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Blocklike Fluorocarbon and Hydrocarbon Copolymer Films via Surface-Initiated ATRP and Postpolymerization Reactions

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ABSTRACT: We report a new method to prepare ultrathin blocklike copolymer films on metal surfaces with molecularly optimized surface and barrier properties. Copolymer films containing various fluorocarbon and/or hydrocarbon side chains were created by a one-step surface-initiated polymerization of poly(hydroxyethyl methacrylate) (PHEMA) followed by straightforward derivatization steps. Exposure of PHEMA to perfluorobenzoyl chloride results in a perfluoroaryl-modified PHEMA film that exhibits high conversion and outstanding barrier properties but does not present an oleophobic surface. We have previously demonstrated that fluorinated esters created in this manner may be hydrolyzed back to PHEMA by brief exposure to base. Controlled hydrolysis results in regeneration of PHEMA in the outer surface region that can be subsequently rederivatized with alkyl or fluoroalkyl acid chlorides to create copolymer films with tailored surface composition. Surface properties are solely affected by the species used during rederivatization while barrier properties result from the combined conversion, structuring, and surface properties of the copolymer film.

Introduction

Block copolymer thin films are often prepared by sequential polymerization of different monomers using controlled, surface-initiated polymerizations.[1−3] These films exhibit properties that are dependent on monomer choice and have applications in lithographic masks, membranes, responsive coatings, and photonic devices.[1,4−6] However, the sequential polymerization steps utilized during formation of these films are time- and labor-intensive processes and tend to result in diminished block thicknesses due to progressively lower reinitiation efficiencies.[1]

Scheme 1. Controlled Hydrolysis and Acylation Reactions to Form Blocklike Copolymer Films from a Base PHEMA Film on Gold

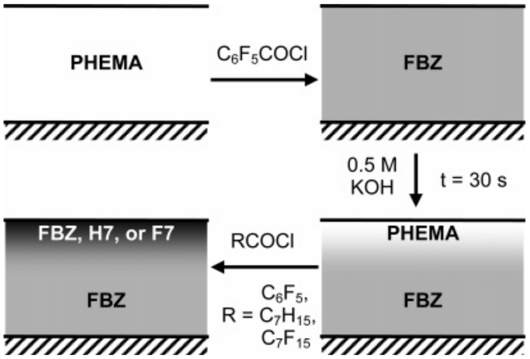

Table 1. Advancing Contact Angles (deg) for Water and Hexadecane (HD) and Critical Surface Energy (γ_C) for Modified PHEMA Films on Gold

film[a]	$\theta_A(H_2O)$ (deg)	θ_A(HD) (deg)	γ_C (mN/m)	ref
H1	70	<10		16
H7	104	<10		16
H11	113	16	∼27	16, 17
H13	117	21	∼26	16, 17
H15	117	44	24	16, 17
H17	115	47	23	16, 17
F1	90	49	21	17
F3	110	67	15	14
F7	128	79	9	14
FBZ	90	<10		14

[a] H represents alkyl modifications, F represents fluoroalkyl modifications, and FBZ represents a perfluorobenzoyl modification; the accompanying number indicates the carbon chain length of the modification.[14,16,17]

Herein, we demonstrate a method that requires only a single polymerization step but can yield copolymer films having blocklike properties and controlled thickness up to several hundred nanometers (Scheme 1). As the starting point, poly(hydroxyethyl methacrylate) (PHEMA) films are grown from gold surfaces using surface-initiated, water-accelerated atom transfer radical polymerization (ATRP).[7−11] The use of PHEMA allows, by simple postpolymerization chemical reactions, the addition of numerous side chains to tune film properties. We and others have shown that the hydroxyl side chains of the PHEMA film can be derivatized by reaction with various species, including fluorocarbon and hydrocarbon acid chlorides, an imidazole, and trimethylchlorosilane, to produce films with a wide range of wettabilities (Table 1).[10,12−18] Here, we modify PHEMA with pentafluorobenzoyl chloride (C_6F_5COCl) to generate a film denoted as FBZ that contains perfluoroaryl side groups on ∼80% of the side chains.[14] Of significance here, when fluorocarbon acid chlorides such as FBZ are employed in the modification of PHEMA, the resulting fluorinated esters created via the acylation reaction are susceptible to hydrolysis in basic solutions.[14] By controlling the base concentration and exposure time, hydrolysis of fluorinated PHEMA films can be conducted in a diffusion-limited manner, only removing fluorinated ester groups near the outer surface. Since this hydrolysis regenerates hydroxyl groups, the outer portions of the film can be subsequently rederivatized with a second moiety (i.e., another fluorocarbon or hydrocarbon) to create blocklike copolymer films (Scheme 1). The choice of modifying species allows surface (Table 1) as well as barrier properties to be

