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Adsorbed Monolayers Based On Functionalized Diblock Copolymers

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Introduction. A host of technologies require surfaces with organic coatings whose chemical reactivity or surface energy can be precisely controlled. In this report we describe a new method of tailoring surface chemistry which is based on adsorbed monolayers of functionalized block copolymers. This approach complements currently available methods such as the use of plasmas, small molecule coupling agents, and Langmuir−Blodgett films. Polymeric monolayers offer added mechanical strength and stability at elevated temperatures compared to small molecule assemblies.[1−4] In addition, the present method is extremely flexible. It can be applied to a wide range of substrates and enables a large range of chemical functionalities to be incorporated into the exposed surface layer.

It has been known for some time that different blocks within block copolymers have an inherent tendency to segregate due to the unfavorable interaction between different monomer types. This is the case even when monomers which differ only slightly in chemical structure are employed. This fact has been used to produce and explore a variety of microphase-separated bulk structures.[5] In addition, the segregating tendancy within block copolymers has led to interesting behavior near surfaces.[6−11] It has been shown that block copolymers tend to straddle interfaces and as such have been used to lower the interfacial tension between components in polymer blends[12] and to promote adhesion between polymers and solid surfaces,[13] among others. Furthermore, films of block copolymers on smooth surfaces have been shown to exhibit a rich variety of morphologies similar to those found in bulk samples, including lamellar[7−9] and various micellar[10,11] structures. In this work the segregating tendancy of block copolymers is used to achieve layering within a single monolayer.

Much attention has been devoted to the study of monolayers of block copolymers in which one block adsorbs preferentially onto a substrate from a selective solvent.[6,14−17] However, to date, the block copolymers investigated have possessed either no reactive chemical functionality or only a very limited range of functional groups. This has greatly limited the scope of technologies which could be impacted. The present work employs a general synthetic method for incorporating functional groups within the blocks. Diblock copolymers of this type can be designed to adsorb onto a variety of substrates including most metal and mineral surfaces by incorporating metal ligands or alkoxysilyl groups, among others, onto one of the blocks. The second, nonadsorbing block can be prepared with a wide rangeof functional groups to perform specific desired functions, such as amines which are commonly used to bond with thermoset resins. However, the presence of functional groups on both blocks allows the possiblity for both blocks to have specific attractive interactions with the substrate. Therefore the detailed structure of the monolayer, as opposed to only the adsorbed amount, must be determined. In particular, the degree of segregation of the two blocks normal to the surface is a principle focus of this work. A layered structure will indicate that the functional groups of the second block do not adsorb onto the substrate and thus are available at the surface for further reactivity.

In this work living ring-opening metathesis polymerization (ROMP) has been used to synthesize a variety of functionalized block copolymers. The synthesis of well-defined block copolymers with narrow polydispersity containing a variety of chemical functionalities has only become possible recently with the development of specialized catalysts in the 1980s by Grubbs and Tumas[18] and Shrock.[19] Figure 1a shows a generic living ROMP synthesis of a diblock copolymer. The functionalized monomers are derived from cyclopentadiene. The versatility arises from the fact that the initiators in the ring-opening polymerization step can tolerate a wide variety of functional groups, in contrast to other living polymerization techniques such as anionic polymerization. For this work, blocks containing secondary amines, imidazoles, triazoles, triethoxysilyl groups, methyl esters, and nitriles have been synthesized. Full details regarding the synthesis of these polymers will be reported in subsequent publications.

Such functionalized block copolymers can be designed to adsorb onto substrates from a dilute solution to form monolayers in which the two blocks segregate normal to the surface into separate layers. This is demonstrated here for diblock copolymers functionalized with imidazole and secondary amine groups adsorbing onto copper mirrors. The chemical structure of this copolymer is shown in Figure 1b. In this case, while both chemical functionalities have some affinity for copper, the imidazole group has a much stronger interaction with the substrate. Indeed, imidazoles are known to form a charge transfer complex with copper and have found use as corrosion inhibitors.[20] The imidazole- and amine-functionalized blocks each have molecular weights of 15 kg/mol, based upon stoichiometry.[21] The imidazole-functionalized block is capped with a *p*-methoxybenzene group, while the amine-functionalized block is terminated with dimethyltoluene. For characterization of the adsorbed layers, a block copolymer sample was prepared in which the amine-functionalized block was selectively deuterated. Approximately 14 out of a

