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Surface-Induced Selective Delamination of Amphiphilic ABA Block Copolymer Thin Films

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ABSTRACT: We demonstrate the unforeseen property of selective adhesion/delamination of amphiphilic block copolymer films in coating hydrophobic and hydrophilic substrates. When spin-coated from THF solutions onto hydrophilic substrates (e.g., glass and O₃-treated silicon wafer), amphiphilic poly-(oligoethylene glycol methyl ether methacrylate) (POEGMA)-based ABA block copolymers **1** and **2** formed thin films with hydrophobic surfaces. Upon exposure to water, these films undergo a fast rearrangement to a hydrophilic surface before they delaminate from the substrate. In contrast, when deposited on a hydrophobic substrate (e.g., Au, Si, Ag), the same copolymer films do not undergo any surface rearrangement and remain as coherent thin films on the substrate. From contact angle measurements it becomes clear that the delamination is accompanied by a rapid surface rearrangement from a hydrophobic to hydrophilic nature. This rearrangement is not observed for the copolymer over hydrophobic surfaces despite the identical constitutions of the copolymers and identical microphase-separated surface morphologies. It is shown that within the range of polymers investigated this behavior was only observed for POEGMA-containing triblock copolymers. Moreover, it is also shown that in order to show this delamination behavior the polar A-block must be large compared to the apolar B-block. On the basis of XPS and AFM data, we propose that this selective adhesion/delamination is a direct consequence of the self-organization of the block copolymers in the polymer thin films.

Introduction

The ability of copolymers consisting of chemically distinct polymeric segments to undergo microphase separation as a result of enthalpically driven segregation has led to a remarkable range of nanostructured morphologies being catalogued and studied.¹ Consequently, such materials have been the subject of intense study for over 10 years.² Block copolymer thin films show many of the morphologies displayed by the bulk materials, but substrate and surface effects can play a much more pronounced role in the self-organization, particularly for very thin films. A large number of potential applications for these self-organizing thin films have been proposed and demonstrated. Examples include applications as lithographic masks,³ photonic materials,⁴ and nanostructured membranes.⁵ In this paper we will demonstrate the unforeseen property of selective adhesion/delamination of amphiphilic block copolymer films in coating hydrophobic and hydrophilic substrates. This selective adhesion/delamination is a direct consequence of the self-organization of the block copolymers, resulting from the chemical structure and

so, we believe, from the bulk, surface, and substrate energetic interactions.

Experimental Section

Materials. Poly[(oligoethylene glycol methyl ether methacrylate)-*block*-methylphenylsilane-*block*-(oligoethylene glycol methyl ether methacrylate)], POEGMA-PMPS-POEGMA, poly(hydroxyethyl methacrylate-*block*-methylphenylsilane-*block*-hydroxyethyl methacrylate), PHEMA-PMPS-PHEMA, and poly(methyl methacrylate-*block*-methylphenylsilane-*block*-methyl methacrylate), PMMA-PMPS-PMMA, samples were synthesized according to procedures previously described.⁶ Poly[(oligoethylene glycol methyl ether methacrylate)-*block*-styrene-*block*-(oligoethylene glycol methyl ether methacrylate)], POEGMA-PS-POEGMA, samples were synthesized using atom transfer radical polymerization techniques⁷ (see Supporting Information).⁸

All solvents were commercial products (Biosolve Ltd., The Netherlands) and were used as received.

Film Preparation. Glass substrates (microscope cover glasses, diameter = 16 mm, Menzel-Glasser, Germany) were first cleaned by ultrasonic treatment in acetone, rubbing with soap, rinsing in demineralized water, sonication in 2-propanol, and finally UV/ozone treatment. The substrates were then transferred to a N₂ glovebox, where first a Cr (3 nm) and then another metal (Au or Ag) layer (20 nm) were deposited by thermal evaporation under vacuum (5 × 10⁻⁶ mbar, 1 ppm of O₂, and <1 ppm of H₂O). The silicon wafers were cleaned by sonication in 2-propanol (hydrophobic surface), followed when required by UV ozone treatment (hydrophilic surface).

