2732 *Macromolecules* 2010, *43*, 2732–2738
DOI: 10.1021/ma1000749

Macromolecules
ARTICLE

Perfectly Alternating Amphiphilic Poly(*p*-phenylene) Graft Copolymers by Combination of Controlled Radical Polymerization and Suzuki Coupling Processes

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Received January 11, 2010; Revised Manuscript Received February 12, 2010

ABSTRACT: The preparation of amphiphilic poly(*p*-phenylene) (PP) possessing completely and perfectly alternating hydrophilic poly(ethylene oxide) (PEO) and hydrophobic polystyrene (PS) side chains is described. First, PS macromonomer with suitable functionality for polyphenylation was prepared by atom transfer radical polymerization (ATRP). The antagonist macromonomer, PEO, was synthesized by etherification reaction. Both macromonomers were reacted in the final stage via Suzuki cross coupling in the presence of $Pd(PPh_3)_4$ as catalyst to form the desired amphiphilic graft copolymer (M_n: 32 400 g/mol and M_w/M_n: 2.28). The intermediates obtained in various stages and graft copolymers were characterized by ^1H NMR and IR analysis. The optical absorption properties of the polymer were monitored with UV, and an additional absorption at around 280−320 nm evidenced the formation of PP chain. Thermal properties of PP were investigated by DSC. The thermogram displayed two transitions at 51.98 and 89.60 °C, indicating the presence of both PEO and PS structures in the copolymer. The perfectly alternating hydrophilic PEO and hydrophobic PS side chains were observed by AFM measurements to nanophase-separate in thin films.

Introduction

A great deal of interest has been paid to the conjugated polymers because of their applications in electronic conductivity and optoelectronic devices such as light-emitting diodes (LEDs),[1,2] transistors,[3] solid-state lasers,[4] waveguides,[5] solar cells,[6] and chemical and biomolecular sensors.[7] Poly(*p*-phenylene)s (PPs) are typical conjugated polymers in combination with excellent mechanical properties and thermal and thermo-oxidative stability. They are potentially one of the most useful polymers for organic conducting materials because of their extended planar conjugated π system, along with high strength and high heat resistance. Other interesting and significant properties of PPs are liquid crystallinity[8] and photo- and electroluminescence.[9] Current methodologies for the direct synthesis of various PPs are primarily based on nickel-[10−12] and palladium-mediated[13] cross-coupling reactions largely because of their preservation of regiochemistry and nearly quantitative yields.[8−10,12] Unfortunately, PPs are insoluble in many organic solvents, which limit their processability. Therefore, attachment of conformationally mobile alkyl side chains to the backbone has been important because it has allowed the controlled synthesis of soluble and processable PPs with high molecular weight. To improve the solubility of PPs, a series of functionalized PPs pendant alkyl groups has been reported.[14−17] Moreover, our group reported the synthesis of PP-type graft copolymers[18] by using the macromonomer technique via controlled polymerizations such as atom transfer radical polymerization (ATRP)[19−21] or ring-opening polymerization (ROP).[22−25]

Among various controlled radical polymerization methods developed in the past decade, ATRP[26−29] seems to be the most extensively used method because of its easy manipulation, ability to control molecular weight and structure, and applicability to a wide range of monomers. In our previous works, we reported the synthesis of PPs with polystyrene (PS) side chains starting from ATRP initiators, namely, 1,4-dibromo-2,5-bis(bromomethyl)benzene[19] or benzene-2,5-dibromomethyl-1,4-bis(boronic acid propanediol diester).[30]

Amphiphilic copolymers with hydrophilic and hydrophobic segments have been extensively investigated because of their unique self-organization characteristics and wide range of potential applications.[31] In the area of polymer chemistry, amphiphilic copolymers are identified to display various attractive properties such as surface activity and aggregate formation.[32,33] Statistical copolymer of PPs substituted with oligo(oxyethylene) side chains were synthesized as a novel polymer electrolytes by Wegner and coworkers.[34,35] Then, Zhang et al.[36] reported amphiphilic PP having nonpolar hexyloxy and polar oligo(ethylene glycol) chains at every other repeating unit. PPs having alternating sugar and alkyl substituents were synthesized by Suzuki coupling and an increased rotational flexibility of the main chain phenyl rings with respect to the PP having only glucose substitutents has been demonstrated.[37] However, in both cases, the hydrophobic groups were short alkyl chains. Additionally, several reports in the literature concern the preparation of amphiphilic poly(phenylene ethylene)s (PPEs) possessing a hydrophobic alkyl side chain together with polar,[38] poly(ethylene oxide) (PEO),[39−41] or cationic[42,43] side chains. Computer simulations of polymers having chemically incompatible alternating side chains showed local phase separation of the two different side chains without any long-range order along the backbone.[44,45] To the best of our knowledge, there are no examples of amphiphilic PPs with alternating polymeric side chains.

Herein, we describe the synthesis and characterization of novel alternating amphiphilic PP graft copolymers by Suzuki polycondensation reaction of hydrophilic PEO and hydrophobic PS macromonomers through aryl dihalide and aryldiboronic acid

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functional groups. The morphology of the synthesized PPs in ultrathin films is interpreted in terms of local phase separation between the two chemically incompatible side chains.