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altered to varying degrees and provides fundamental information on the effect of a dense outer block on the overall barrier properties of the film.[14,16,18] As compared to use of a single functionality within polymer films, a combination of groups to simultaneously optimize all areas of effectiveness in applications provides the ultimate ability to engineer surfaces and films at the molecular level.

In the interest of creating hydrophobic, oleophobic barriers via simple, controlled reactions, FBZ was chosen as the base film because it exhibits desirable barrier properties while presenting a surface that is oleophilic (wetted by hexadecane) and only moderately hydrophobic (undesirable for use as a nonwetting coating).[14] Therefore, the properties of this film may be dramatically altered by modification with an outer block. In addition, FBZ is readily hydrolyzed but accommodates a slower, more easily controlled hydrolysis as compared with perfluoroalkyl modifications since it is slightly more stable (β but no α fluorine atoms). The highly blocking barrier properties of FBZ are important to achieving a controlled hydrolysis and preventing the KOH solution from penetrating into the fluorocarbon region of the film.[14]

Baker, Bruening, and co-workers[18] have recently demonstrated that alumina membranes coated with thin (<200 nm) hydrocarbon- and fluorocarbon-modified PHEMA films exhibit remarkable separation factors (as high as 500) in the pervaporation of volatile organic compounds (i.e., benzene or ethyl acetate) from water. The ability to control both surface and barrier properties, as described herein, could ultimately be useful to affect molecular partitioning and diffusivities and, perhaps, tailor separation efficiencies in a molecule-specific manner. While postpolymerization reactions within films on a surface can occasionally be found in the literature,[3,10,12,13,18,19] no analogous scheme was found for the preparation of blocklike copolymer films from a homopolymer film.

Experimental Section

Materials. CuCl (99.995+%), $CuBr_2$ (99.999%), 2,2′-bipyridine (bpy, 99+%), 2-hydroxyethyl methacrylate (HEMA, >99%), pyridine (99+%), potassium hydroxide (KOH, 85+%), $K_3Fe(CN)_6$ (99+%), $K_4Fe(CN)_6 \cdot 3H_2O$ (99%), and hexadecane (99%) were used as received from Aldrich. *N*,*N*-Dimethylformamide (DMF, 99.9%), isooctane (99%), octanoyl chloride ($C_7H_{15}COCl$, 99%), pentadecafluorooctanoyl chloride ($C_7F_{15}COCl$, 98%), pentafluorobenzoyl chloride (C_6F_5COCl, 98%), trifluoroacetic anhydride ($(CF_3CO)_2O$, 99+%), dichloromethane (99.9%), and Na_2SO_4 (anhydrous) were used as received from Fisher. Gold shot (99.99%) and chromium-coated tungsten filaments were obtained from J&J Materials and R.D. Mathis, respectively. Silicon (100) wafers (Montco Silicon) were rinsed with ethanol and deionized water and dried with nitrogen. Ethanol (AAPER, absolute) was used as received. Deionized water (16.7 MΩ·cm) was purified with a Modu-Pure system and used as a solvent during polymerization and for rinsing. An initiator-terminated disulfide, $(BrC(CH_3)_2COO(CH_2)_{11}S)_2$, was synthesized as described in the literature.[20]

Preparation of Gold Substrates. Gold substrates were prepared by evaporating chromium (100 Å) and gold (1250 Å) in sequence onto silicon (100) wafers at rates of 1−2 Å s^{-1} in a diffusion-pumped chamber with a base pressure of 4×10^{-6} Torr. After removal from the evaporation chamber, the wafers were typically cut into 1.5 cm × 4 cm pieces.

