1, although there is consistency between $M_{\rm NMR}$ and $M_{\rm GPC}$ values, molecular weight distributions of both macromonomers are slightly broad due to the fact that polymerizations start with



SCHEME 3 Synthesis of polystyrene (PS) macromonomer by ATRP.



SCHEME 4 Synthesis of poly(*p*-phenylene) (PP) with alternating poly(perfluorooctylethyl acrylate-*co*-methyl methacrylate) [P(FEA*co*-MMA)] and polystyrene (PS) side chains by Suzuki polycondensation reaction.

benzylic halides, which lead to inefficient initiation.⁵⁸ However, as far as the ultimate aim is concerned, sufficient control of over the molecular weight and desired functionality for the next Suzuki coupling step were achieved.

In the final step, P(FEA-*co*-MMA) and PS based macromonomers were reacted via Suzuki polycondensation in the presence Pd(PPh₃)₄ as catalyst (Scheme 4). The structure of the obtained fluorinated PP was investigated by ¹H NMR, GPC, UV, fluorescence, and DSC analysis. Figure 1 shows ¹H NMR spectra of PP and its precursors. Even if the backbone protons of PP appear together with the aromatic protons of PS, the spectrum shows signal of both macromonomers [Fig. 1(a)]. Typical GPC profiles of precursors and resulted polymer are shown in Figure 2. GPC trace of the new polymer is shifted to higher molecular weights, as compared to the starting P(FEA-*co*-MMA) and PS macromonomers. GPC trace of PP did not show any PS precursor trace indicating its quantitative reaction. The slight shoulders on both sides of the chromatogram suggest chain growth in different lengths during PP formation.

Figure 3 shows the FTIR spectra of PS, P(FEA-*co*-MMA), and PP containing these two precursors as side chains. In the spectrum of PS [Fig. 3(a)], aromatic overtone and C—H stretching of PS as well as B—O peak at 1262 cm^{-1} are



FIGURE 2 (a) GPC traces of polystyrene (PS) macromonomer, (b) poly(perfluorooctylethyl acrylate-*co*-methyl methacrylate) [P(FEA-*co*-MMA)] macromonomer, and (c) poly(*p*-phenylene) (PP).



FIGURE 3 (a) FTIR spectra of polystyrene (PS) macromonomer, (b) poly(perfluorooctylethyl acrylate-*co*-methyl methacrylate) [P(FEA-*co*-MMA)] macromonomer, and (c) poly(*p*-phenylene) (PP).



FIGURE 4 (a) UV spectra of poly(perfluorooctylethyl acrylate*co*-methyl methacrylate) [P(FEA-*co*-MMA)] macromonomer, (b) polystyrene (PS) macromonomer, and (c) poly(*p*-phenylene) (PP) in CH₂Cl₂.

detectable. Characteristic absorption peaks of P(FEA-*co*-MMA) at 1727 and 1144 cm⁻¹ corresponding to C=O and C—F bond, respectively, are clearly observed in the PP spectrum at 1731 and 1146 cm⁻¹.

UV absorption spectra of macromonomers and corresponding PP recorded in CH_2CI_2 solutions with same concentrations are shown in Figure 4. While P(FEA-*co*-MMA) macromonomer does not show significant absorption, the PS based macromonomer has intense absorption at around 262 nm associated with phenyl ring. UV spectrum of PP has a peak with higher intensity at wavelength close to the absorbance wavelength of PS macromonomer because of the presence of supplementary phenylene rings in the main chain. Moreover, absorption shoulders at 270 and 375 nm further evidence for the formation of a PP chain.

Furthermore, fluorescence properties of PP and macromonomers were investigated. As shown in Figure 5, while



FIGURE 5 (a) Normalized excitation and (b) emission fluorescence spectra of poly(p-phenylene) (PP) in CH_2CI_2 at room temperature.



FIGURE 6 (a) DSC traces of poly(perfluorooctylethyl acrylate*co*-methyl methacrylate) [P(FEA-*co*-MMA)] macromonomer, (b) polystyrene (PS) macromonomer, and (c) poly(*p*-phenylene) (PP).

P(FEA-*co*-MMA) and PS macromonomer did not show any fluorescence properties, PP gave a strong fluorescence emission. The excitation spectrum of PP presented a maximum at 260 nm, and emission spectrum obtained at this excitation wavelength had a maximum at 351 nm.

Also, the thermal behavior was investigated by DSC (Fig. 6). Glass transition temperatures (T_g) were measured during the second heating cycle (from 0 to 200°C) at 10°C/min under nitrogen flow. PS and P(FEA-*co*-MMA) macromonomers show the typical glass transitions at 100 and 65°C, respectively. PP displayed the two transitions at 66 and 104°C indicating microphase separation of the two side chain grafts from the backbone. No evidence of a mesophase formation was detected for P(FEA-*co*-MMA) and PP. The random incorporation of 77 mol % of MMA units in the copolymer introduced constitutional disorder, which impeded formation of a mesophase structure typical of the fluorinated homopolymer.^{44,59}

The wetting behavior of the polymers was studied by measurements of the static contact angle θ of thin films (200–400 nm thickness) using water and *n*-hexadecane as wetting liquids (Table 2). The films were spin-coated onto glass slides, dried under vacuum overnight, and then annealed for 12 h at 120°C to achieve equilibrium morphologies.