Experimental Section

Materials. Styrene (S, 99%, Aldrich) was passed through a basic alumina column to remove the inhibitor. 2,5-Dibromotoluene (98%, Aldrich), *N*-bromosuccinimide (NBS, 99%, Merck), PEO monomethylether (M_n: 2000, Fluka), sodium hydride (97%, Aldrich), *n*-butyl lithium (*n*-BuLi (2.5 M solution in hexane), Acros), trimethylborate (≥99%, Merck), 1,3-propanediol (≥99%, Fluka), $NaHCO_3$ (Aldrich), $Pd(PPh_3)_4$ (Merck), benzoyl peroxide (Aldrich), CuBr (98%, Acros), 2,2 dipyridyl (bpy, ≥99% Acros), magnesium sulfate anhydrous ($MgSO_4$, ≥99.0%, Aldrich), and silicagel 90 (Fluka, 0.2 to 0.5 mm) were used as received. Carbon tetrachloride (CCl_4, ≥99.0%, Aldrich) was distilled over phosphorus pentoxide and stored over 4 Å molecular sieves. Hexane (95.0%, Carlo Erba) was distilled over sodium wire. Tetrahydrofuran (THF, ≥ 99.0%, Fluka) was dried over potassium hydroxide and distilled over sodium wire and benzophenone.

Synthesis of 1,4-Dibromo-2-(bromomethyl)benzene (1). 1,4-Dibromo-2-(bromomethyl)benzene was synthesized according to modified procedure.[30] 2,5-Dibromotoluene, (5.0 g, 20 mmol), NBS (3.9 g, 22 mmol), and benzoyl peroxide (0.10 g, 0.4 mmol) were heated under reflux in 20 mL of CCl_4 under nitrogen for 4 h. The reaction mixture was filtered to remove succinimide, and the succinimide was washed with a supplementary amount of CCl_4 and finally with a little quantity of CH_2Cl_2. The combined organic solutions were washed several times with water and than dried over $MgSO_4$. The solvent was removed by rotary evaporator. The product was purified by passing through a silica gel column using diethylether as an eluent. Finally, the product was obtained as white crystals after recrystallizing twice from petroleum ether (Yield: 38%). m.p.: 89.2 °C. ^1H NMR ($CDCl_3$): 4.51 (s, 2H, CH_2Br), 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). Benzene-2-methyl-1,4-bis(boronic acid) was synthesized according to modified procedure.[15] 2,5-Dibromotoluene, (22 g, 87.0 mmol) was heated under reflux in 140 mL of *n*-hexane under nitrogen for 2 h. The solution was allowed to cool to room temperature for 30 min. The reaction mixture was then cooled to −78 °C, and *n*-BuLi (96 mL, 24 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 room temperature for 3 h. After being stirred at room temperature for 12 h, the solution was heated to reflux temperature under nitrogen for 2 h. Then, the solution was cooled to room temperature for 30 min. The reaction mixture was further cooled to −78 °C, and trimethylborate ($B(OCH_3)_3$) (100 mL, 870 mmol) was added. The solution was allowed to warm to room temperature for 3 h before the reaction was quenched with the addition of 2 M HCl. The two phases were separated, and the water phase was extracted with four portions of diethyl ether and then dried over $MgSO_4$ and evaporated to yield the boronic acid as a white solid, which was used without further purification. Yield: 50%. ^1H NMR ($CDCl_3$): 2.29 (3H, *CH*$_3$), 7.90 (bs, 4H, OH), 7.38 (1H, aromatic), 7.56 (1H, aromatic), 7.73 (1H, aromatic). 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 (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 propanediol diester). Benzene-2-methyl-1,4-bis(boronic acid propanediol diester) was synthesized according to modified procedure.[46] 1,3-Propanediol (10.5 mL, 144 mmol) and 10.8 g of 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 $MgSO_4$. The solvent was removed in vacuo to afford a light-yellow solid. Recrystallization from hexane. Yield: 18%. m.p.: 116.3 °C. ^1H NMR ($CDCl_3$): 2.08−1.99 (t, 4H, O−CH$_2$−*CH*$_2$−CH$_2$−O), 4.17−4.13 (t, 8H, O−*CH*$_2$−CH$_2$−*CH*$_2$−O), 2.37 (s, 3H, CH_3), 7.50 (s, 1H, aromatic), 7.65 and 7.68 (2H, aromatic). IR (cm^{-1}): 3053−3019 (aromatic CH stretching), 2955−2926 (aliphatic qCH stretching), 1483 (aromatic C=C stretching), 1421 (vibration of Ph-B bond), 1392, 1372 (B−O in $B(OH)_2$), 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 modified procedure.[30] Benzene-2-methyl-1,4-bis(boronic acid propanediol diester) (1.80 g, 6.9 mmol), NBS (1.5 g, 8.3 mmol), and benzoyl peroxide (0.03 g, 0.14 mmol) were heated under reflux in 15 mL of CCl_4 under nitrogen for 24 h. The reaction mixture was filtered to remove succinimide and washed with a small amount of CCl_4 and CH_2Cl_2. The combined organic solutions were washed several times with water and then dried over $MgSO_4$. The solvent was removed by rotary evaporator. The product was purified by passing through a silica gel column using diethylether as an eluent. Finally, the product was obtained as white crystals after recrystallizing twice from diethyl ether. Yield: 30%. ^1H NMR ($CDCl_3$): 2.10−2.02 (m, 4H, O−CH$_2$−*CH*$_2$−CH$_2$−O), 4.20−4.12 (m, 8H, O−*CH*$_2$−CH$_2$−*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 strecthing), 1481(aromatic C=C stretching), 1425 (vibration of Ph-B bond), 1393 (vibration of B−O), 1313−1150 (starching of C−O linkages), 1097, 1023, 928, 822, 798, 724, 687, 653.