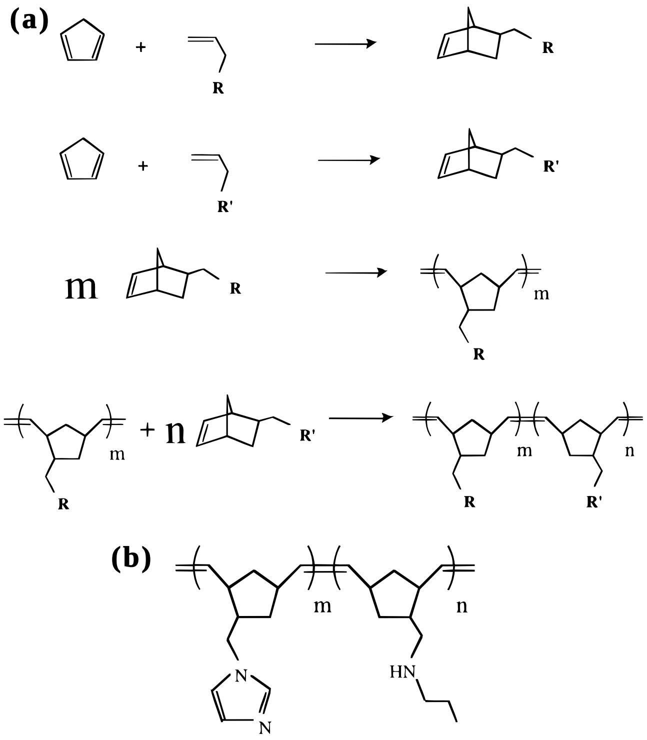

Figure 1. (a) Generic synthesis of a functionalized diblock copolymer by living ROMP. Specialized catalysts developed by Grubbs and Tumas[18] and Schrock[19] allow a wide variety of pendant functional groups to be incorporated. (b) Chemical structure of the diblock copolymer used in the adsorption studies in Figures 2 and 3. To allow a detailed characterization of the adsorbed conformation, the amine-functionalized block was selectively deuterated.

possible 19 protons of the amine monomer were replaced with deuterium. Copper mirrors were prepared by sputtering ~150 Å films onto polished silicon wafers. The copolymer was adsorbed from an 80/20 (by weight) methanol/water solution at a weight fraction of 2×10^{-4}. The addition of water decreases the solvent quality and enhances adsorption. After exposure to the copolymer solution for 5 min, the copper mirrors were removed from solution and allowed to air dry, and then were rinsed exhaustively with methanol, a good solvent for both blocks of the copolymer. The segregation of the blocks normal to the surface was verified using neutron reflection (POSY II reflectometer, Argonne National Labs and SPEAR reflectometer, Los Alamos National Laboratories) and time-of-flight secondary ion mass spectroscopy (TOF-SIMS).

For the analysis of the reflectivity data, model profiles were approximated by a series of slabs of constant neutron scattering length density. The reflectivity was calculated from the stack of layers using the Fresnel equations, with Debye–Waller (DW) factors employed at each interface to account for either in-plane roughness or a smooth gradient in scattering length density between layers.[22] Best fits were obtained using a nonlinear least squares fitting algorithm (Marquardt). The reflectivity was first obtained for the bare copper film. The resulting copper profile was then fixed in the analysis of the data following adsorption of the copolymer.

Results and Discussion. Neutron reflectivity from a bare copper mirror and after adsorption of the copolymer film are shown in Figure 2a. The data cover nearly 6 orders of magnitude in reflectivity and are displayed as reflectivity × q^4 for clarity. The neutron scattering length density profile for the copolymer-coated substrate is shown in Figure 2b. A bilayer profile for the copolymer film is required to fit the reflectivity data in Figure 2a. These two layers correspond to the protonated imidazole-functionalized block and the deuterated amine-functionalized block. Profiles involving only a single layer or multilayers are not consistent with the data. The imidazole-functionalized block forms a 20 Å layer adjacent to the copper surface while the amine-functionalized block forms a 33 Å layer at the air interface. The neutron scattering length density of each layer is roughly half the values calculated for homopolymers of each block at melt density (1.4×10^{-6} and 5.3×10^{-6} Å^{-2} for the imidazole- and amine-functionalized blocks, respectively). This indicates that the layers are not densely close-packed, but that substantial air is present within the monolayer. This contrasts with typical small molecule self-assembling monolayers where high-density lateral packing of the molecules can be obtained. In the present method, somewhat higher densities can be obtained by increasing the concentration of the adsorbing solution. The variation of the layer thicknesses and densities with