Films of (co)polymers **1–4** were prepared by spin-coating from THF solutions (5 mg/mL) on glass (cleaned by ultrasonic treatment in acetone and 2-propanol), silicon wafer, and on metal-coated glass substrates. Spin-coating was carried out

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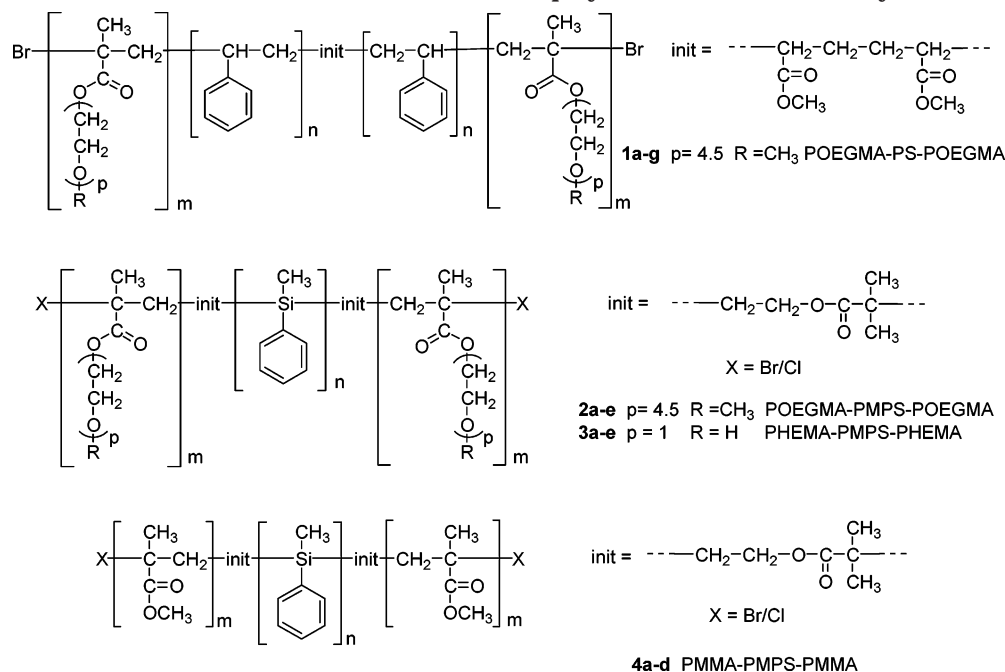
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Chart 1. Structure of ABA Block Copolymers Used in This Study



using a spin-coater from Headway Research Inc. for 50 s at a rotation speed of 1500 rpm.

To investigate the changes in the copolymer films after exposure to water by XPS and AFM, films of **2a** spin-coated on glass and on gold substrates were soaked in Millipore water for 1 and 25 min, respectively. Water remaining on the sample films was removed by centrifugal force through spinning the sample at 1500 rpm.

Contact Angle Measurements. Contact angles were measured on a Drop Shape Analysis DSA 10 apparatus from Krüss, using the sessile drop method at room temperature. Measurements were carried out within 10 s (2 records/s) after placing a water droplet on the film surface and were repeated at least three times on different positions of the same sample.

For gold and glass surfaces without any polymer a decrease in contact angles (θ) of 1–2° within 10 s was recorded (controls).

Tapping Mode Atomic Force Microscopy. Tapping mode AFM measurements were performed using a MultiMode scanning probe microscope (Nanoscope III) from Digital Instruments, Inc. (Santa Barbara, CA). The samples were probed using NSG 10 or NSG 11/A “Golden” silicon cantilevers (NT-MTD, Moscow, Russia), with a force constant of 11.5 N/m.

X-ray Photoelectron Spectroscopy. XPS measurements were performed in a VG-Escalab 200 spectrometer using an aluminum anode (Al K α = 1486.6 eV) operating at 510 VA with a background pressure of 2×10^{-9} mbar. Spectra were acquired at 0° and 60° with respect to the surface normal. The carbon 1s region was fitted in CasaXPS using 3 Gaussian/Lorentzian synthetic peaks representing the hydrocarbon (a), oligoether (b) and carboxyl function (c) in the POEGMA-PMPS-POEGMA **2** block copolymer (Figure 4).

All spectra are presented after charge correction and intensity calibration setting the C 1s peaks corresponding to hydrocarbon (a) at a binding energy of 285.0 eV and a peak area of 1000.

The samples for XPS have been prepared following the procedure described above (see Film Preparation), with the only difference that square glass plates (30 \times 30 mm²) were used as substrates instead of the round glass plates (diameter = 16 mm).