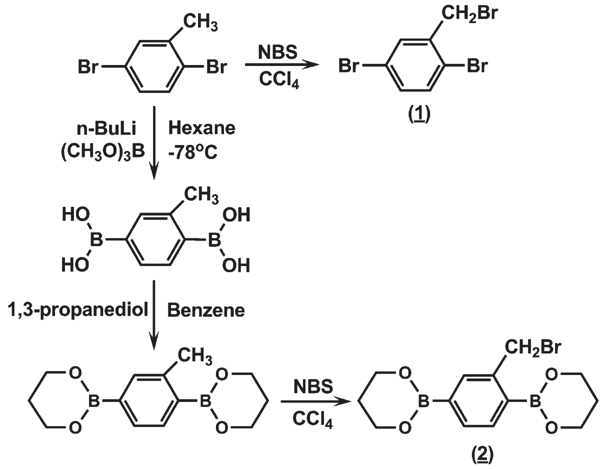
Preparation of Poly(ethylene oxide) Macromonomer (M1) by Etherification Reaction. Sodium hydride (0.024 g, 1.1 mmol) was added to PEO (2.0 g, 1.0 mmol) in dry 25 mL of THF, and the reaction mixture was stirred at 0 °C under nitrogen for 30 min. 1,4-Diboromo-2-(bromomethyl)benzene (**1**) (0.66 g, 2.0 mmol) in dry 10 mL of THF was added portionwise to the solution. The mixture was kept stirring at room temperature for 24 h. The solution was extracted with water, and the organic layer was dried over anhydrous $MgSO_4$ and CH_2Cl_2 was removed by rotary evaporation. The mixture was precipitated in diethyl ether, and the solid formed was collected after filtration and dried at room temperature in a vacuum overnight. ^1H NMR ($CDCl_3$): 3.34 (s, 3H, O*CH*$_3$), 3.70 (m, 4H, O−*CH*$_2$*CH*$_2$−O), 4.55 (s, 2H, Ar-*CH*$_2$), 7.33 (1H aromatic), 7.37 (1H aromatic) 7.64 (1H, aromatic). IR (cm^{-1}): 2946−2884 (aliphatic CH stretching), 1466 (aromatic C=C stretching) 1360−1341 (CH_2 vibration), 1279−1147 (C−O−C stretching of ether lineages), 1060, 1028, 960, 841.

Preparation of Polystyrene Macromonomer (M2) by ATRP. A Schlenk tube was charged with CuBr (0.040 g, 0.27 mmol), bpy (0.13 g, 0.83 mmol), initiator (**2**) (0.090 g, 0.27 mmol), and styrene (4.5 g, 24 mmol). Three freeze−pump−thaw cycles were performed, and the tube was stirred in an oil bath at 110 °C for 50 min. After the given time, the mixture was diluted with THF. Then, the copper complex was removed by passing through a neutral alumina column, and THF was removed by rotary evaporation. The mixture was precipitated in methanol, and the solid was collected after filtration and dried at room temperature in a vacuum overnight (32%, $M_{n,GPC}$ = 9150, M_w/M_n = 1.4). ^1H NMR ($CDCl_3$): 2.26−1.17 (aliphatic of PS, O−CH$_2$−*CH*$_2$−CH$_2$−O, Ar−*CH*$_2$), 4.13 (t, 8H, O−*CH*$_2$), 4.47 (bs, 1H, Ph*CH*−Br), 6.47−6.57 (2H aromatic of PS), 7.04−7.46 (3H 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.

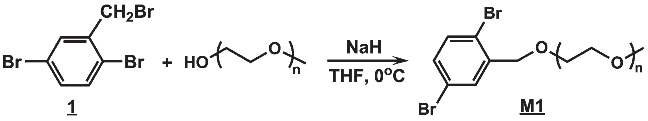
Synthesis of Amphiphilic Poly(*p*-phenylene) by Suzuki Polycondensation Reaction. A 100 mL three-necked round-bottomed flask equipped with a condenser, a septum, nitrogen inlet−outlet, and magnetic stirrer, was charged with 20 mL of 1 M $NaHCO_3$ solution and 30 mL of THF. The solvents were previously degassed by bubbling nitrogen over a period of 30 min. The mixture was refluxed under nitrogen for 3 h. A 20 mL three-necked round-bottomed flask equipped in the same way as the previous one was charged under inert atmosphere with PS-based macromonomer (0.25 g, 0.028 mmol), PEO-based macromonomer (0.07 g, 0.028 mmol), $Pd(PPh_3)_4$ (0.7 mg, 5.8×10^{-4} mmol), and 3 mL of the solvent mixture introduced with a syringe through the septum. The reaction was maintained with vigorous stirring and with the exclusion of oxygen and light at reflux. After 48 h, a supplementary amount of 5 mL of the solvent mixture was added through the septum and stirred 1 day more. After this time, the polymer was obtained by precipitation in methanol, and the solid was collected after filtration and dried at room temperature in a vacuum overnight (0.21 g, 66%,). ^{1}H NMR ($CDCl_3$): 1.85−1.43 (m, aliphatic of PS), 3.64 (s, O−CH_2−CH_2−*O* of PEO), 7.20−6.57 (m, aromatic of PS and PP). IR (cm^{-1}): 3059, 3025 (aromatic CH stretching), 2923, 2849 (aliphatic CH stretching), 1937, 1867, 1798, 1665 (out-of-plane C−H deformation), 1583, 1492, 1452 (aromatic C=C stretching), 1390−1313 (CH_2 vibration), 1267−1125 (C−O−C stretching) 760.

