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Bioinspired Catecholic Copolymers for Antifouling Surface Coatings

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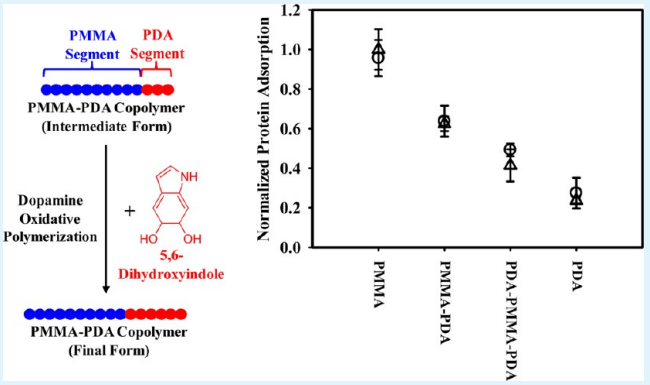
Supporting Information

ABSTRACT: We report here a synthetic approach to prepare poly(methyl methacrylate)-polydopamine diblock (PMMA-PDA) and triblock (PDA-PMMA-PDA) copolymers combining mussel-inspired catecholic oxidative chemistry and atom transfer radical polymerization (ATRP). These copolymers display very good solubility in a range of organic solvents and also a broad band photo absorbance that increases with increasing PDA content in the copolymer. Spin-cast thin films of the copolymer were stable in water and showed a sharp reduction (by up to 50%) in protein adsorption compared to those of neat PMMA. Also the peak decomposition temperature of the copolymers was up to 43°C higher than neat PMMA. The enhanced solvent processability, thermal stability and low protein adsorption characteristics of this copolymer makes it attractive for variety of applications including antifouling coatings on large surfaces such as ship hulls, buoys, and wave energy converters.



KEYWORDS: *polydopamine, PMMA, melanin, coatings, antifouling*

INTRODUCTION

Mussel-inspired catechol chemistry has attracted tremendous attention in recent years[1] for promoting adhesion of coatings on organic and inorganic surfaces,[2] modifying low surface energy substrates,[3] making free radical scavenging nanoparticles,[4] etc. It is interesting to note that the ortho-dihydroxyphenyl group, referred to as a "catechol" group, is also a common structural feature in natural melanins derived from oxidative polymerization of 5,6-dihydroxyindole (DHI) and 5,6-dihydroxyindole-2-carboxylic acid (DHICA),[5,6] or synthetic melanin-like polymers[7] derived from different monomers like L-3-(3,4-dihydroxyphenyl)-alanine (L-dopa), dopamine, etc. (Scheme 1a). The catecholic unit is assumed to be a key structural unit responsible for many different functions of melanins and this has led to renewed interest in catechols and catechol derivatives.[1] (It is likely that quinones and catechols are present simultaneously in these molecules in a reversible manner depending on conditions.) Recent reports on mussel adhesive proteins postulate a significant role of catechol bearing L-dopa, that is present in significant quantity at the foot of *Mytilus edulis*, in the strong tethering ability of mussels to various surfaces.[2] This stimulated great interest in using catecholic molecules like dopamine for surface immobilization schemes and antifouling surfaces,[8] where the substrates were dip-coated with dopamine based initiators followed by surface initiated polymerization and grafting of a variety of polymer brushes like polyethylene glycol (PEG), and other peptidomimetic polymers.[8,9] Recently, Jiang et al. developed a zwitterionic poly(carboxybetaine) with biomimetic adhesive catechol groups that can be applied to surfaces via the convenient "graft to" approach.[10] Although these approaches used dopamine units merely for anchoring antifouling polymers like PEG to the substrate, a more recent report demonstrated that polydopamine coatings by themselves enhance the fouling resistance on water purification membranes.[11]

Gradual growth and accumulation of biomass, commonly referred to as "biofouling", is a major problem affecting surfaces that are in contact with fluids containing proteins, cells, and microorganisms. Biofouling is also a serious problem in marine environments where the increased drag due to biofouling can result in a 40% fuel consumption increase in large commercial vessels[12] with hull corrosion and crevice formation as other costly detrimental effects. Furthermore, leaching of active ingredients such as copper and organic biocides from traditional antifouling coatings on marine vessels has led to increasingly stringent regulation of these biocidal coatings.[13] This has stimulated tremendous interest in the development of nonbiocidal technologies to control fouling. Though the above-mentioned approaches which involve dip-coating substrates with dopamine or dopamine initiators (followed by growth of antifouling polymers in some cases) can be a convenient antifouling approach for smaller surfaces like filtration membranes and medical implants, they are less applicable to larger surfaces like ships, buoys, and wave energy converters. We believe that grafting polydopamine (PDA) onto other commonly used