Results and Discussion

We have observed that, when spin-coated from THF solutions onto hydrophilic substrates (e.g., glass and O₃-

treated silicon wafer) without further treatment (i.e., annealing), amphiphilic poly(oligoethylene glycol methyl ether methacrylate) (POEGMA)-based ABA block copolymers **1** and **2** (Chart 1) formed thin films with hydrophobic surfaces. Upon exposure to water, these films underwent a fast rearrangement to a hydrophilic surface before they delaminated from the substrate. The delamination resulted in polymer fragments floating in the water as was observed by optical microscopy. In the case of **2a–d**, this process could be monitored also by following the decrease of the characteristic UV band of the PMPS at 340 nm as a function of time of exposure to water.⁹ In contrast, when deposited on a hydrophobic substrate (e.g., Au, Si, Ag), the same copolymer films did not undergo any surface rearrangement and remained as coherent thin films on the substrate (Figure 1).

The thin films of block copolymers **1** and **2** were prepared by spin-coating from THF solutions (5 mg/mL) onto the different substrates and were studied as cast. The films of the polysilane derived copolymers **2a–d**

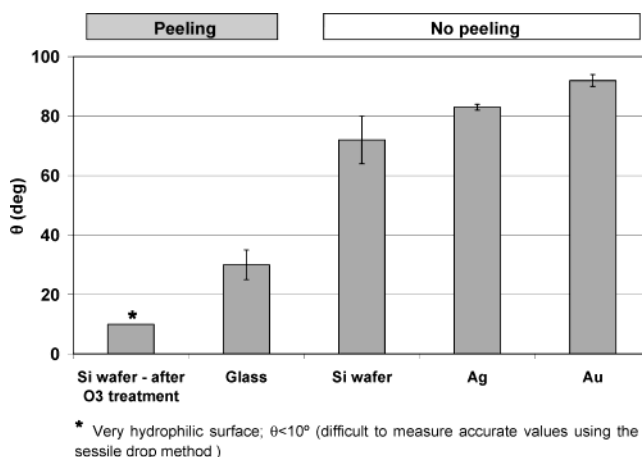


Figure 1. Water contact angles (θ) of different substrates. The block copolymer films (**1a–e**, **2a–d**) selectively delaminate only from the substrates with a hydrophilic surface upon immersion in H₂O.

Table 1. Molecular Weight Characteristics of the ABA Block Copolymers (Structures Given in Chart 1)

copolymer	M_n^a	M_w/M_n^a	$DP_{A\text{ block}}^b$	$DP_{B\text{ block}}^a$	r^c
1a	30 000	1.26	79	86 ^b	5.33
1b	40 200	1.31	56	75 ^b	4.42
1c	34 600	1.46	25	75 ^b	1.97
1d	13 300	1.27	16	75 ^b	1.20
1e	15 200	1.45	13	75 ^b	1.03
1f	21 000	1.12	27	200 ^b	0.78
1g	37 000	1.20	16	204 ^b	0.45
2a	12 600	1.8	23	32	3.63
2b	18 700	1.75	26	58	2.23
2c	21 000	2.1	29	70	2.08
2d	10 900	1.5	10	32	1.57
2e	16 900	1.6	18	70	1.29
3a	9 600	1.5	28	32	1.91
3b	6 600	1.5	7	32	0.48
3c	6 000	1.5		32	0.58 ^d
3d	12 500	1.55	17	70	0.53
3e	10 300	1.9	10	70	0.31
4a	24 700	1.67	86	43	3.31
4b	11 000	1.60	34	29	2.23
4c	14 500	1.80	40	43	3.08
4d	10 000	1.85		43	0.92 ^d

^a From SEC measurements (polystyrene standards) unless otherwise noted. ^b From ¹H NMR spectroscopic analysis in CDCl₃. ^c r = weight ratio calculated from ¹H NMR using formula ($2M_n$ A block/ M_n B block) unless otherwise noted. ^d Weight ratio calculated from SEC using formula ($2M_n$ A block/ M_n B block).