Characterization. ^{1}H NMR spectra of 5−10% (w/w) solutions in $CDCl_3$ with $Si(CH_3)_4$ as an internal standard were recorded at room temperature at 250 MHz on a Bruker DPX 250 spectrometer. Gel permeation chromatography (GPC) measurements were obtained from a Viscotek GPCmax Autosampler system consisting of a pump, a Viscotek UV detector and a Viscotek 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 PS standards. FT-IR spectra were recorded on a Perkin-Elmer FT-IR Spectrum One B spectrometer. UV spectra were recorded on a Shimadzu UV-1601 spectrometer. Fluorescence measurements were carried out using a Hitachi F-4500 fluorescence spectrophotometer, and the excitation and emission spectra of PP were recorded in CH_2Cl_2 at room temperature. Differential scanning calorimetry (DSC) was performed on Perkin-Elmer Diamond DSC calibrated with indium. Glass-transition temperatures were measured after a first heating (from −50 to 150 °C) and cooling (from 150 to −50 °C) cycle. Thermograms were recorded during the second heating cycle (from −50 to 300 °C) at 10 °C/min under nitrogen flow. DSC calibration was performed with indium, and the transition temperature (T_g and T_m) was determined at the midpoint between upper and lower intersection of the baseline with the tangent to the transition step. For atomic force microscopy (AFM) measurements, PP films were spin coated on silicon substrates from 0.5 to 1.0 mg/mL solutions in CH_2Cl_2. Hydrophilic silicon substrates were obtained by UV-ozone treatment for 30−40 min. Height and phase images were taken by NT-MDT Solver P47 in tapping mode with ultra sharp Si cantilevers having force constant of 48 N/m.

Scheme 1. Synthesis of Aryl Dihalide (1) and Aryl Diboronic Acid (2) Compounds by Using *N*-Bromosuccinimide (NBS) in the Bromination Step



Scheme 2. Preparation of Poly(ethylene oxide) (PEO) Macromonomer (M1) by Etherification Reaction in Tetrahydrofuran (THF)



Results and Discussion

The overall strategy, as presented in Scheme 1, is based on the preparation of functional precursors and macromonomers suitable for the phenylation process by Suzuki coupling. First, the precursor (**1**) for the PEO-based macromonomer (**M1**) was synthesized through bromination of methyl group of 2,5 dibromotoluene with *N*-bromosuccinimide (NBS) in CCl_4 solution. The ATRP initiator (**2**), namely, benzene-2-bromomethyl-1,4-bis(boronic acid propanediol diester), was obtained by multiple step reactions. For this purpose, benzene-2-methyl-1,4-bis-(boronic acid) was synthesized from the same starting compound for **1** by using *n*-BuLi, followed by reaction with trimethylborate at −78 °C. Refluxing of the diboronic acid compound with 1,3-propanediol using a Dean−Stark trap afforded bis(boronic acid propandiol diester). Apparently, the esterification reaction enhanced the solubility of the initial boronic acid compound in CCl_4 and consequently esteems the subsequent bromination reaction with NBS in this solvent. The FT-IR analysis of the related compounds indicated that the OH stretching of $-B(OH)_2$ group gives a broad peak at ~3202 cm^{-1} (Figure S1 of the Supporting Information). The aromatic CH stretching is located at 3029 cm^{-1}. The vibration of phenyl boronic acid linkage Ph-B gives a strong peak at 1446 cm^{-1}. The absorption bands at 1388 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, and the vibrations of Ph−B and B−O are still observed at 1421 and 1392 cm^{-1}, respectively. The structures of intermediates were also confirmed by ^{1}H NMR analysis (Figure S2 of the Supporting Information). The peak at 7.90 ppm corresponding to boronic acid protons completely disappeared after the ester formation (Figure S2a of the Supporting Information). In the spectrum of bis(boronic acid propanediol diester), methylene and methyl protons resonanced at 4.17 and 2.05 ppm, respectively (Figure S2b of the Supporting Information). Bromination of methyl group of benzene-2-methyl-1,4-bis(boronic acid propanediol diester) was clearly evidenced by the shifting of the peak corresponding to the

Table 1. Molecular Weight Characteristics of Poly(*p*-phenylene) and Its Precursors

polymers	M_{nNMR} (g/mol)[a]	M_{nGPC} (g/mol)[b]	M_w/M_n[b]
PEO macromonomer[c]	2650[d]	2400	1.03
PS macromonomer[e]	8250[f]	9150	1.40
poly(*p*-phenylene)[g]	nd[h]	32400	2.28

[a] Calculated by using ^{1}H NMR spectra. [b] Determined by GPC based on polystyrene standards. M_n: number-average molecular weight; M_w: weight-average molecular weight. [c] Functionalization was performed by etherification reaction. Molecular weight and molecular weight distribution of starting PEO were measured as 2200 and 1.03, respectively. [d] Determined by using the ratio between aromatic protons of (**1**) and methylene protons of PEO from ^{1}H NMR spectrum. [e] Polymerization conditions; bulk, $[M]_0/[CuBr]_0/[L]_0 = 86/1/3$ at 110 °C. Bipyridine used as a ligand. [f] Determined by using the ratio between methylene protons of (**2**) and aromatic protons of PS from ^{1}H NMR spectrum. [g] Suzuki polycondensation was performed using Pd(0) catalyst at 90 °C for 5 days. [h] Not determined.