Polymerization. Gold substrates were first placed in a 1 mM ethanol solution of $(BrC(CH_3)_2COO(CH_2)_{11}S)_2$ for 24 h. The initiated samples were then rinsed with ethanol, dried with nitrogen, and placed in vials that were subsequently degassed and backfilled with nitrogen. A Cu^I/Cu^{II}/bpy (69 mM CuCl, 20 mM $CuBr_2$, 195 mM bpy) system in a 50:50 v:v water/HEMA solution was used for polymerization.[10] The mixture was placed in a Schlenk flask sealed with a rubber septum and was degassed by performing three freeze−pump−thaw cycles. This was followed by transfer of the solution via cannula into vials containing up to six samples each. After polymerizing for 12 h at room temperature, the samples were thoroughly rinsed with water and DMF and then dried with nitrogen. As measured by ellipsometry with samples from two different batches, the average PHEMA film thickness was 224 ± 10 nm under these conditions.

Reactions To Form Blocklike Copolymer Films. Gold surfaces with PHEMA films were exposed to 20 mM solutions of C_6F_5COCl with 25 mM pyridine in dichloromethane for at least 3 h to give FBZ films with high conversion (∼80%) of hydroxyl groups to esters. After acylation, the films were rinsed with dichloromethane and ethanol and dried with nitrogen. Controlled hydrolysis of the films was achieved by exposing FBZ to a 0.5 M KOH ethanolic solution for 30 s, followed by rinsing with water and ethanol and drying with nitrogen. The partially hydrolyzed films (PHEMA/FBZ) were then placed in solutions containing 20 mM C_6F_5COCl, $C_7H_{15}COCl$, or $C_7F_{15}COCl$ along with 25 mM pyridine for 3 h to form FBZ/FBZ, H7/FBZ, or F7/FBZ films, respectively. Dichloromethane was used as solvent for C_6F_5COCl and $C_7F_{15}COCl$ solutions while isooctane was the solvent for $C_7H_{15}COCl$ solutions. To make the terpolymer film, F7/FBZ+F1, FBZ films were placed in a 20 mM solution of trifluoroacetic anhydride and 25 mM pyridine in dichloromethane for 3 h to form FBZ+F1. These films were then subjected to partial hydrolysis and reaction with $C_7F_{15}COCl$, as described above, to form F7/FBZ+F1.

Characterization Methods. Polymer film properties were evaluated using the following methods throughout the various reaction steps to track changes in film properties. Reflectance absorption infrared spectroscopy (RAIRS) was performed using a Bio-Rad Excalibur FTS-3000 infrared spectrometer. The p-polarized light was incident at 80° from the surface normal. The instrument was run in single reflection mode and equipped with a Universal sampling accessory. A liquid nitrogen-cooled, narrow-band MCT detector was used to detect reflected light. Spectral resolution was 2 cm^{-1} after triangular apodization. Each spectrum was accumulated over 500 scans with a deuterated octadecanethiol-d_{37} self-assembled monolayer on gold as the background. For all films, water subtraction was performed to remove peaks resulting from atmospheric moisture, and the hydroxyl peak area (as calculated from 3050 to 3700 cm^{-1}) was subsequently used to estimate conversion as demonstrated previously.[14] Even with relatively small peak areas involved, estimated conversion for modified PHEMA films is quite consistent, allowing reactive modifications to be made while tracking conversion throughout (see Supporting Information for a detailed example of conversion estimation). Conversions indicated represent the average and standard deviation of at least seven independent sample preparations.

Ellipsometry measurements were taken on a J.A. Woollam Co. M-2000DI variable angle spectroscopic ellipsometer with WVASE32 software for modeling. Measurements at three spots per sample were taken with light incident at a 75° angle from the surface normal using wavelengths from 400 to 800 nm. Optical constants for a bare gold substrate, cut from the same wafer as the samples to be characterized, were measured by ellipsometry and used as the baseline for all polymer film samples. Film thickness of the polymer layer on samples, regardless of modification, was fit to a two-term Cauchy layer model, allowing the modeling software to fit thickness as well as the two Cauchy terms defining the refractive index, n. Typical values for n from the modeling software ranged from 1.40 to 1.44.

A Rame-Hart contact angle goniometer with a microliter syringe was used to measure advancing contact angles on static drops of water and hexadecane on the polymer surfaces. The needle tip of the syringe remained inside the liquid drop while measurements were taken on both sides of ∼5 μL drops.