(POEGMA–PMPS–POEGMA) all exhibited contact angles with water (θ) in the range $90 \pm 10^\circ$, pointing to a rather hydrophobic film surface. However, for the films spin-coated on glass, a decrease of $35 \pm 5^\circ$ was recorded within 10 s, indicating a fast rearrangement of the film surface.¹⁰ In the same time period, the films deposited on hydrophobic substrates showed a decrease of only $1\text{--}10^\circ$, thus retaining their hydrophobic character. A rapid decrease in the water contact angles was also observed for the polystyrene derived polymers **1a–e** (POEGMA–PS–POEGMA) when spin-coated on glass, whereas only a small change was observed when they were deposited on hydrophobic substrates (e.g., Au, Ag, hydrophobic Si wafer). In the latter case the films surfaces were hydrophobic ($\theta = 90 \pm 10^\circ$) with the exception of the films of **1e** that exhibited a more hydrophilic surface ($\theta = 60 \pm 1^\circ$).¹¹

This substrate-induced difference in stability of the polymer films appeared to be dependent on the hydrophilic:hydrophobic weight ratios between the blocks (r) which are given in Table 1. The spin-coated films of the copolymers with low values of r (i.e., **1f**, **1g**, and **2e**) did not show any surface rearrangement or delamination behavior on hydrophobic or on hydrophilic substrates. Films of these polymers all revealed rather hydrophobic surfaces as was deduced from the water contact angles, which were stable and ranging from $\theta = 80^\circ$ to 90° (only for **1g**: $\theta = 67 \pm 1^\circ$).

Control films were prepared from a series of ABA block copolymers: poly(hydroxyethyl methacrylate-*block*-methylphenylsilane-*block*-hydroxyethyl methacrylate), PHEMA–PMPS–PHEMA (**3**), poly(methyl methacrylate-*block*-methylphenylsilane-*block*-methyl methacrylate), PMAA–PMPS–PMMA (**4**), and poly(methacrylic acid-*block*-methyl methacrylate-*block*-methacrylic acid), PMAA–PMMA–PMAA.¹² These films were all stable in aqueous media both when spin-coated on glass and on gold, with stable values for θ of $85 \pm 5^\circ$ (**3** and **4**) and of $65 \pm 5^\circ$ (for PMAA–PMMA–PMAA), similar to the case of the “nonpeeling” block copolymers

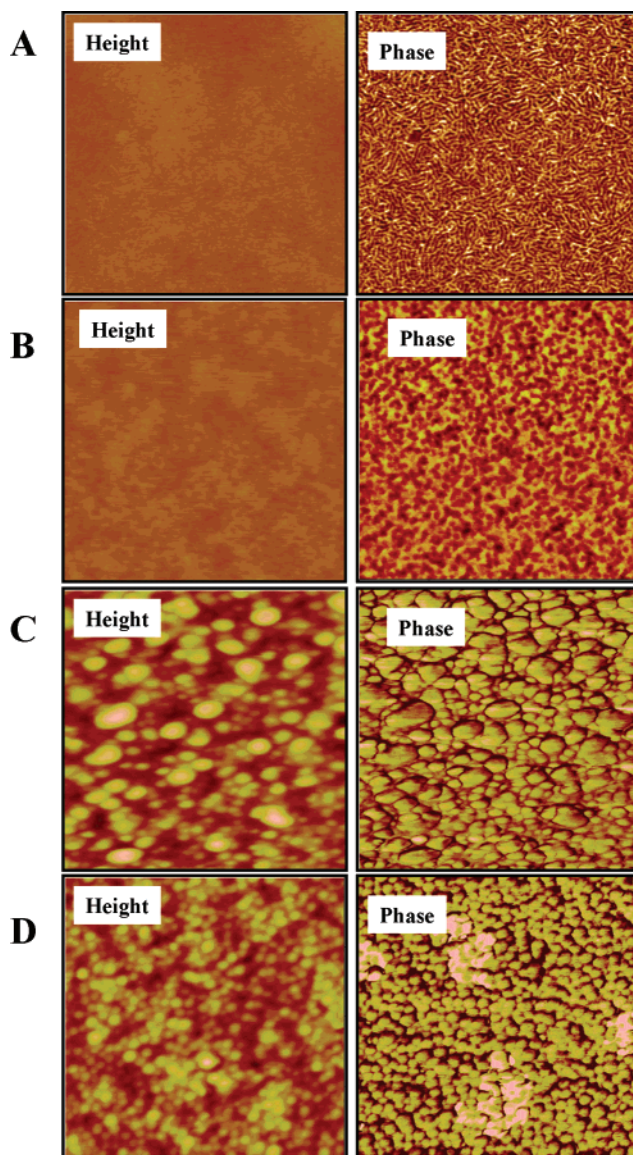


Figure 2. Tapping mode AFM height and phase images of films of (A) **2a**, (B) **1e**, (C) **2e**, and (D) **1g** copolymers spin-coated on glass from THF solution with a concentration of 5.0 mg/mL. Scan area: $1 \times 1 \mu\text{m}^2$. Vertical scale of height images: 40 nm; phase shift: 40° .