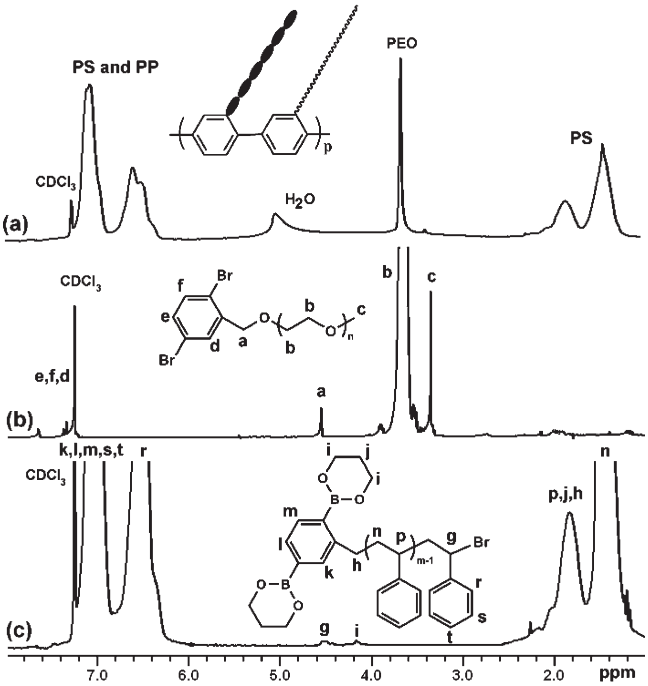
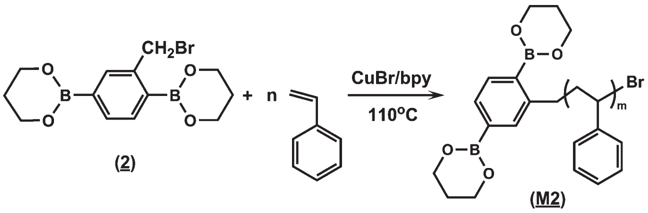


Figure 1. ^{1}H NMR spectra of (a) poly(*p*-phenylene) (PP) and (b) its precursors poly(ethylene oxide) (PEO)-based macromonomer (**M1**) and (c) polystyrenre (PS)-based macromonomers (**M2**) in $CDCl_3$.

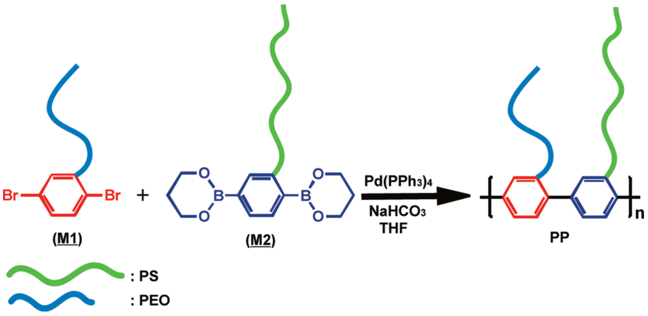
methyl protons at 2.47−4.89 ppm (Figure S2c of the Supporting Information). The aromatic protons were noted at 7.25−7.68 ppm in all of the related spectra. After the bromination reaction, the resulting initiator, **2**, was used as an ATRP initiator and also Suzuki coupling reagent.

PEO-based macromonomer (**M1**) was obtained by etherification reaction between **1** and monohydroxy functional PEO (Scheme 2). This macromonomer, having two bromine atoms directly connected to the central benzene ring, is suitable for Suzuki polycondensation with a diboronic ester in the presence of palladium catalyst. As can be seen from Table 1, the molecular weight of the polymer was slightly increased by the etherification reaction. The observed increase is due the incorporation of the aromatic group at the chain end. The polydispersity remained unchanged, indicating that there was no degradation or coupling during the etherification reaction. More reliable evidence of functionalization of PEO was obtained by ^{1}H NMR analysis. The spectrum presented in Figure 1b contains characteristic bands of PEO at 3.34 (OCH_3) and 3.70 ppm ($O-CH_2CH_2-O$) as well as aromatic protons of central benzene ring at 7.24−7.64 ppm. Functionalization efficiency of PEO was found to be 94%, as calculated by using the ratio between aromatic protons to methylene protons of repeating units. Moreover, the aromatic-CH_2 groups are in the vicinity of O atoms of the first PEO repeating unit, and the corresponding protons give a clear signal at 4.55 ppm.

Scheme 3. Preparation of Polystyrene (PS) Macromonomer (M2) by ATRP Using CuBr/Bipyridine (CuBr/bpy) Catalyst System



Scheme 4. Synthesis of Amphiphilic Poly(*p*-phenylene) (PP) by Suzuki Polycondensation Reaction



The ATRP of styrene using the CuBr/bpy catalytic system provide PS as a second precursor preserving two boronic ester functionalities, which is useful for Suzuki coupling in combination with PEO-based macromonomer (Scheme 3). The results of polymerization are shown in Table 1. There is a good agreement between molecular-weight-obtained GPC measurement and ^{1}H NMR calculation. Furthermore, ^{1}H NMR spectrum of PS macromonomer indicates the boronic ester structure at the chain end as showing a peak at 4.13 ppm corresponding to methylene protons of boronic ester structures (Figure 1c).