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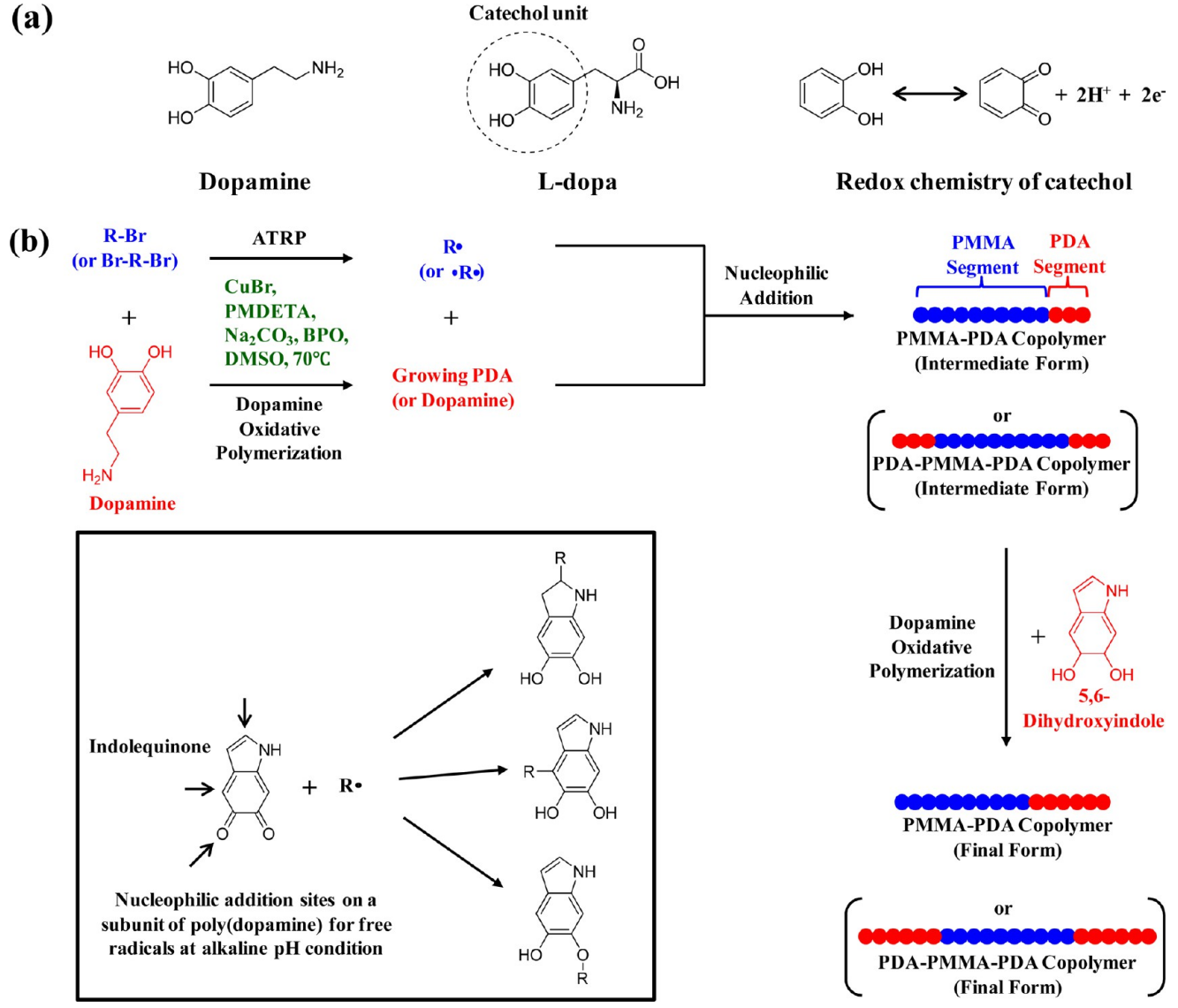
Scheme 1. (a) Chemical Formula of Dopamine and L-dopa, and Redox Chemistry of Catechol; (b) Copper-Catalyzed and pH-Induced Nucleophilic Addition of PMMA Radicals to Polydopamine, Combined with Dopamine Oxidative Polymerization[a]



[a]R-Br or Br-R-Br, prepared by ARGET ATRP, was used as a macroinitiator for generating a carbon nucleophile. R represents the PMMA chain. The boxed inset shows the nucleophilic addition sites on a subunit of PDA.

coating polymers such as PMMA could enable facile spray coating of large objects such as ship hulls with PDA containing polymers in the same way paints are applied, rendering them fouling resistant. To this end, we developed a synthetic approach to prepare poly(methyl methacrylate)-polydopamine diblock (PMMA-PDA) and triblock (PDA-PMMA-PDA) copolymers only from commercially available monomers. The resulting block copolymers show enhanced chemical processability, mechanical stability and good fouling resistance. These structured polymers, derived from modern controlled polymerization methods, differ from previous approaches[14,15] where specialized dopa/dopamine containing monomers were synthesized and incorporated into random copolymers.

EXPERIMENTAL SECTION

Materials. Anisole, methyl methacrylate (MMA), copper(II) bromide, cyclopentanone, ethyl 2-bromoisobutyrate (EBIB), and calcium hydride were purchased from Acros Organics. Dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), hexanes, dimethylformamide (DMF), sodium carbonate, and glass slides were obtained from Fisher Scientific. Benzene, dimethyl 2,6-dibromoheptanedioate (DMDBHD), copper(I) bromide, tin(II) 2-ethylhexanoate ($Sn(EH)_2$), dopamine-HCl, N,N,N′,N′,N″-pentamethyldiethylenetriamine (PMDETA), benzoyl peroxide (BPO), PMMA (M_w = 350 000 g/mol), phosphate buffered saline (PBS, pH 7.4), and basic alumina were purchased from Sigma-Aldrich. Tris[2-(dimethylamino)ethyl]amine (Me_6TREN) was synthesized following a published procedure.[16] Fluorescein conjugated bovine serum albumin (BSA-FL) was purchased from Life Technologies. Ultrapure water (18.2 MΩ cm) was obtained from a Thermo Scientific Barnstead E-pure water purification system. 10 mM Tris-HCl (pH 8.5) was prepared as needed. Anisole, MMA, and DMSO were purified by stirring with basic alumina and calcium hydride for 2 h and then filtered before use. Soluene was purchased from Perkin-Elmer and used as received.

Synthesis of PMMA Macroinitiators Using Activators Regenerated by Electron Transfer Atom Transfer Radical Polymerization (ARGET ATRP). MMA was initiated in anisole using either EBIB or DMDBHD, to synthesize a mono-functional macroinitiator

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(PMMA-Br) and a bi-functional macroinitiator (Br-PMMA-Br), respectively. For the synthesis of PMMA-Br, MMA (41.3 mL, 383 mmol), EBIB (625 μL, 4.3 mmol), copper(II) bromide (9.5 mg, 0.043 mmol), Me_6TREN (109 μL, 0.43 mmol), and anisol (39.7 mL) were placed in a schlenk flask and degassed by argon bubbling for 40 min. Polymerization was triggered by adding $Sn(EH)_2$ (138 μL, 0.43 mmol) to the flask. The sealed flask was placed in an oil bath maintained at 70 °C. After 10 h, the polymerization was quenched with liquid nitrogen and the flask was opened to air. The mixture was diluted with THF and then passed through a basic alumina column three times to remove the copper complex. The polymer was precipitated by adding a large amount of hexane. Dissolution and precipitation were repeated three times and then the polymer was lyophilized using benzene. The purified polymer was analyzed using an Agilent 1100 series chromatography setup (Agilent Technologies, USA). Size exclusion chromatography (SEC) calibration curves were obtained with PMMA standards from Polymer Laboratories. In addition, Br-PMMA-Br was synthesized using a similar procedure with shorter reaction time (5 h) and different molar ratios of MMA/DMDBHD/$CuBr_2$/Me6TREN/$Sn(EH)_2$ = 55/1/0.01/0.1/0.1 in anisole (50 wt % in the solution).