1f–g and **2e**. These experiments indicate that the observed phenomena are not common for amphiphilic ABA block copolymers in general, and we tentatively propose that the presence of the POEGMA block may be critical. However, a broader range of ABA amphiphilic block copolymers needs to be tested in order to reach a definite conclusion.

To further investigate this remarkable behavior, the surfaces of the pristine films of a series of POEGMA–PMPS–POEGMA and POEGMA–PS–POEGMA copolymers were analyzed by tapping mode AFM. These measurements revealed smooth surfaces ($\sigma_{\text{rms}} \approx 0.5$ nm for a scan area of $1 \times 1 \mu\text{m}^2$) displaying lateral microphase separation for all the polymers exhibiting the selective peeling behavior (Figure 2A,B). Microphase separation has previously been demonstrated for the PMPS derived materials by thermal analysis.⁶ Surprisingly, similar morphologies were observed for films spin-coated on glass and on gold. An image analysis based on the Power Spectrum Density¹³ leads to comparable values of the correlation lengths ($\xi = 15$ nm) on both

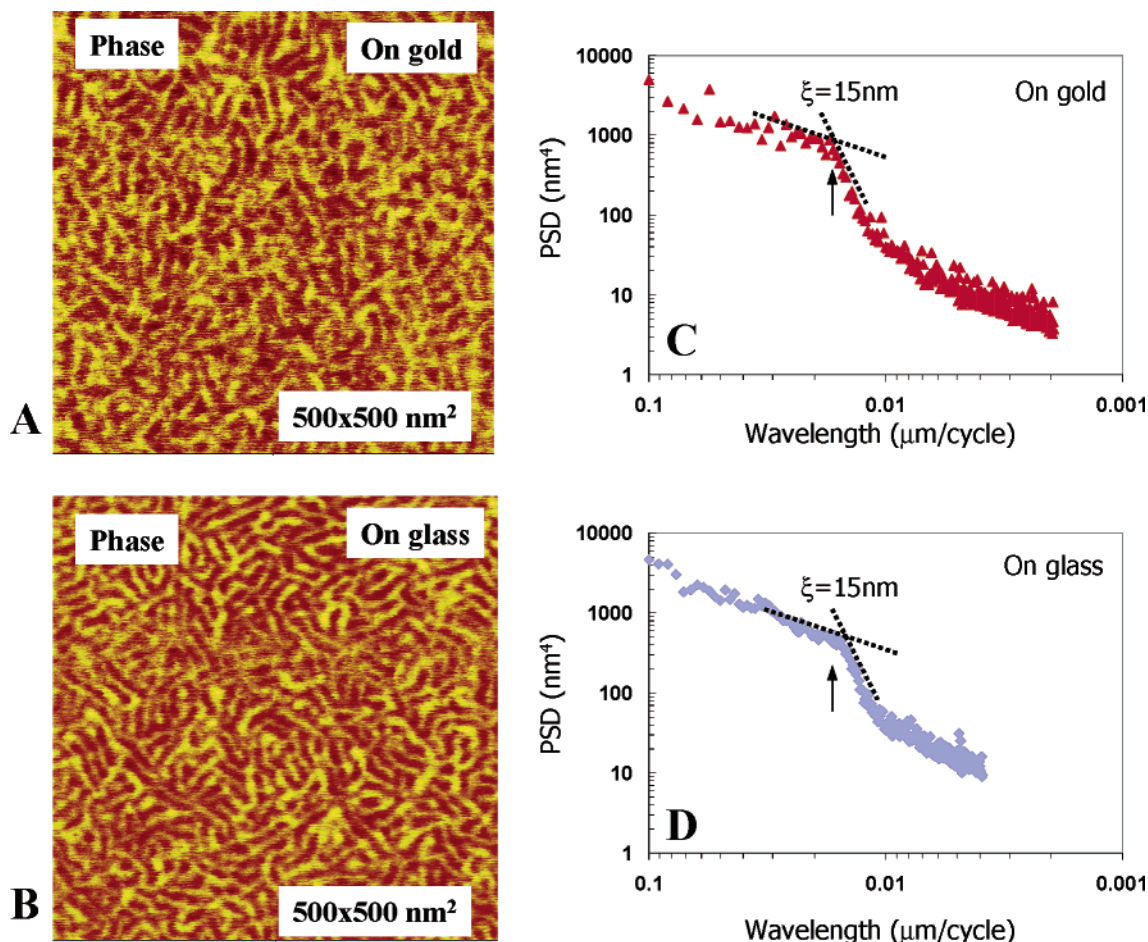


Figure 3. (A, B) Tapping mode AFM phase images of films of **2a** spin-coated on gold (A) and on glass substrate (B). Phase shift: 40°. (C, D) Two-dimensional power spectral density (PSD) curves calculated from the phase images. Correlation length (ξ) is around 15 nm both for the polymer film deposited on gold and for the film on glass, indicating the same domain size.