Hydrophilic PEO- and hydrophobic PS-based macromonomers were reacted via Suzuki polycondensation in the presence $Pd(PPh_3)_4$ as catalyst to form desired amphiphilic copolymer (Scheme 4). The structure of amphiphilic PP was investigated by ^{1}H NMR, GPC, UV, fluorescence, DSC, and the thin film morphology by AFM analysis. ^{1}H NMR spectra of PP and its precursors PEO- and PS-based macromonomers were collected in Figure 1. Even if the protons of the PP backbone appear together with aromatic protons of PS, the spectrum shows characteristic signals of both macromonomers (Figure 1a).

Moreover, GPC trace of the PP was shifted to higher molecular weights (lower elution volume) as compared with that of starting PEO- and PS-based macromonomer (Figure 2). GPC measurement of PP was performed after the reprecipitation from methanol. This treatment is expected to remove the unreacted PEO macromonomer. However, unreacted PS would have remained in the mixture because of the similar solubility behavior with the resulting PP arising from its high PS character. The absence of a peak corresponding PS macromonomer at high elution volume is another indication for the successful coupling process. Because of the comblike structure of the poly(phenylene)s obtained from the corresponding macromonomers, the values of M_n and M_w/M_n calibrated with linear standard polymers should be taken as a minimum estimation.[47]

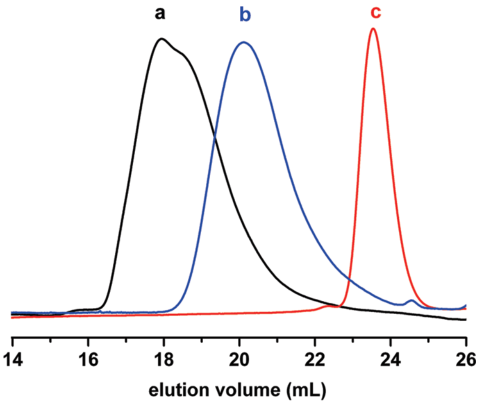


Figure 2. (a) GPC traces of poly(*p*-phenylene) (PP) and its precursors (b) polystyrene (PS)-based macromonomer (**M2**) and (c) poly(ethylene oxide) (PEO)-based macromonomers (**M1**).

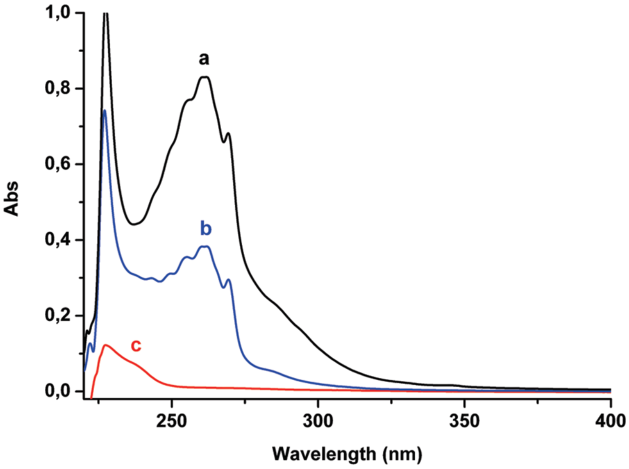


Figure 3. UV spectra of (a) poly(*p*-phenylene) (PP) and its precursors (b) polystyrene (PS)-based macromonomers (**M2**) and (c) poly(ethylene oxide) (PEO)-based macromonomer (**M1**) in CH_2Cl_2.

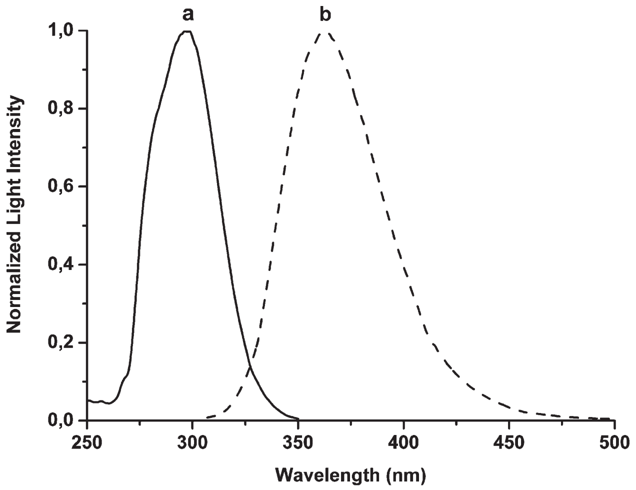


Figure 4. (a) Normalized excitation and (b) emission fluorescence spectra of poly(*p*-phenylene) (PP) in CH_2C_2 at room temperature.

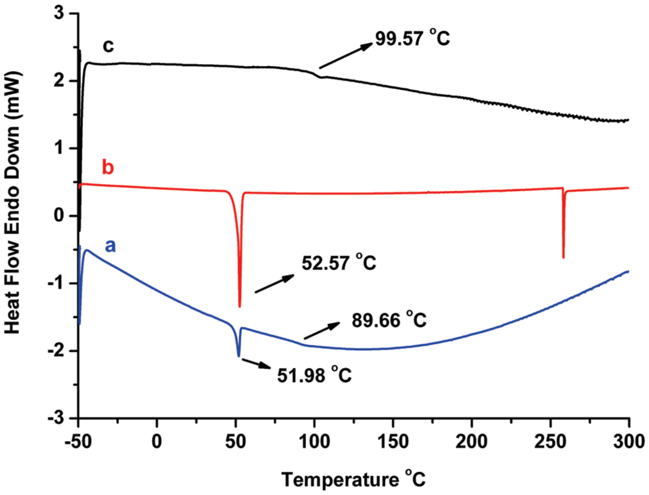


Figure 5. DSC traces of (a) poly(*p*-phenylene) (PP) and its precursors (b) poly(ethylene oxide) (PEO)-based macromonomer (**M1**) and (c) polystyrene (PS)-based macromonomers (**M2**).