Synthesis of PMMA-PDA and PDA-PMMA-PDA Copolymers. For the synthesis of PMMA-PDA copolymer, two schlenk flasks were prepared simultaneously. PMMA-Br (2.5 g, 0.26 mmol) was fully dissolved in DMSO (20 mL) by stirring for 4 h. Dopamine-HCl (1.2 g, 6.4 mmol), PMDETA (81 μL, 0.39 mmol), sodium carbonate (341.2 mg, 0.05 M), BPO (1.55 g, 6.4 mmol), and DMSO (44.4 mL) were added to another schlenk flask, and also stirred for 4 h. The solution color immediately turned black due to the pH-induced oxidative dopamine polymerization. Subsequently, oxygen was removed from both flasks by three freeze-pump-thaw cycles, and then copper(I) bromide was added to the flask containing dopamine in a glove box. PMMA-Br solution was transferred to the other flask containing copper(I) bromide catalyst to trigger the coupling reaction between Br ended PMMA and dopamine or partially grown PDA, and the reaction was conducted at 70 °C for 2 days under vigorous stirring. The reaction was stopped by removing heat, quenching with liquid nitrogen, and opening the flask to air. The mixture was diluted with DMF and then run through a basic alumina column to remove the copper and ligand. Subsequently, the resultant solution was concentrated by evaporating solvents at 100 °C under vacuum using a rotary evaporator. The polymer was precipitated by addition to a large amount of methanol and washed several times by ultrapure water and methanol to remove residual Na_2CO_3, BPO, dopamine monomer, and pure PDA unattached to PMMA. The purified copolymer was finally dried under vacuum at room temperature until a constant weight was reached. For synthesis of PDA-PMMA-PDA copolymer, two times molar ratio of dopamine-HCl and CuBr/PMDETA was used to grow PDA on both ends of PMMA. PDA-PMMA-PDA synthesis used a similar procedure with dopamine-HCl/Br-PMMA-Br/CuBr/PMDETA = 50/1/3/3 with BPO content = 1 molar equivalent based on dopamine-HCl in DMSO solution (10 mL per 1 mmol of dopamine-HCl). Dark brown powder was obtained with 48-57% yield for both copolymers. All polymers were analyzed using an Agilent 1100 series SEC equipped with refractive index (RI) and photoabsorbance detectors.

UV−Vis Spectroscopy. Photoabsorbance of PMMA-Br, PMMA-PDA, PDA-PMMA-PDA was obtained from a 1 mg/mL solution in DMF using a UV−visible spectrophotometer (Evolution 220, Thermo Scientific).

Solubility Test. A variety of good solvents for PMMA were chosen for this test. PMMA-PDA, PDA-PMMA-PDA and pure PDA (4 mg/mL) were separately placed in glass vials containing test solvent, and stirred for 12-24 h. Good solubility was confirmed by observing clear solution (no insoluble particles visible to the eye) at a concentration of 4 mg/mL. PDA-PMMA-PDA required a longer time to dissolve in the solvents than PMMA-PDA since the content of PDA in PDA-PMMA-PDA is much higher than that of PMMA-PDA.

Thermogravimetric Analysis (TGA). Thermal decomposition behavior of the copolymers was investigated using a thermogravimetric analyzer (DSC/TGA 1, Mettler Toledo). Samples were heated from 30 °C to 1000 °C at 20 °C/min under nitrogen atmosphere.

Differential Scanning Calorimetry (DSC). Samples were heated and scanned under a continuous nitrogen purge (50 mL/min) at 10 °C/min within the temperature range of 25−200 °C using a Mettler Toledo DSC 1. The glass transition temperature (T_g) for each sample was taken as the midpoint step increment in the specific heat of the second heating cycle.

Protein Adsorption. Solutions of PMMA (Sigma-Aldrich, M_w = 350 000 g/mol), PMMA-PDA, and PDA-PMMA-PDA in cyclopentanone were prepared at a concentration of 4 wt %. Films were spin-coated onto glass slides (25×25 mm) at 2000 rpm for 60 s and annealed at 140 °C for 10 h under vacuum to remove residual solvents. Pure PDA thin films were formed on glass slides by dip-coating the substrate during oxidative polymerization.[2] Glass slides were placed in isopropyl alcohol and cleaned by ultrasonication, and then thoroughly rinsed with acetone and methanol. Dopamine solution (2 mg/mL) in 10 mM Tris-HCl (pH 8.5) was prepared, and glass slides were immersed in the solution. The solution was continuously stirred for 3 days. The solution color turned black by alkaline pH-induced oxidative polymerization of dopamine. PDA-coated glass slides were rinsed with ultrapure water and dried with air. Film thickness measurements were carried out at multiple locations on each sample using a profilometer (Dektak 6M Stylus Profiler, Veeco Instruments Inc.) (PMMA: 186 nm, PMMA-PDA: 105 nm, PDA-PMMA-PDA: 107 nm, PDA dip-coating: 57 nm). For short-term protein adsorption tests, films on glass slides were incubated in the 1 mg/mL BSA-FL solution in 7.4 pH PBS at 4 °C for 60 min, and rinsed several times with ultrapure water.[17] The short-term tests were conducted for both dry and water-aged films, separately. The water-aged films were prepared by immersing dry films in ultrapure water for 24 h prior to incubation in BSA-FL. For long-term protein adsorption tests, dry thin films were incubated with BSA-FL (0.5 mg/mL) in 7.4 pH PBS at 4 °C for one week, and then gently washed several times with ultrapure water. All films were air-dried over night before fluorescence testing. All these procedures were carried out in the darkness to avoid photo-bleaching. Fluorescence spectroscopy was performed on polymer films on a Photon Technologies QuantaMaster 40 with a photomultiplier tube detection system with 2 nm excitation slits and 4 nm emission slits. The excitation and emission wavelengths used were 450 nm and 560 nm, respectively. The fluorescence intensity of each film of PMMA, PDA-PMMA, PDA-PMMA-PDA, and PDA was measured before and after immersion, and the intensity before incubation was subtracted from the intensity after immersion so as to take background fluorescence into account.[18] Finally, the intensities were normalized with the average fluorescence intensity of a protein adsorbed PMMA film (non-water aged), which had been annealed and then immediately incubated in BSA-FL solution similarly.