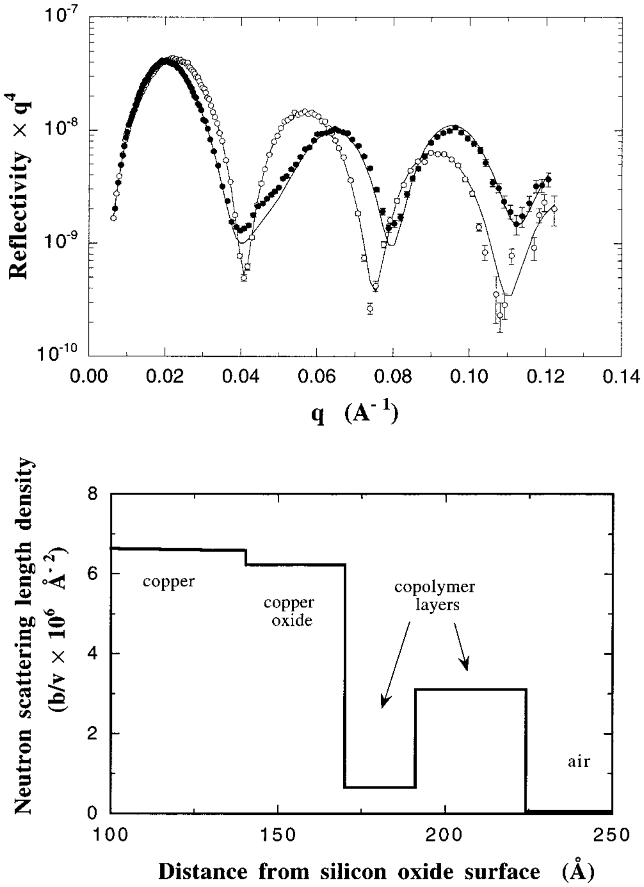

Figure 2. (a) Neutron reflectivity from a bare copper mirror (○) and after adsorption of the diblock copolymer (●). The data cover nearly 6 orders of magnitude in reflectivity and are presented as reflectivity × q^4 for clarity. The curves through the data correspond to best fits using model scattering length density profiles. (b) Best-fit scattering length density profile for the copolymer-coated substrate of Figure 2a. The profile indicates that the two blocks segregate into layers parallel to the substrate surface, with the deuterated amine-functionalized block at the air surface. The best-fit yields DW factors of 13 and 15 Å at the copper oxide/imidazole block and amine block/air interfaces, respectively, and a DW factor less than 5 Å between the two blocks. A DW factor of 12 Å is obtained from the reflectivity from the bare copper surface before deposition.

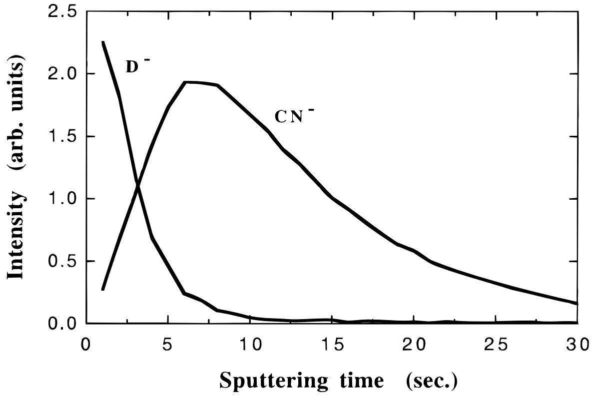

Figure 3. Time-of-flight SIMS data from a sample prepared in a fashion identical to that used for the reflectivity study in Figure 2. The D^- signal correponds to the deuterated amine-functionalized block, while the CN^- ions arise from the protonated imidazole-functionalized block. Beyond a sputtering time of 30 s, only copper ions (not shown) are detected in appreciable quantities. These data confirm the layering of the two blocks on the surface.

block molecular weights, concentration, solvent quality, and other details of the adsorption protocol is currently under investigation.