surfaces (see Figure 3). The thickness of the films was determined after scratching the film surface (**2a**, **2e**) to be 35 ± 5 nm.

AFM imaging of a film of **2a** that had been soaked in water for 25 min showed the detachment of the polymer from glass. However, the polymer film was still present in some regions with the nanostructure observed for the pristine films still visible. In contrast, the polymer film on gold appeared unchanged.

Nevertheless, in the case of the “nonpeeling” polymers (**1f**, **1g**, **2e**), the films were relatively rough ($\sigma_{\text{rms}} = 4\text{--}5$ nm) and exhibited a granular surface morphology without regular microphase-separated structures at the surface of the films. These block copolymers have hydrophilic:hydrophobic weight ratios of ~ 1 or less and contain a middle hydrophobic block (PS or PMPS) longer than the hydrophilic block (POEGMA). This allows the formation of micelle-like structures in which the hydrophobic block encapsulating the POEGMA blocks is present at the film surface as a result of a lower surface energy.¹⁴ We speculate that this makes it more difficult for water to penetrate into the films and to induce delamination.

XPS spectra acquired at 0° with respect to the surface normal revealed identical chemical compositions for the upper 7–10 nm of the pristine films of **2a** when spin-coated both on glass and on gold-covered glass (Figure 4). The chemical composition of both these film surfaces deviated only slightly from the calculated bulk composition of the polymer film. On the film surface the C 1s

signal corresponding to the polymer backbone and the phenyl groups (a) was slightly enhanced compared to the C–O (b) and O=C–O (c) peaks, which indicates a slight accumulation of the PMPS block at the surface of the copolymer film. However, for spectra acquired at 60°, this increase becomes significant, pointing to an enrichment of the unfunctionalized carbon content at the outermost surface of the film. Indeed, it is known that for amphiphilic block copolymers the segments of lower surface energy (e.g., the hydrophobic polymer chains) accumulate at the outermost surface region of the copolymer films under dry conditions.^{10,15}

After exposure to water of a film spin-coated on glass, the relative intensity of the C–O peak (b) increased, indicating a clear shift to a higher POEGMA content of the surface top layer (Figure 4). Moreover, an additional Si peak corresponding to SiO₂ (glass) was visible in the spectrum of the polymer film soaked in water. This is in accordance with the optical microscope observations that showed the appearance of holes in the polymer film on glass. The surface reconstruction of amphiphilic block copolymer films upon exposure to water is a known phenomenon.¹⁰ After wetting, the hydrophilic domains migrate toward the surface in order to reduce the free energy of the water/polymer interface. However, in our case no change in the XPS spectrum of the polymer film spin-coated on gold was observed after exposure to water. This indicates that no significant surface rearrangement of the copolymer occurs in the film when gold is used as a substrate.