Water Stability and Structural Characterization of Thin Films. Thin films of PMMA-Br, PMMA-PDA and PDA-PMMA-PDA were spin-coated (2000 rpm, 60 s) on silicon wafers (15 × 15 mm) from cyclopentanone solutions (4 wt %), and annealed at 140 °C for 10 h under vacuum. In addition, free and pure PDA was synthesized according to a reported procedure,[4] and dissolved in Soluene (Perkin-Elmer) at a concentration of 4 wt %. The pure PDA film was then spin-coated onto a silicon wafer at 2000 rpm for 60 s, and dried in the hood. PDA was also deposited by oxidative polymerization on a silicon wafer by simple immersion of the substrates into the polymerizing dopamine solution (2 mg/mL) in 10 mM Tris-HCl (pH 8.5) for 3 days.[2,19] The thickness of the films was measured using a spectroscopic ellipsometer (VB-400 VASE Ellipsometer, J. A. Woollam Co., Inc.) using wavelengths from 382 to 984 nm with a 65° angle of incidence (PMMA-Br: 103 nm, PMMA-PDA: 114 nm, PDA-PMMA-PDA: 94 nm, PDA dip-coating: 52 nm). The thickness of the spin-coated PDA film was difficult to measure due to macroscopic surface roughness. An optical microscope (Olympus BX60) with a camera was used to collect micrographs of the thin films at low (10×) and high (50×) magnifications. The water stability of the films was investigated by immersing them in ultrapure water for two days or in slightly alkaline 10 mM Tris-HCl (pH 8.5) for one week.

Surface Properties of Thin Fims. Water contact angles were measured with a Ramé-Hart, inc. NRL C.A. goniometer (model #100-00). The volume of the water drop used for the measurement was 6 μL. An X-ray photoelectron spectroscopy (XPS, KRATOS Axis Ultra)

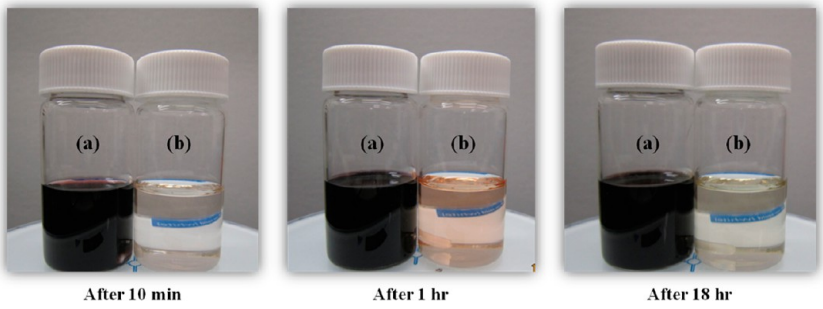

Figure 1. Photographs illustrating the effect of sodium carbonate on dopamine oxidative polymerization reaction: (a) with or (b) without sodium carbonate (53 mg, 0.05 M). Dopamine-HCl (75 mg, 0.40 mmol), BPO (97 mg, 0.40 mmol), and DMSO (10 mL) added in all cases.

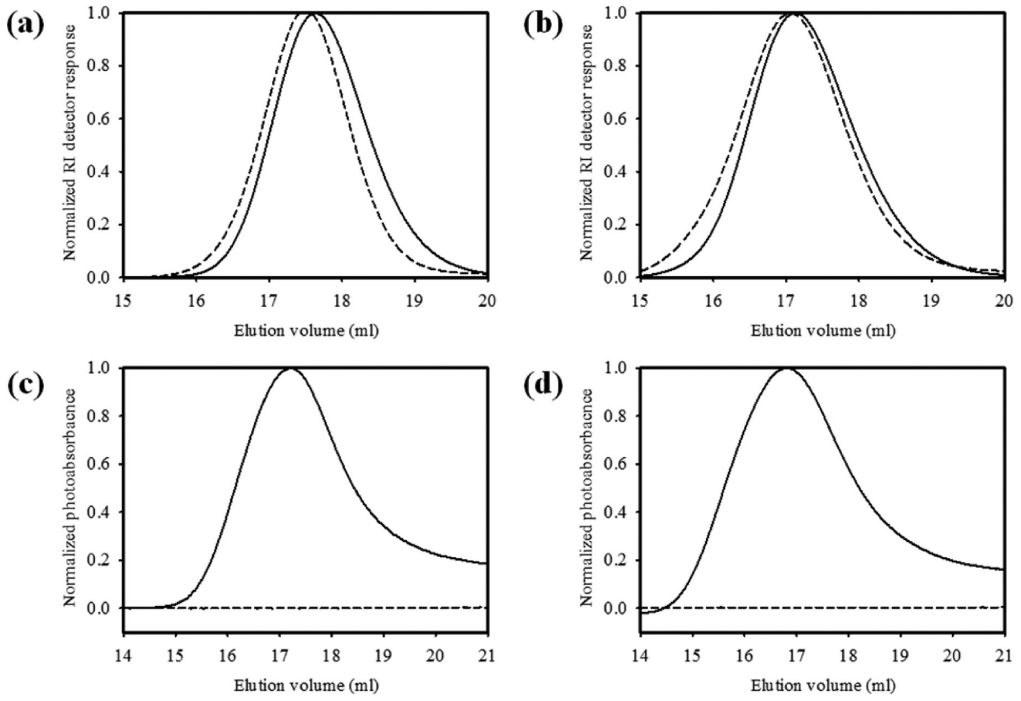

Figure 2. Size exclusion chromatograms (RI signal) of (a) PMMA-Br and (b) Br-PMMA-Br macroinitiators before (solid line) and after (dashed line) chain extension with PDA. SEC traces from light absorbance (λ: 450 nm) for (c) PDA-PMMA (solid line), PMMA-Br (dashed line), (d) PDA-PMMA-PDA (solid line), and Br-PMMA-Br (dashed line).

instrument using a monochromatic Al Kα X-ray source ($h\nu$ = 1486.5 eV) was used to analyze the surface composition of the films. The photoelectron take-off angle was normal to the surface of the sample and 45° with respect to the X-ray beam. High-resolution spectra were collected and the pressure in the analysis chamber was typically 2×10^{-9} Torr during data acquisition.