UV absorption spectra of macromonomers and corresponding PP registered in solutions with the same concentrations are shown in Figure 3. Whereas PEO-based macromonomer does not show significant absorption, the PS-based macromonomer has intense absorption at ~262 nm. The UV spectrum of PP has a peak with higher intensity at wavelengths close to that of PS-based macromonomer because of the presence of supplementary phenylene rings in the main chain. Moreover, additional absorption at around 280−320 nm is further evidence of the presence of PP chain.

Furthermore, fluorescence properties of PP and macromonomers were investigated in Figure 4. Whereas PEO- and PS-based macromonomers do not show any fluorescence properties, PP shows the strong fluorescence properties. The excitation spectrum of PP had the maximum at 299 nm, and emission spectrum obtained for the excitation wavelength at this value had a maximum at 366 nm.

Also, the thermal behavior of the polymers was investigated by DSC (Figure 5). Glass-transition temperatures (T_g) were measured after a first heating (from −50 to 150 °C) and cooling (from 150 °C to −50 °C) cycle. Thermograms were recorded during the second heating cycle (from −50 to 300 °C) at 10 °C/min under nitrogen flow. PS-based macromonomer shows a typical T_g at 99.57 °C, and low-molecular-weight-PEO-based macromonomer exhibits only a melting temperature (T_m) at 52.57 °C. PP displayed two transitions at 51.98 and 89.60 °C. The first transition belongs to T_m of the PEO segment, and the latter is consistent with T_g of PS segment.

Ultrathin films (thickness <20 nm) of PP spin coated on silicon substrates from CH_2Cl_2 solutions showed nanostructured morphology at the top surface. Figure 6 shows the AFM height and phase pictures of a 19.0 nm thick PP film. The top surface had ~1 to 2 nm peak-to-peak roughness originating from circular holes of ~1 to 2 nm deep. Although the in-plane distribution of these holes were not regular, the distance between the neighboring holes were on the average 65 ± 15 nm, as determined by Fourier transformation of the AFM phase image. We attribute such morphology to the presence of nanophase separation between the PS and the PEO side chains of PP. Phase-separated PS and PEO side chains tend to either side of the PP backbone. The tendency of the PEO side chains for the underlying silicon substrate and the PS side chains for the air/film interface then orient the molecules in such a way that layers of PEO/PP backbone/PS forms parallel to the substrate. Perfect alternation of PEO and PS side chains on the backbone allows interdigitation between same-type side chains of neighboring layers. An incomplete top surface layer of the film would then show holes whose depth would be equal to the PS layer thickness. R_g of PS macromonomers ($M_n \approx 8250{-}9150$ g/mol) is ~1 nm, which is

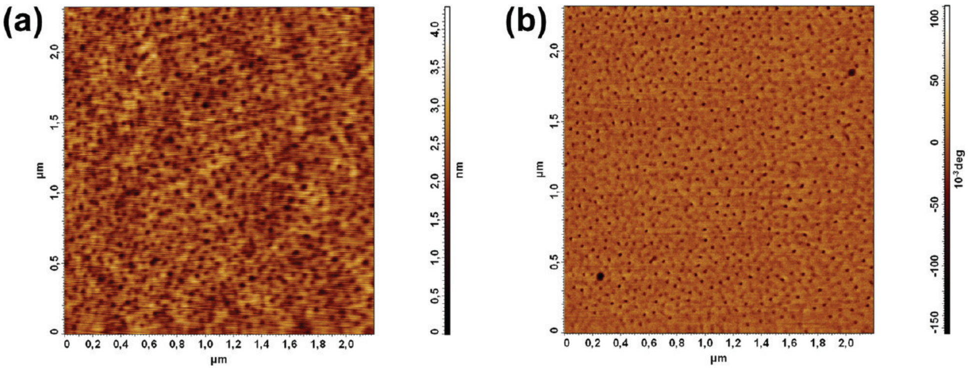


Figure 6. (a) AFM height and (b) phase pictures of 19.0 nm thick poly(*p*-phenylene) (PP) film on silicon substrate.