The roughnesses and the widths of the interfaces are important aspects of the monolayer structure. The best-fit model yields DW factors of 13 and 15 Å at the copper oxide/imidazole block and amine block/air interfaces, respectively. A DW factor less than 5 Å is required between the two blocks. A DW factor of 12 Å is obtained from the reflectivity from the bare copper surface before deposition. These values can represent contributions from both in-plane roughness and gradients in scattering length density between the layers. Independent information regarding the roughnesses of the layers was obtained by analyzing the off-specular scattering and also from atomic force microscopy (AFM). Of the two factors mentioned above, only in-plane roughness produces off-specular scattering. The intensity of off-specular scattering from the copper mirrors with and without the copolymer monolayer is similar, and significantly increased relative to that for a bare silicon wafer (DW $\cong$ 5 Å). With X-rays, using the method of Weber and Lengeler,[23] we obtain rms roughness values ranging from 15−20 Å for ~1000 Å thick sputtered copper films. From AFM, the topographies of the bare copper film and the copolymer-coated film are very similar, with a peak-to-valley difference of ~45 Å, reasonably consistent with the rms roughness obtained from the specular reflectivity. No sharp features which might have indicated surface micelles were observed.[10,11] Thus, the DW factors for the copper oxide/imidazole block and amine block/air interfaces appear to represent in-plane roughness, the value of which is only slightly greater than that of the bare copper surface. The smaller DW factor for the interface between the two blocks indicates a lower level of roughness than that for the other interfaces.

The layering of the blocks normal to the surface is further confirmed with TOF-SIMS, shown in Figure 3. In this technique, the sample is bombarded with successive pulses of heavy ions, gallium ions in the present case, and the charged ions dislodged from the sample are accelerated to a detector. Extremely high mass resolution allows identification of the individual species sputtered off by each pulse. The intensity of each species is determined as a function of sputtering time, and thus, increasing depth into the sample. In Figure 3, the negatively charged deuterium ions are indicative of the deuterated amine-functionalized blocks. The intensity of all deuterium-containing ions (others not shown) peak in the limit of zero sputtering time and thus arise from the surface layer. A second organic layer, indicated by the negatively charged CN species, lies between the deuterium-containing amine block and the copper. The CN^- species can only arise from the imidazole-functionalized blocks, since that material is the only organic component in the system which does not contain deuterium. While quantitative information about layer thicknesses, compositions, and densities is difficult to obtain from this technique, the results clearly show the segregation of the two blocks into separate layers. Similar layered conformations have been observed for other systems as well, such as diblock and triblock copolymers functionalized with amines and alkoxysilyl groups adsorbed onto silicon oxide.

The layered conformation of the copolymers can be understood by considering the unfavorable interaction between the two monomer types, which causes the blocks to segregate, and the irreversibility of the imidazole/copper interaction. That the imidazole groups form strong, irreversible complexes with copper is demonstrated by the fact that the monolayer-covered surfaces can be washed exhaustively with a good solvent without removal of the monolayer. Another factor which may affect the conformation of the adsorbed copolymers is the difference in surface energy between the two blocks, or between the backbone and the pendant groups. Indeed, the segregation of low-energy end groups to the air surface of homopolymer melts has been previously demonstrated using surface tension measurements.[24] In the present work, the surface energies of the two pendant functional groups are quite different, with the imidazole group having a much higher surface energy than the *n*-propylamine group.[25] Thus, the surface energy difference is another factor, in addition to the strength of interaction with copper, which would favor the imidazole block at the copper surface and the amine block at the air surface. The relative contributions of these two factors, and the conformations which result when the two factors are in opposition, will be subjects of future study. It is also possible that the amine backbone portion of the monomers, or the dimethyltoluene end groups, may occupy the surface region in preference to the amine pendant functional groups. This degree of segregation, or preferential orientation of the monomers, cannot be determined on the basis of the present data.

The fact that the copolymers adsorb as monolayers with the two chemically functionalized blocks segregating normal to the surface invites a range of potential applications. Specialized adhesion promoters for thermoset resins and metal or mineral surfaces are an obvious application.[26] As in the example above, one block can also be designed to inhibit corrosion of the substrate in addition to simply anchoring the copolymer to the surface. Microsensors constitute another area of potential application.[27] The ability to incorporate a variety of functional groups onto the nonadsorbing block and to control the layer thicknesses through the block molecular weights should allow tailoring of the sensitivity to a variety of organic and inorganic analytes. Applications may also be found in the areas of biosensors[28] or model biomembrane fabrication.[1] In this case, the mobility of the nonadsorbing block should allow adsorbing macromolecules the freedom to rearrange their conformations, which can be critical.[29] Finally, applications can be envisioned for technologies requiring control over wetting and lubrication properties. Once again, the versatility of the synthetic technique allows films with good mechanical strength to be applied to a variety of substrates and provides for tailoring of surface energies and chemical interactions.

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