RESULTS AND DISCUSSION

Our synthetic approach to make these block copolymers involved two steps (Scheme 1). First, PMMA with a bromine end group at one or both ends of the PMMA chain was synthesized using established ARGET ATRP procedures.[20−24] PMMA with the Br end group, obtained by precipitation and purification, was then transferred into a polymerizing dopamine solution. Copper(I) bromide was used to remove the Br end-group from PMMA macroinitiators (dormant form) and to generate a carbon nucleophile as a PMMA free radical (active form), which then coupled with dopamine monomers or growing PDAs in solution. Since fully grown PDAs have very limited solubility in organic solvents, one can expect poor reaction conversion when coupling already synthesized PDA with PMMA macroinitiators. In fact, direct coupling of pure PDA and PMMA-Br in DMSO was attempted and it was observed that PDA was attached to PMMA but at very low PDA content, as confirmed by UV-Vis photoabsorbance of the purified product. Radical scavenging properties of quinones and the nucleophilic addition of carbon-centered radicals to quinones are well-known.[25,26] Recent studies have described Michael addition chemistries between *o*-quinone and nucleophilic groups such as thiols and amines for mussel-inspired layer-by-layer assembly of multilayer films,[2,27−29] and the same catechol chemistry with carbon nucleophiles as an electron donor instead of a heteroatom nucleophile was employed in this study. The dopamine or growing PDA segments linked to PMMA chains (intermediate form) were further polymerized with dopamine monomers in the solution. Eventually, PMMA-Br and Br-PMMA-Br macro-initiators resulted in PMMA-PDA diblock and PDA-PMMA-PDA triblock copolymers (final form), respectively (Scheme 1b), which were then thoroughly purified. Typically, dopamine polymerization is conducted in aqueous conditions.[2,4] However, in this work, dopamine oxidative polymerization was carried out

in DMSO, using published procedures for the synthesis of melanin-like polymers but with slight modifications.[7,30] Sodium carbonate was added for neutralization of dopamine-HCl to develop a basic solution.[4] The oxidized quinone form of catechol is favorable for dopamine self-polymerization and the Michael addition reaction (Scheme 1b boxed insert).[2,27−29] The oxidized form is postulated to drive the transformation of dopamine monomer toward 5,6-dihydroxyindole, which upon further oxidation and intermolecular crosslinking yields a heterogeneous polymer.[2] Wei et al. also reported that dopamine polymerization is promoted and activated at high pH in the presence of oxidants such as an ammonium persulfate.[31] We also found that dopamine solutions in DMSO quickly turn black in the presence of Na_2CO_3, suggesting that an alkaline pH is essential for spontaneous dopamine polymerization (Figure 1).

SEC equipped with RI and photoabsorbance detectors was used to confirm the formation of copolymer. A homogeneous shift of the SEC RI traces toward higher molecular weight suggests PDA attachment to the PMMA macroinitiator (Figure 2a, b). Although PMMA macroinitiators show no photoabsorbance (Figure 2c, d), PDA exhibits a broad band photoabsorbance in the UV and visible wavelengths. Both RI and photoabsorbance peaks appearing at the same elution volume confirms that PDA is covalently linked to PMMA (Figure 2c, d). (The ∼0.2 min offset in peak location of the photoabsorbance trace compared to the RI trace is due to intermediate tubing between the two detectors). The number average molecular weights (M_n) of PMMA-Br and Br-PMMA-Br macroinitiators were 9600 and 14 300 g/mol, respectively, with corresponding polydispersity indices (PDI) of 1.46 and 1.49. After PDA attachment the M_n of PMMA-PDA and PDA-PMMA-PDA were 12 900 g/mol (PDI = 1.31) and 17 100 (PDI = 1.48) (based on PMMA standard calibration), respectively. PDA contents of PMMA-PDA and PDA-PMMA-PDA by nitrogen combustion analysis were 7.8 and 9.3 wt %, respectively.

As further evidence for the successful coupling of PDA to the PMMA macroinitiator, we observed a broad band monotonic photoabsorbance for the copolymers, which is characteristic of PDA and other natural and synthetic melanins (Figure 3).[5,32]

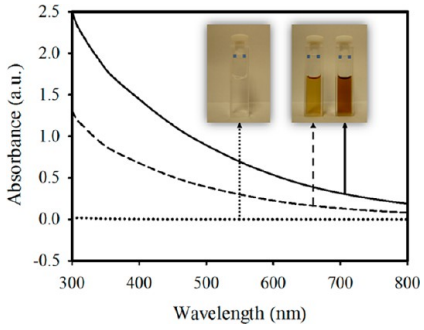

Figure 3. UV−Vis absorbance spectra of PMMA-Br (dotted line), PMMA-PDA (dashed line), and PDA-PMMA-PDA (solid line) in DMF at 1 mg/mL.

The absorbance intensities were found to increase with PDA content in the copolymer and, as expected, the PDA-PMMA-PDA triblock copolymer solution in DMF was much darker than PMMA-PDA at identical concentrations (inset in Figure 3). It is simply deduced that PDA-PMMA-PDA triblock copolymer could contain roughly twice the amount of PDA in each molecule compared to PMMA-PDA diblock copolymer when Br-PMMA-Br and PMMA-Br have roughly similar molecular weights.