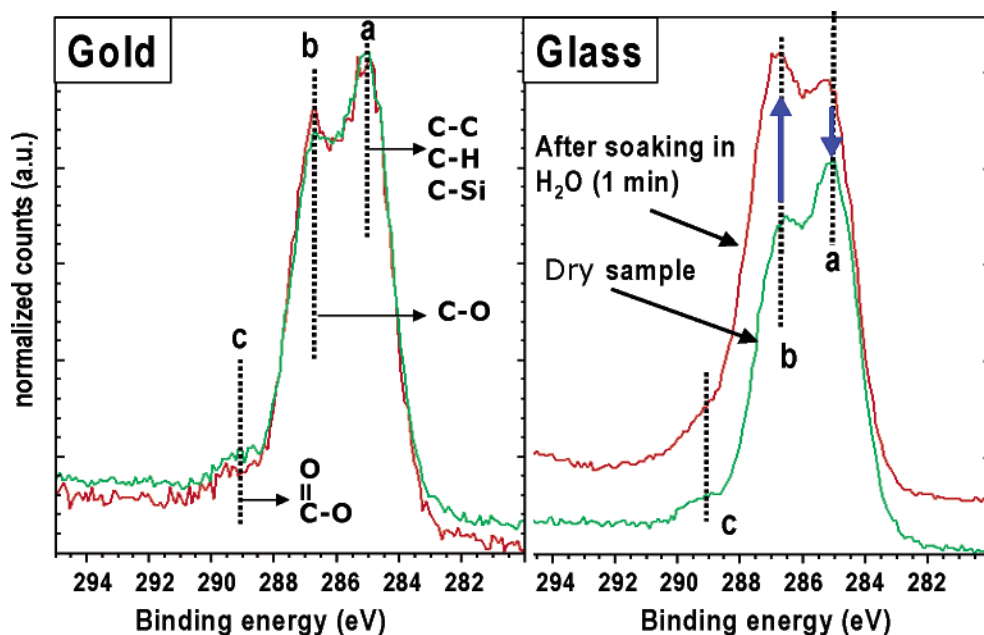


Figure 4. Carbon peak (C 1s) in the XPS spectra of **2a** films spin-coated on gold and on glass as spin-coated (green) and after immersion in water for 1 min (red). Spectra acquired at 0° with respect to the surface normal.

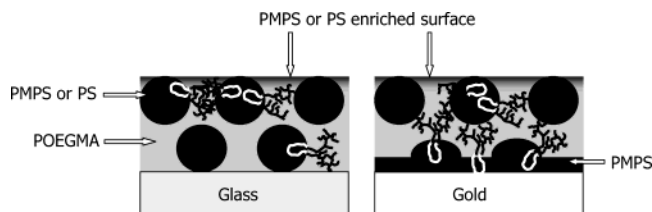


Figure 5. Postulated models for the self-organization of the delaminating ABA block copolymers over gold and glass substrates (cross section).

The most common morphologies encountered for microphase-segregated block copolymers include spherical, cylindrical, gyroid, and lamellar structures.^{1,2} The exact morphology is determined by the relative volume fractions of the distinct polymeric segments. In thin films as well as the volume symmetry of the copolymer, the symmetry of the surface energy conditions must be taken into consideration.¹⁶ All of these morphologies have been observed in block copolymer thin films.¹⁷ However, where strongly asymmetric and antisymmetric boundary conditions exist for block copolymers (as they do for our copolymers), unusual hybrid morphologies have been predicted and observed.¹⁸ We postulate that an antisymmetric hybrid structure exists in our films, as illustrated in Figure 5. This would explain both the apparent identical surface morphologies over gold and glass as well as the selective delamination from glass. At the surface of the film of **2a** (Figures 2A and 3), the hydrophobic and hydrophilic blocks phase separate into elongated objects that could be either perpendicular lamellae or cylinders lying parallel to the surface. We think that the most probable morphology would consist of cylinders parallel to the surface. AFM investigations revealed the presence of a thin layer of one of the blocks at the interface of the copolymer film with air. Light tapping AFM showed a featureless phase image, and the microphase-separated structures (Figure 2a) were visible only when using harder tapping conditions. The slight accumulation of PMPS block (lower surface energy than POEGMA) at the outermost layer of the polymer film is also supported by the angle-

resolved XPS measurements presented above. At the gold surface, however, a parallel lamellar organization occurs with at least one layer of the hydrophobic segment (polysilane or polystyrene) at the substrate. This layer behaves as a hydrophobic seal for the metal and prevents water from reaching the interface, and consequently the copolymer film remains attached. At the glass surface POEGMA resides, allowing for permeation of water and the subsequent detachment of the copolymer film. The surface reorganization of the films over the glass surface is a result of the reorientation of the OEGMA chains pointing toward the substrate to the surface. The reason for the lack of such reorganization of the POEGMA segments over the gold substrate is at this stage not clear but may be related to the poor permeability of water through the film and/or physical constraints to swelling/reorganization imposed by the morphology. The proposed organization consequently would lead to constraints with respect to the rearrangement of the film over gold as compared to glass.

The block copolymers synthesized for these studies were prepared by controlled radical polymerization techniques.^{7,8} They must therefore be considered less well-defined as compared to block copolymers prepared by living polymerization methods, as is also demonstrated by the relative polydispersity indices shown in Table 1. As the possibility of contamination of the ABA samples with homopolymer and AB diblock copolymer could be of relevance to the phenomenon described in this paper, it is important to consider the likelihood of such contamination.