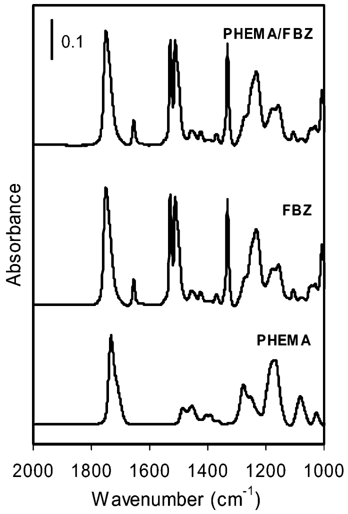

Figure 1. RAIR spectra for PHEMA, FBZ, and PHEMA/FBZ. Modification of PHEMA to form FBZ results in additional C−O stretching from 1100 to 1300 cm^{-1}, C−F stretching around 1350 cm^{-1}, aromatic C−C stretching between 1500 and 1700 cm^{-1}, and additional C=O stretching from the newly formed ester at 1749 cm^{-1}. Hydrolysis of FBZ to form PHEMA/FBZ results in no significant change in this low wavenumber region of the IR spectrum.

Reported values and ranges represent the average and standard deviation of values obtained from at least six independent sample preparations.

Electrochemical impedance spectroscopy (EIS) was performed with a Gamry Instruments CMS300 impedance system interfaced to a personal computer. A flat cell (EG&G Instruments) was used to expose only 1 cm^2 of each sample to an aqueous solution containing electrolyte and redox probes while preventing sample edges from being exposed. The electrochemical cell consisted of an aqueous solution of 1 mM $K_3Fe(CN)_6$, 1 mM $K_4Fe(CN)_6\cdot 3H_2O$, and 0.1 M Na_2SO_4 with a Ag/AgCl/saturated KCl reference electrode, a gold substrate counter electrode, and a gold substrate containing the film to be studied as the working electrode. All data were collected in the range from 10^{-2} to 10^4 Hz using 10 points per decade and were fit with an appropriate equivalent circuit model[14] to determine resistance and capacitance values. Reported values and ranges for resistance and capacitance represent the average and standard deviation of values obtained from at least five independent sample preparations.

Results and Discussion

Controlled Hydrolysis of Fluorocarbon-Modified Films. A 220 nm PHEMA film was exposed to a 20 mM solution of pentafluorobenzoyl chloride in dichloromethane for at least 3 h to generate an FBZ film with perfluoroaryl groups on the side chains. As we have previously shown, ~80% of the PHEMA hydroxyl groups are converted to perfluoroaryl groups, which are signified in the reflectance−absorption infrared spectra by a new carbonyl peak at ~1749 cm^{-1}, aromatic C−F stretching peaks between 1200 and 1350 cm^{-1}, and peaks for fluorinated C−C aromatic ring stretching from 1500 to 1700 cm^{-1} (Figure 1).[14] The FBZ film was then hydrolyzed for 30 s in 0.5 M KOH ethanolic solution to form PHEMA/FBZ (outer/inner block as shown in Scheme 1). As indicated by IR conversion estimates based on changes in the hydroxyl peak area, this brief exposure resulted in minimal overall film hydrolysis with only ~5% of fluorinated ester groups in FBZ hydrolyzed to alcohols. Accordingly, the IR spectrum (Figure 1) for this film still indicated a predominately FBZ composition. From ellipsometric measurements (Table 2), film thickness dropped ~15 nm upon hydrolysis, which is consistent with a ~20 nm layer of regenerated hydroxyl groups remaining atop the film. While the overall hydrolysis was minimal, the effect at the outer few angstroms was significant, as the advancing water contact angle indicated that surface properties reverted entirely to those of a PHEMA film. This complete conversion at the outer surface and slight change in conversion overall is consistent with a diffusion-limited hydrolysis (as suggested in Scheme 1). As additional evidence of a diffusion-limited hydrolysis reaction, the surface properties (dependent only on the outer 5 Å of surface composition) of the films become those of PHEMA after only 1 s in 0.5 M KOH/ethanol, a condition in which ≤1% of the perfluorobenzoyl groups were hydrolyzed. The slight extent of this reaction combined with the rapid and complete conversion of surface properties is consistent with a fast surface reaction. A reaction-limited process would not likely cleave the entire surface layer of fluorinated esters in such a short amount of time but instead would diffuse into the bulk film, hydrolyze groups randomly, and only completely hydrolyze the surface on a longer time scale.[21]