Thermal Analysis. The copolymers also displayed interesting thermal behavior (Figures 4 and 5). The peak decomposition temperatures of PMMA-PDA and PDA-PMMA-PDA were 16 and 43 °C higher, respectively, than that of neat PMMA (Figure 4c, d). PMMA is known to degrade under elevated temperature by radical initiated chain scission followed by chain unzipping.[33−36] The free radical scavenging behavior of melanin is well known and it was recently demonstrated how this feature could be exploited in thermo-oxidative stabilization of PMMA and other thermoplastic polymers by simply blending 0.5−5 wt % natural or synthetic melanins into the polymers.[32] It is interesting to note that coupling PDA, which has a similar catecholic group as melanin, onto the ends of PMMA also results in enhanced thermal stability. The thermal degradation mechanism of PMMA has been extensively studied, and Kashiwagi et al. suggested three steps of mass loss of free radically polymerized PMMA.[35] Initial thermal degradation at low temperature is ascribed to weak links and unsaturated end groups generated during termination of free radical polymerization, followed by random chain scission at high temperature.[32] Figure 4c and d show a substantial increase in the peak decomposition temperature after chain extension of PMMA macroinitiators by PDA, but there was little or no enhancement in the onset decomposition temperature. PMMA macroinitiators prepared by ARGET ATRP and their respective copolymers do not have unsaturated chain ends and head-to-head linkages from a chain termination step which is susceptible to depolymerization.[34] Most of the PMMA chain ends are saturated and occupied by bromides, initiator fragments, or PDA. Therefore, the major thermal degradation mechanism of the macroinitiators and copolymers involves only random chain scission, and hence the thermal stabilization effect was observed mainly in the peak decomposition temperature, not in the onset (Figure 4c, d).

PMMA-PDA and PDA-PMMA-PDA copolymers also displayed two distinct T_gs, which is a typical characteristic of a block copolymer. Although PMMA macroinitiators and pure PDA have a T_g of about 110−115 °C and 100 °C respectively, the copolymers had two separate T_g values, one around 100 °C and another around 117 °C (Figure 5 and Table 1) corresponding to PDA blocks (red arrows) and PMMA blocks (blue arrows) respectively. Pure PDA exhibits multistep T_g behavior whose origin is unknown but which is clearly reproduced in the block copolymers.

Solvent Solubility. One significant advantage of coupling polydopamine to a common coating polymer like PMMA is the enhanced solvent solubility of the copolymer. While PDA doesn't dissolve in many organic solvents except for moderate solubility in DMF and DMSO, which has been ascribed to strong hydrogen bonding and π-stacking among the subunits,[37] the copolymers dissolve in a variety of good solvents for PMMA (THF, DMF, cyclopentanone, toluene, acetone, methylene chloride, etc.) (Table 2 and Figure 6). The enhanced solubility of these copolymers in organic solvents as compared to that of PDA has significant processing advantages. Smooth thin films could be made by spin-coating the copolymer solutions from cyclopentanone or toluene on silicon wafers and glass slides, comparable to neat PMMA films, while spin-coated pure PDA films and PDA films deposited during oxidative polymerization exhibited macroscopic and microscopic surface roughness, respectively (Figure 7). These films were then used for water stability, surface characterization, and protein adsorption tests.

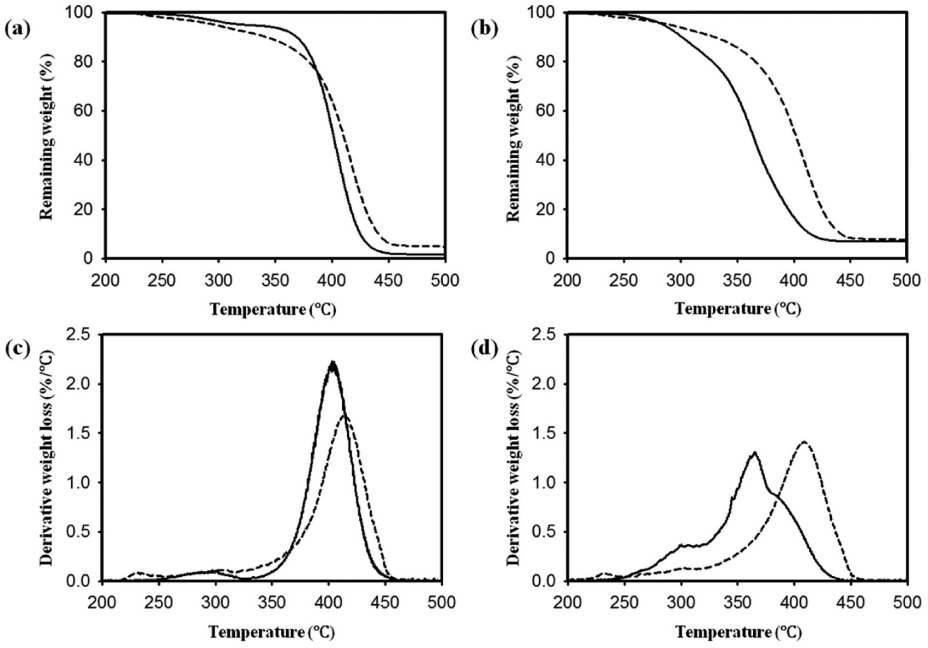

Figure 4. Thermogravimetric analysis of (a) PMMA-Br (solid line) and PMMA-PDA (dashed line), and (b) Br-PMMA-Br (solid line) and PDA-PMMA-PDA (dashed line). Derivative thermogravimetric analysis of (c) PMMA-Br (solid line) and PMMA-PDA (dashed line), and (d) Br-PMMA-Br (solid line) and PDA-PMMA-PDA (dashed line). All samples were heated in a nitrogen atmosphere at 20 °C/min.