For both the PMPS- and PS-based polymers a high degree (>95%) of end-group functionalization has been determined,¹⁹ and also high initiator efficiencies for these and similarly end-functionalized macroinitiators have been observed.^{9,20} Consequently, contamination of the samples with significant amounts of homopolymer is not likely. If so, fractionation by precipitation using selective solvents during workup for both the PMPS and PS ABA block copolymers would remove any small quantities of homopolymer. However, the possibility of contamination by a small but significant percentage of

AB diblock copolymer for the PMPS materials and to a lesser degree for the PS materials cannot be excluded without extensive analysis (e.g., MALDI-TOFF) and/or fractionation of the products.²¹

Nevertheless, blends of ABA block copolymers with a minor component of AB diblock copolymer where the molecular weight ratios, $\delta = N_1/N_2$, are less than 5 (N_1 and N_2 are degrees of polymerization of the two block copolymers) should not show any macrophase separation according to previously reported investigations into block copolymer blends.²² The AB diblocks may show an increased mobility leading to their preferential accumulation at the surfaces of the films in preference to the ABA blocks. But as these polymers are built from the same chemical constituent blocks, no large effect would be expected from such an event. A comparison of the effect of the block structure (e.g., AB vs ABA vs blends) on the self-organization and delamination of these films is underway.

At present, it is not clear whether the glass transition temperatures of the respective blocks play a role in the reorganization and delamination behavior. The POEGMA block possesses a low glass transition temperature, viz. -31 to -39 °C for the PMPS-POEGMA copolymers^{6a} and -51 °C for the homopolymer.²³ In contrast, PMMA ($T_g = 105$ °C²⁴), PHEMA ($T_g = 110$ °C²⁵), and PAA ($T_g = 109$ °C¹⁹) all have high glass transition temperatures which implies that the mobility of these chains may be considered highly hindered compared to that of the POEGMA. However, the situation is complicated by the fact that the T_g s of the glassy hydrophilic blocks are likely to drop upon exposure to water vapor.²⁶ Irrespective, the lower mobility of the glassy blocks may lead to an inability of the PHEMA- and PAA-containing copolymers to reorganize which will prevent delamination.

It should be noted, however, that the discussion is further complicated by the fact that the T_g in the bulk in many cases is different from that observed in thin films (<80 nm). For example, the T_g s of PMMA and PS have been observed to increase above those of bulk polymers at high interfacial energies and decrease for low interfacial energies.²⁷ In the present study the blocks of the copolymers may have up to four separate interfacial energies (e.g., the OEGMA chains may be phase separated from the PMPS/PS, the surface, the substrate, and the PMA backbone), and furthermore the effect of water swelling of the hydrophilic blocks needs to be considered. Consequently, the actual T_g values may be considerably different from those encountered in the bulk. A more detailed study into the T_g behavior in such block copolymer thin films will be carried out to address these issues in the context of the delamination phenomena described here.

Preliminary annealing experiments performed on some of the PMPS(POEGMA)₂ **2a-d** copolymers (165 °C, 2.5 h) revealed a significant change in the wetting properties of the polymer films. The surface of the films spin-coated on glass had become hydrophobic ($\theta = 85 \pm 10^\circ$), while the films deposited on gold became more hydrophilic ($\theta = 30-50^\circ$, depending on the composition of the copolymer). Moreover, the selective adhesion behavior was lost, as no delamination was observed after annealing. These observations support the proposed model in which the film stability is related to the morphology. Further studies on the effect of annealing and the solvent used in deposition on the morphology of the copolymer films will be completed in the future.

Conclusion

Polystyrene and poly(methylphenylsilane) derived ABA amphiphilic block copolymers possessing poly-[oligo(ethylene glycol methyl ether) methacrylate] outer segments with suitable hydrophilic:hydrophobic block ratios display selective adhesion to gold, silver, and clean (nonoxidized) silicon surfaces. In contrast, delamination is observed for these polymers from hydrophilic surfaces such as glass and oxidized silicon. Delamination is accompanied by a rapid surface rearrangement from a hydrophobic to hydrophilic nature that is not observed for the copolymer over hydrophobic surfaces despite the identical constitutions of the copolymers and identical microphase-separated surface morphologies. This phenomenon offers a unique approach to the selective coating of metal patterned surfaces with copolymers whose functionality and properties may be varied.

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Supporting Information Available: Typical syntheses of α,ω -dibromopolystyrene and POEGMA-PS-POEGMA. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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