Rederivatization of Hydrolyzed FBZ Films and Engineered Surface Properties. Other diblocklike copolymer films were formed by exposing PHEMA/FBZ films to solutions of octanoyl chloride or pentadecafluorooctanoyl chloride to rederivatize the outer film surface and form H7/FBZ or F7/FBZ, respectively (see Scheme 1). PHEMA/FBZ or films rederivatized to form FBZ/FBZ served as experimental controls. A terpolymer film, F7/FBZ+F1, was engineered by backfilling with a short-chain modification (trifluoroacetic anhydride) to have elevated hydroxyl conversion before controlled hydrolysis and rederivatization with F7 at the outer film surface. After copolymerization, hydroxyl conversion estimates from the IR hydroxyl peak area (Table 2) returned to the same levels as before hydrolysis, indicating that essentially all regenerated hydroxyl groups had been successfully rederivatized. However, since the films still contain a predominate FBZ composition, only slight changes are observed in the low wavenumber region of the IR spectra (Figure 2). Spectra for F7/FBZ and F7/FBZ+F1 each show the appearance of a peak at 1790 cm^{-1} that corresponds to α-fluorination of the carbonyl group to produce $-OC(O)CF_2-$ linkages and an increase in CF stretching at 1250 cm^{-1} over that of the FBZ/FBZ control.[15] In comparing H7/FBZ to FBZ/FBZ, the lack of spectral changes in the C−H bending region (1400−1500 cm^{-1}) or in the C−H stretching region (not shown) is attributed to the weak absorbance of the short hydrocarbon groups, which we have also observed in homogeneous H7 films.[16] As a supporting note,[22] modification of PHEMA/FBZ with octadecanoyl choride to produce longer hydrocarbon side groups results in distinct C−H stretching peaks at 2920 and 2851 cm^{-1}, consistent with an outer crystalline hydrocarbon region (not shown).[23]

Copolymer film thickness (Table 2) increased significantly upon reacting the outer film portions with fluorocarbon or hydrocarbon groups which, as we have noted before, results from the polymer chains extending to accommodate the additional volume of long side chains.[14] In fact, increases in film thickness generally scale with the molecular volume or mass of the derivatizing species (F7 > H7 > FBZ). Upon comparison of

Table 2. Conversion, Thickness, Advancing Water and Hexadecane Contact Angles, and Film Resistance (R_f) and Capacitance (C_f) of Modified PHEMA Blocklike Copolymer Films

film	conversion (%)	thickness (nm)	$\theta_A(H_2O)$ (deg)	θ_A(HD) (deg)	log R_f ($\Omega \cdot cm^2$)	C_f (nF/cm^2)
PHEMA		224	75 ± 3	<10	3.0 ± 0.3	640 ± 200
FBZ	81 ± 2	394	90 ± 2	<10	8.1 ± 0.6	9 ± 2
PHEMA/FBZ	76 ± 2	379	75 ± 2	<10	8.2 ± 0.5	11 ± 2
FBZ/FBZ	80 ± 2	390	92 ± 2	<10	8.2 ± 0.3	9 ± 1
H7/FBZ	82 ± 3	402	106 ± 3	<10	8.8 ± 0.4	8 ± 1
F7/FBZ	82 ± 3	444	128 ± 2	77 ± 2	9.1 ± 0.5	7 ± 1
F7/FBZ+F1	87 ± 2	448	127 ± 2	77 ± 2	10.0 ± 0.4	8 ± 1

copolymer wetting data in Table 2 with those for homogeneous films in Table 1, reaction of the small portion of regenerated hydroxyl groups yielded the surface properties expected for PHEMA films modified exclusively with those acid chlorides.[14,16] The surface groups of the copolymer films were chosen to be increasingly hydrophobic (PHEMA < FBZ < H7 < F7) in order to demonstrate the ability to tune surface properties by creating copolymer films in this manner. Of the surfaces investigated here, only F7/FBZ and F7/FBZ+F1 with advancing hexadecane contact angles of 77° also exhibit oleophobic behavior, consistent with results for a homogeneous F7 film, where the fluorocarbon chains lie normal at the air−film interface and result in an extremely low critical surface energy of 9 mN/m.[14]