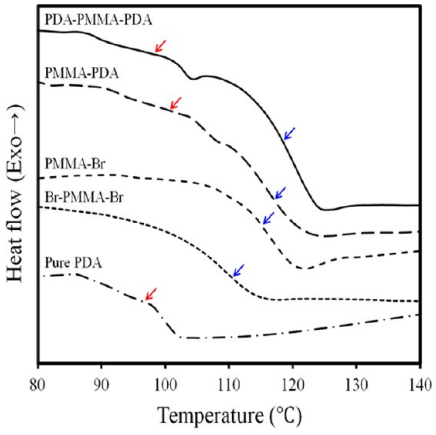

Figure 5. Differential scanning calorimetry (DSC) thermograms of PMMA-Br, Br-PMMA-Br, PMMA-PDA, PDA-PMMA-PDA, and pure PDA. T_g for each sample, taken as a midpoint of specific heat increment from the second heating run, was indicated by an arrow.

Table 1. Glass Transition Temperatures of PMMA Macroinitiators and Their Respective Copolymers

polymer	T_g (°C)
PMMA-Br	115
Br-PMMA-Br	111
PMMA-PDA	101/117
PDA-PMMA-PDA	98/118
Pure PDA	97

Thin Film Surface Characterization. Water contact angle measurements were conducted to examine the surface wetting properties of the copolymer films. As shown in Figure 8, the static contact angles of PMMA-PDA (68.3°) and PDA-PMMA-PDA (64.7°) copolymers decreased by 6-10° compared to neat PMMA (74.6°), which clearly indicates that PDA incorporation made the surface of the copolymer coating more hydrophilic.

Table 2. Solubility Chart of PMMA-PDA, PDA-PMMA-PDA, and Pure PDA in various Organic Solvents[a]

	solubility[b]		
solvent	PMMA-PDA	PDA-PMMA-PDA	Pure PDA
acetone	○	○	×
acetonitrile	○	○	×
anisole	○	○	×
benzene	○	○	×
2-butanone	○	○	×
chlorobenzene	○	○	×
chloroform	○	○	×
cyclopentanone	○	○	×
DMF	○	○	△
DMSO	○	○	△
methylene chloride	○	○	×
toluene	○	○	×
THF	○	○	×

[a]Good solubility was determined by a clear solution (no insoluble particles visible to the eye) at the concentration of 4 mg/mL (Experimental). [b](○, good, △, limited, ×, poor).

XPS spectra of the thin films also confirmed that the surface composition changes with incorporation of PDA (see Figure S1 in the Supporting Information). The N 1s peak was present in thin films of PMMA-PDA and PDA-PMMA-PDA copolymers but not PMMA-Br precursor. These two experiments serve to confirm the presence of PDA directly confirm on the surface and suggest that strategies to attach additional antifouling polymers such as PEG to the PDA at the surface by Michael addition could be successful.

Thin Film Protein Adsorption Studies. The copolymer films also showed strong antifouling behavior (Figure 9). Thin films of commercial PMMA and two copolymers were spin-coated, while PDA films were dip-coated on glass slides during dopamine polymerization. We used a commercial PMMA with high molecular weight as control instead of PMMA macro-

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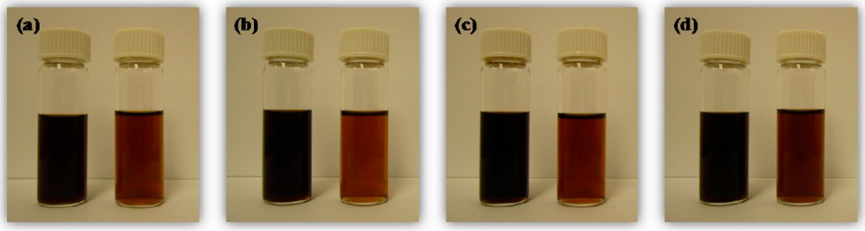

Figure 6. Photographs of solutions of PDA-PMMA-PDA (left) and PMMA-PDA (right) copolymers in (a) acetone, (b) cyclopentanone, (c) DMF, and (d) THF at a concentration of 4 mg/mL.

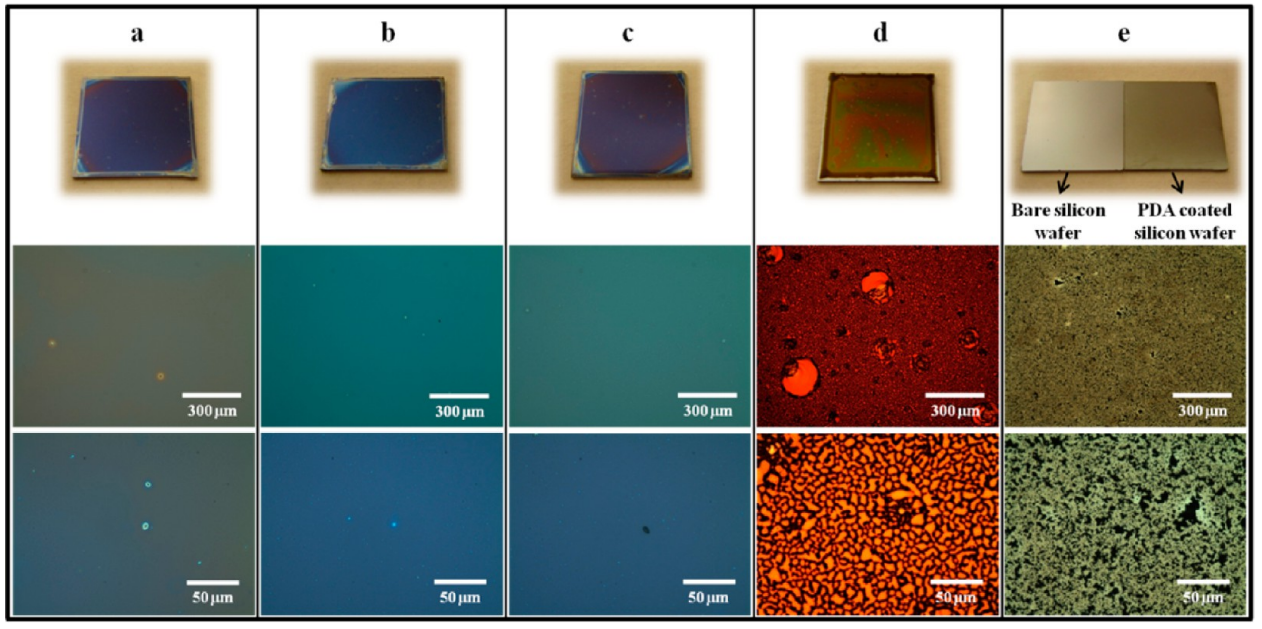

Figure 7. Photographs (top row) and optical microscopy images (bottom two rows) of spin-coated thin films of (a) PMMA-Br, (b) PMMA-PDA, (c) PDA-PMMA-PDA, (d) pure PDA, and (e) PDA films deposited during oxidative polymerization on silicon wafers at low (10×, middle row) and high (50×, bottom row) magnification. Each column includes three images of the same film at different imaging conditions.