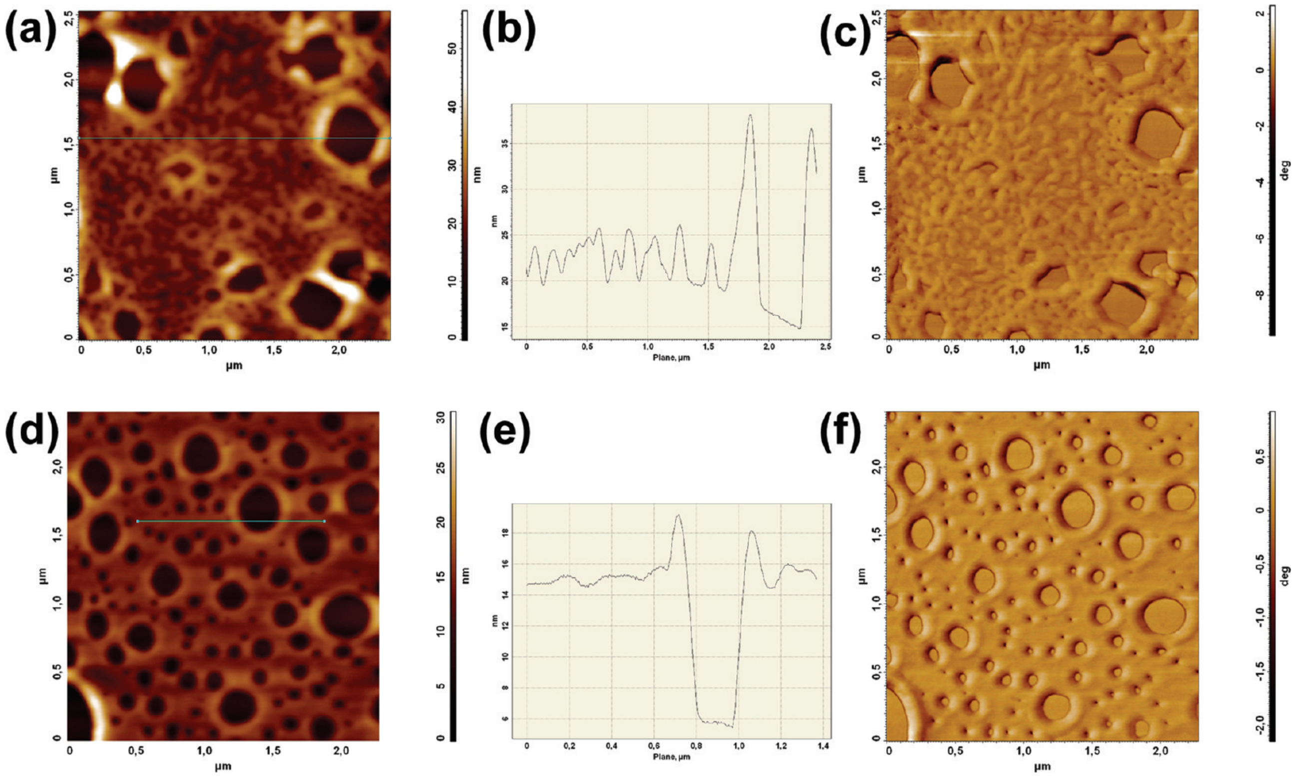


Figure 7. AFM height and phase pictures of 10.6 nm thick poly(*p*-phenylene) (PP) films on (a−c) untreated silicon and on (d−f) UV-ozone treated silicon: (a) height picture on untreated Si, (b) the surface roughness profile along the line shown in part a, (c) phase picture on untreated Si, (d) height picture on UV-ozone treated Si, (e) the surface roughness profile along the line shown in part d, and (f) phase picture on UV-ozone treated Si.

in good agreement with the observed depths of the holes on the top surface. The average distance of ~65 nm between the holes cannot be related to the molecular structure. This might arise because of different solubility of PS and PEO in CH_2Cl_2 and the evaporation of the solvent during the spin coating process.

To check further the nanophase separation between the perfectly alternating PEO and PS side chains and the influence of the substrate interface in orienting the layers, we investigated the morphology of even thinner films on untreated and UV-ozone-treated silicon substrates. UV-ozone treatment makes the silicon substrate surface more hydrophilic by the addition of −OH groups. The tendency of the hydrophilic PEO side chains for the substrate will then be stronger. Figure 7 shows the AFM height and phase pictures of 10.6 nm thick PP films on untreated silicon wafers (a and c) and UV-ozone treated silicon wafers (d and f). Spin coating from relatively dilute PP solution (c = 0.5 mg/mL) resulted in incomplete coverage. Uncoated circular regions (holes) having diameter between 0.1 and 0.5 μm were observed on both substrates. The PP film on untreated silicon consisted of ~5 nm thick smooth film on top of which there were ~5 nm peak-to-peak undulations (Figure 7b), indicating an incomplete and rough top surface. On the contrary, the PP film having the same thickness on hydrophilic silicon substrate showed a smooth ~10 nm thick film between the circular holes. The peak-to-peak roughness of the top surface was ~1 nm (Figure 7e). The difference in the roughness of the top surfaces of PP films for different substrates is also clearly seen in the phase pictures of Figure 7c,f. Another difference observed between the two spin-coated films is in the smoothness of the circumference of the large uncoated holes: the holes on untreated silicon have rougher circumference including some kinks, whereas the holes on hydrophilic silicon had smoother circumference. This shows that the film on hydrophilic silicon is better equilibrated by the tendency of the PEO side chains for the substrate such that the incomplete top layers disappeared at the expense of enlarged holes.

In summary, we have demonstrated the potential of Suzuki cross coupling reactions as a versatile synthetic route to prepare completely and perfectly alternating amphiphilic graft copolymers. The well-defined macromonomers of hydrophilic PEO and hydrophobic PS equipped with the opponent functional groups were readily coupled in the presence of palladium catalyst. The structures of such complexed graft copolymers have been fully characterized. Because of the extended conjugation arising from the polyphenylene formation, they exhibit a bathochromic shift in both absorption and emission spectra. The perfectly alternating hydrophilic PEO and hydrophobic PS side chains were observed by AFM measurements to nanophase separate in thin films. The perfectly designed amphiphilic nature of the PP graft copolymers, and the optical properties imply that they may find many applications in various fields.

Acknowledgment. We thank Istanbul Technical University for the financial support and the authors (A.L.D and Y.Y.) thank Turkish Academy of Sciences for financial support.

Supporting Information Available: FT-IR and ^{1}H NMR spectra of dihalide and aryl diboronic acid compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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