Engineered Barrier Properties of Copolymer Films. Previous work has shown that improving conversion of hydrophilic hydroxyl groups reduces the presence of water and ion-diffusing pathways and results in dramatic improvement in the barrier properties (higher R_f and lower C_f) of modified PHEMA films.[16] Controlled film hydrolysis and subsequent surface modification provide a route to hold overall conversion constant while investigating the effect of surface composition on barrier properties. To conduct this study of surface effects on barrier properties, we performed electrochemical impedance spectroscopy (EIS) on the copolymer films upon exposure to an aqueous solution of 1 mM $K_4Fe(CN)_6 \cdot 3H_2O$, 1 mM $K_3Fe(CN)_6$, and 0.1 M Na_2SO_4. The impedance spectra for all the copolymer films, as well as for PHEMA and FBZ, are presented as Nyquist plots in Figure 3. As shown in the inset, copolymer films with similar surface hydrophilicity to FBZ exhibit comparable barrier behavior, as indicated by the similar scale for Nyquist plots of FBZ, PHEMA/FBZ, and FBZ/FBZ. For comparison, the Nyquist plot of PHEMA is also presented in the inset of Figure 3 but exists at significantly lower Z values than can be reasonably seen on the scale of the plot. The Nyquist plots for the diblocklike films modified with more hydrophobic and structured surface compositions (H7/FBZ, F7/FBZ, and F7/FBZ+F1) exhibit distinctly higher impedances.

To extract physical film parameters, the spectra for all modified PHEMA films were fit with a Randles equivalent circuit model having film resistance (R_f) and capacitance (C_f) in parallel with one another and in series with a solution resistance (R_s).[14] The PHEMA spectrum was fit with an equivalent circuit containing two time constants, one for the initiator and one for the polymer film, as established previously.[14] As shown quantitatively in Table 2 and based on equivalent circuit fits of the impedance spectra for the films, R_f for the diblocklike copolymer films increases with increasing surface hydrophobicity (F7/FBZ > H7/FBZ > FBZ/FBZ ≈ PHEMA/FBZ). Simply modifying the outer few nanometers of the film to contain hydrophobic chains produces an order of magnitude difference in R_f between F7/FBZ and PHEMA/FBZ. Among films with similar bulk composition and surface hydrophobicity (FBZ,

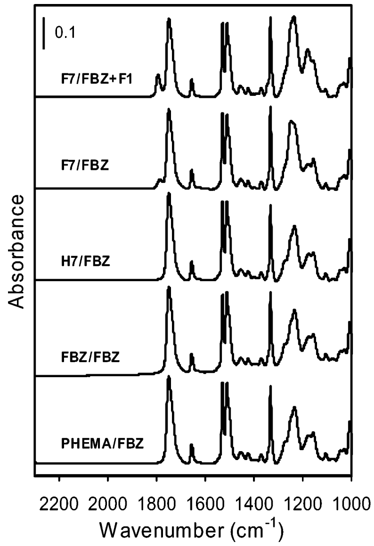

Figure 2. RAIR spectra for copolymer and terpolymer films. Rederivatization of PHEMA/FBZ to form copolymer films results in minimal changes. For F7/FBZ, a small amount of CF_2 stretching around 1350 cm^{-1} and an additional C=O peak at 1790 cm^{-1} appear. A terpolymer film, F7/FBZ+F1, exhibits even more CF_3 and C=O stretching atop those for F7/FBZ.

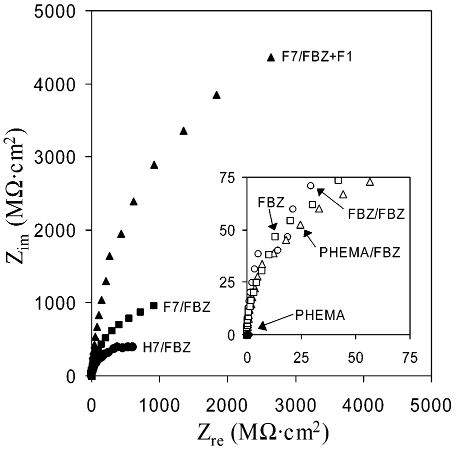

Figure 3. Nyquist plots for the electrochemical impedance behavior of PHEMA, FBZ, all diblocklike copolymer films, and one terpolymer film. All spectra were obtained in the frequency range from 10^{-2} to 10^4 Hz in an aqueous solution containing 1 mM $K_4Fe(CN)_6 \cdot 3H_2O$, 1 mM $K_3Fe(CN)_6$, and 0.1 M Na_2SO_4. The larger view shows only the three best barrier films created in this work: F7/FBZ+F1 followed by F7/FBZ and H7/FBZ. The inset is on a much smaller scale but shows spectra of FBZ, PHEMA/FBZ, and FBZ/FBZ, indicating that the barrier properties of these films do not vary significantly from one another. The spectrum for PHEMA, a much worse barrier than the engineered films, appears at extremely low Z values (<1 $M\Omega \cdot cm^2$) in the inset.