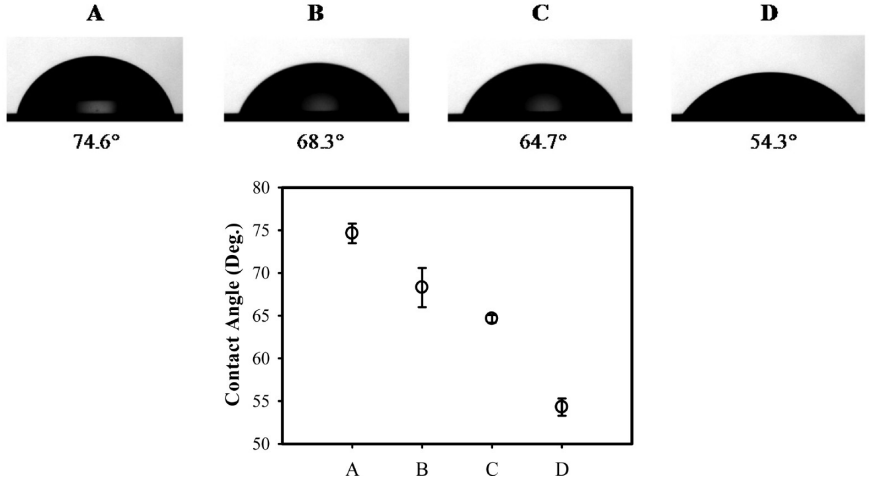

Figure 8. Water contact angle analysis of (a) PMMA (M_w = 350 kg/mol), (b) PMMA-PDA, (c) PDA-PMMA-PDA, and (d) PDA deposited by oxidative polymerization on silicon wafers. Error bars indicate standard deviation from ten measurements.

initiators for this protein adsorption test due to its better stability in water. Protein adsorption behavior was determined using a previously reported procedure[17] by incubating the films in BSA-FL (0.5 mg/mL in pH 7.4 PBS buffer) at 4 °C for 7 days. PMMA films showed the strongest fluorescence intensity from BSA-FL adsorption, but significantly lower intensities were measured from the copolymer films indicating less protein adsorption. Normalizing the data with the fluorescence intensity of neat PMMA films, we observed an 40−50% reduction in protein adsorption for the copolymer films. For reference, the protein

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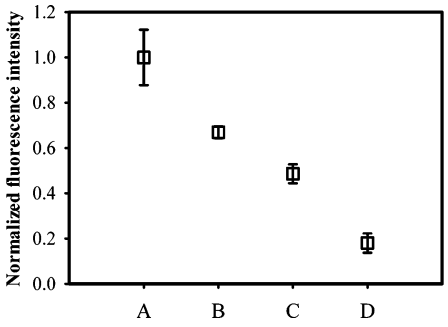

Figure 9. Normalized fluorescence intensity of thin films of (A) PMMA (M_w = 350 kg/mol), (B) PMMA-PDA, (C) PDA-PMMA-PDA, and (D) PDA deposited by oxidative polymerization, incubated in a 0.5 mg/mL BSA-FL solution at 4 °C for one week.

adsorption of pure PDA was also determined and we found that PDA-PMMA-PDA copolymer performs reasonably close in antifouling behavior to pure PDA deposited by dip-coating (Figure 9). Protein adsorption tests conducted for 60 min before or after aging the films in ultrapure water for 24 h showed similar antifouling behavior (see Figure S2 in the Supporting Inforamtion). It is important to note here that the copolymers have much better chemical processability than PDA and can be easily spray coated onto large objects or objects with complicated geometries using common organic solvents. Another significant advantage of this block copolymer architecture is the superior stability of the PMMA-PDA and PDA-PMMA-PDA films both in pure water (pH 6.8−6.9) and slightly alkaline conditions (pH 8.5) (see Figures S3 and S4 in the Supporting Information). Although films of PMMA macroinitiator precursors, having similar molecular weight to the copolymers, fractured and dewetted from the substrates upon immersion in water, the copolymer films had superior stability in ultrapure or slightly alkaline water. Though PDA deposited on a silicon wafer by oxidative polymerization was stable in ultrapure water, preformed PDA dissolved in Soluene (Perkin-Elmer), a special solvent mixture that dissolves melanins, and then spin-coated on a silicon wafer also fractured and delaminated in both ultrapure and alkaline water (see Figure S3 and S4 in the Supporting Information). This highlights the fact that PDA and PMMA complement each other in this copolymer architecture to result in a stable and easily processable antifouling coating. Whereas PMMA adds mechanical stability and chemical processability, PDA provides wet substrate adhesion capabilities and antifouling behavior.[2,38]

CONCLUSIONS

A synthetic approach to prepare catecholic block copolymer architectures containing PMMA and PDA has been established. Chromatography, photoabsorbance and thermal analysis studies confirm successful coupling of PDA to PMMA ends to make block copolymers. Although the solubility of PDA in organic solvents is very limited, the copolymers show very good solubility in a variety of organic solvents which could provide significant processing advantages and facilitate development of PDA containing functional materials. The copolymers can be easily spin-coated into thin films and they have excellent stability in ultrapure water and slightly alkaline conditions as compared to spin-coated PDA. Protein adsorption on the copolymers was 40−50% less as compared to neat PMMA and appeared to be a function of PDA content.

ASSOCIATED CONTENT

Supporting Information

XPS spectra, short-term protein adsorption tests, photographs of thin films, and preparation of thin films. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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