The values of θ with water and *n*-hexadecane are conventionally used to estimate qualitatively hydrophobicity ($\theta_w > \sim 90^\circ$) and lipophobicity ($\theta_h > \sim 60^\circ$), respectively. The fluorinated PP and its precursor P(FEA-*co*-MMA) showed high static contact angles with both interrogating liquids, exhibiting both hydrophobic ($\theta_w = 111^\circ$ and 112° , respectively) and lipophobic ($\theta_h = 67^\circ$ and 69° , respectively) properties. The dual character is typical of fluorinated polymers, as opposed to most other polymers, like polyolefins and PPs, that are hydrophobic, but not lipophobic at the same time (see PS in Table 2). In fact, PS was completely wetted by *n*-hexadecane. On the other hand, dilution of the FEA moieties with PS units in the PP did not affect the self-assembly process of the pendant perfluorinated chains at the surface.

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TABLE 2 Static Contact Angles^a and Surface Tensions^b of Poly(*p*-phenylene) (PP), Poly(perfluorooctylethyl acrylate-*co*-methyl methacrylate) [P(FEA-*co*-MMA)] and Polystyrene (PS)

Film	θ _w (°)	θ _h (°)	γs ^b (mN/m)	γs ^{db} (mN/m)	γs ^{pb} (mN/m)
PP	111 ± 1	67 ± 2	14.1	13.3	0.8
P(FEA- <i>co</i> - MMA)	112 ± 2	69 ± 2	13.4	12.7	0.7
PS	90 ± 2	~ 0	-	-	-

^a Measured with water and *n*-hexadecane.

^b Calculated with the Owens-Wendt-Kaelble method: γ_{s}^{d} is the dispersion component, γ_{s}^{p} is the polar component.

The similarity between the contact angles of the two polymers suggests that the fluorinated polymer grafts were selectively and effectively segregated at the polymer-air interface, thus inducing the same nonwetting character as that of P(FEA-*co*-MMA). The phenomenon of surface segregation is known for a variety of fluorinated polymers and can be exploited in application fields were nonstick, antisoiling, and anti(bio)fouling properties are required.⁶⁰⁻⁶⁷

Measurements of liquid–solid contact angles are commonly used to evaluate solid surface tension $\gamma_{\rm S}$ of polymers. However, the correlation between θ and γ is still a controversial question and none of the different approaches proposed are generally accepted.^{68,69} We followed the additive-component method of the surface tension of Owens, Wendt, and Kaelble (OWK).^{70,71}

In this approach the solid surface tension:

$$\gamma_{\rm S} = \gamma_{\rm S}^{\rm d} + \gamma_{\rm S}^{\rm p} \tag{1}$$

combined with the Young's equation yields:

$$\gamma_{\rm L}(1 + \cos\theta) = 2 \Big[(\gamma_{\rm S}^{\rm d} \gamma_{\rm L}^{\rm d})^{1/2} + (\gamma_{\rm S}^{\rm p} \gamma_{\rm L}^{\rm p})^{1/2} \Big]$$
(2)

where γ^d and γ^p are the dispersion and the polar components of surface tension, respectively. Since, there are two unknowns ($\gamma_S{}^d, \gamma_S{}^p$), it is necessary to use at least two wetting liquids of known $\gamma_L{}^d$ and $\gamma_L{}^p$. The surface tensions and the related components calculated for the polymers are also collected in Table 2.

The values of the $\gamma_{\rm S}$ were consistent with a low surface energy of the polymer films, being 14.1 and 13.5 mN/m for PP and P(FEA-*co*-MMA), respectively. In both cases, the $\gamma_{\rm S}{}^{\rm d}$ component overwhelmed the associated $\gamma_{\rm S}{}^{\rm p}$ component in determining the total surface tension. This behavior is typical of fluorinated surfaces, which experience dispersion forces but prevent polar, for example dipole–dipole or hydrogen bonding interactions. Thus, the surface properties were dominated by the fluorinated component.

CONCLUSIONS

In conclusion, we described the preparation of a novel PP with regularly alternating fluorinated and nonfluorinated

polymer side chains along the aromatic polymer backbone. The method pertains to the elegant combination of ATRP with Suzuki coupling processes. The macromonomers of P(FEA-*co*-MMA) and PS were obtained by ATRP and subsequently used in Suzuki polycondensation to yield desired PP. The structures of such complex macromolecules have been characterized as they showed excellent solubility in common organic solvents at room temperature. High solubility, fluorescence, and low surface tension properties of the PP graft copolymer imply that it is a promising material for many applications where a luminescent PP underlayer is hidden by a hydrophobic and lipophobic overlayer.

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