PHEMA/FBZ, and FBZ/FBZ), R_f does not vary significantly, in agreement with the Nyquist plots for these films. The likely reason for barrier property enhancement with increasing hydrophobicity is the ability of low-energy surfaces to resist penetration by aqueous solutions. Additionally, each of these films (R_f from 10^8 to 10^9 $\Omega\cdot cm^2$) exhibits greater than 5 orders of magnitude improvement in R_f as compared to the base PHEMA film (R_f of 10^3 $\Omega\cdot cm^2$) and up to 1 order of magnitude improvement in R_f as compared to the best homopolymer film, FBZ. C_f increases slightly upon regeneration of surface hydroxyl groups due to greater water penetration into the outer region of the PHEMA/FBZ film. The addition of surface groups having low dielectric constants, however, again reduces C_f, even below the starting value for FBZ. To provide additional points of reference, H7 and F7 homopolymer films exhibit log R_f of 7.0 and 7.4 $\Omega\cdot cm^2$, respectively, and C_f ranging from 9 to 13 nF/cm^2.[14,16] The homopolymer FBZ film (used as the baseline in this study) provides a greater barrier than either of these films due to either higher hydroxyl conversion (vs F7) or film structuring issues (vs H7). By engineering the outer surface region of diblocklike copolymer films based on FBZ, we can achieve coatings with significantly greater resistances and lower capacitances.

Combining backfilling with controlled hydrolysis, as demonstrated with F7/FBZ+F1, enables the preparation of a film with higher overall conversion (87%) while maintaining a hydrophobic/oleophobic surface (Table 2). R_f and C_f derived from an equivalent circuit fit to the EIS spectrum of this film indicate that it does indeed present a greater barrier to ion transport than the other copolymer films (an order of magnitude higher R_f than that of F7/FBZ) or any of the homogeneous films prepared previously.[14,16] The R_f values of films created in this work (up to ~10 G$\Omega\cdot cm^2$) are among the highest of any submicron films reported in the literature[24] and even higher than many films having thicknesses of several microns.[25] These results detail the importance of maintaining a highly hydrophobic surface and minimizing hydrophilic groups throughout to dramatically elevate the resistance of polymer films against ion transfer.

Conclusion

Using a single-step polymerization followed by simple chemical reactions, this approach allows creation of blocklike copolymer films having partially fluorinated bulk composition with a wide range of surface chemical groups (fluorocarbon, hydrocarbon, hydroxyl-rich, etc.) to engineer film properties at the molecular level. This unique methodology for the preparation of copolymer films successfully provides a direct avenue toward the customization of thin films and coatings. Numerous potential applications of these barrier films exist. Simple modification of PHEMA films has already been demonstrated for use in membranes[12,18] and as etch resists.[13] The ability to tune film properties to a greater degree, as evidenced in this work, could provide even higher selectivity and improved performance in these and many other applications.

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Supporting Information Available: Detailed conversion estimation for an example film throughout modification. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) In further support of this claim is the synthesis of F7/FBZ+F1 by first forming FBZ+F1 (with F1 presumably residing in lower regions of the film) followed by hydrolysis. Our previous work has shown that in 0.5 M KOH, films having α-fluorine esters (i.e., F1) hydrolyze instantaneously (~1 s), whereas films having β-fluorine esters (i.e., FBZ) hydrolyze much more slowly (~20 min). Even after 30 s hydrolysis, essentially no F1 functionality was cleaved, as evidenced by the constant intensity of an IR peak at 1790 cm^{-1} due to α-fluorine C═O. In a reaction-limited case, we might expect to see the base solution diffuse into the film and rapidly cleave the F1 chains, but this is not observed.

(22) The crystalline methylene peak positions observed for H17/FBZ also provide indirect proof as to the diffusion-limited behavior of the hydrolysis reaction. Crystallinity implies that the hydrocarbon chains are well-packed and therefore exist together in the outer region of the film.

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