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Hydrophilic Surface Coatings from Acrylic Block Copolymers[†]

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ABSTRACT: A variety of hydrophilic acrylic copolymers have been synthesized and evaluated for their use as hydrophilic surface coatings. The polymers are based on an acrylic backbone onto which oligomeric analogues (degrees of polymerization of 1, 2, or 3) of monomethoxy poly(ethylene glycol) (PEG) have been grafted. The polymers are formed by transesterification of anionically polymerized poly(*tert*-butyl acrylate). Because acrylic acid groups are introduced during the conversion process, these polymers are actually random copolymers of a PEG−acrylate and acrylic acid. These random copolymers are hydrophilic and water-soluble. Triblock copolymers with these random copolymers as the midblock and poly(methyl methacrylate) (PMMA) end blocks have also been synthesized. The hydrophilic polymers corresponding to the midblocks are immiscible with PMMA and have surface energies which are comparable to PMMA. Spun-cast films of the triblock copolymers do not dissolve in water and are quite hydrophilic, as determined by contact angle measurements with water. Direct measurements of adhesive interactions in water show that the block copolymer coatings are able to completely eliminate adhesive interactions in an aqueous environment. Studies of the gelation process of the triblock copolymers in water/ethanol mixtures have also been performed in order to characterize the self-assembly of these materials into physically cross-linked gels.

Introduction

The ability to control the interactions between the surface of a material and water is important in a wide variety applications. In particular, there are two primary reasons why one might want to increase the hydrophilicity of a surface. First, there is an increasing desire to apply coatings to surfaces from aqueous media, a trend which is driven largely by environmental considerations.[1] The aim here is simply to decrease the contact angle of water on the surface of interest so the coating can readily be applied to the surface. Hydrophilic surface modification is also a common strategy for the development of antifouling coatings which are resistant to the absorption and adhesion of proteins, living cells, and other biological entities.[2−4] In physical terms, the goal in these situations is to reduce the thermodynamic driving force for adsorption and adhesion to zero. The presence of the polymer molecules introduces a repulsive interaction between the surface and the potential adhering species. The repulsive forces between a suitably treated surface and a protein molecule or bacterium are similar to the repulsive forces that have been observed between two surfaces with a grafted polymer layer immersed in a good solvent.[5,6] Because protein molecules generally have regions of positive and negative charge, it is important for these applications that the grafted polymer be uncharged, so that electrostatic interactions do not lead to an attractive potential between the protein molecule and the surface. The uncharged water-soluble polymer that has most often been used in these applications is poly(ethylene oxide) (PEO), which in its low molecular weight form is generally referred to as poly(ethylene glycol) (PEG).

To be useful for the applications mentioned above, the hydrophilic polymer responsible for imparting hydrophilic character to the surface must somehow be attached to the surface. In cases involving the application of a water-based coating, the primary requirement is that the hydrophilic coating adheres well to the surface, so that the coating itself will be able to adhere. For the antifouling coatings, the primary requirement is that the hydrophilic polymer does not desorb into the aqueous phase. A variety of methods have been employed in order to attach hydrophilic polymers to surfaces, including the creation of a physically interpenetrated PEO surface layer,[7,8] plasma polymerization of the PEO (or PEO-like) surface layer,[9] various covalent grafting schemes,[10−12] and the use of PEO-containing block or graft copolymers.[13,14] While these approaches have demonstrated the utility of a variety of attachment schemes, they all suffer from various limitations. For example, the covalent grafting and plasma polymerization methods are difficult to adapt to complex geometries. Adsorbed block copolymers can often be displaced from the surface by other molecules, and the surface structure of graft polymers is difficult to characterize. An additional complication for the block copolymer approaches is associated with the relatively high surface energies of most water-soluble polymers. If the copolymer layer is exposed to air for an extended period of time, the water-soluble portions of the molecules will bury themselves under the surface in order to reduce the free energy of the system.[15] If this surface is placed back into water, fouling may occur before the surface is able to reorganize into the desired structure.

Our approach is to use block copolymers consisting of hydrophilic acrylates that are covalently linked to poly(methyl methacrylate). The materials that we have developed are based on polymers that are similar in some respects to poly(ethylene oxide). The hydrophilic

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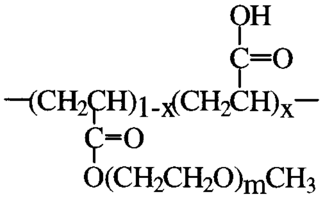

$-(CH_2CH(C(=O)O(CH_2CH_2O)_mCH_3))_{1-x}(CH_2CH(C(=O)OH))_x-$

Figure 1. Schematic representation of the water-soluble PEG-acrylates upon which this work is based. The three different polymers have $m = 1$, 2, or 3 and are referred to as follows: $m = 1$, poly((methoxy monoethylene glycol acrylate)-*r*-(acrylic acid)) (P(MMGA-*r*-AA)); $m = 2$, poly((methoxy diethylene glycol acrylate)-*r*-(acrylic acid)) (P(MDGA-*r*-AA)); $m = 3$, poly((methoxy triethylene glycol acrylate)-*r*-(acrylic acid) (P(MTGA-*r*-AA)).

blocks have side groups which can be viewed as very low molecular weight versions of PEO (or, alternatively, poly(ethylene glycol), or PEG), with structures as illustrated in Figure 1. Our focus has been on acrylic polymers with very low molecular weight side chains, i.e., with $m = 1$, 2, or 3. We refer to the water-soluble blocks as PEG-acrylates. The polymers are similar to the triblock copolymers of PEO and poly(propylene oxide) which have also been used for this purpose.[14] The polymers we have synthesized have two important advantages. First, the PMMA block which anchors the water-soluble block to the surface is glassy, so that the polymers cannot be readily displaced from the surface. Also, the surface energy of the water-soluble block responsible for the antifouling properties is similar to (or in some cases even less than) the surface energy of the PMMA anchoring block. As a result, the driving force for the structure of a block copolymer layer to change when the layer is removed from water is small or nonexistent. The synthesis and characterization of these polymers are described in the following sections, as are the results of preliminary studies on their affect of adhesion in aqueous environments.

Experimental Section

Materials. Methyl methacrylate (MMA) and *tert*-butyl acrylate (tBA) (Aldrich) were purified by addition of triethylalumium or trioctylalumium (Aldrich) until a yellowish color was observed. After degassing by freezing in liquid nitrogen, these monomers were distilled under reduced pressure immediately prior to polymerization. Lithium chloride (Aldrich) was dried in the reaction vessel at 130 °C for 16 h. Tetrahydrofuran (THF) was distilled from fresh sodium benzophenone complex. Acetanilide, 2-methoxyethanol, diethylene glycol methyl ether (Aldrich), and triethylene glycol monomethyl ether (TCI) were used as received.

Polymerization and Modification of Acrylic Polymers. Anionic block copolymerization of MMA and tBA was carried out under a purified argon atmosphere. Diblock copolymers (PMMA−PtBA) were synthesized by using *sec*-butyllithium reacted with 1,1-diphenylethylene as the initiator. The initiator for the triblock copolymers (PMMA−PtBA−PMMA) was produced by reaction of lithium−naphthalene with 1,1-diphenylethylene.[16] The initiators were prepared in THF solution at room temperature and were stirred for 1 day. The final product did not require further purification. The concentration of initiator was determined by the titration of initiator solution with a known amount of acetanilide in THF just before use. Lithium chloride was first introduced into the reaction vessel and dried as previously described. THF was then transferred into the reaction vessel, followed by the addition of a few milliliters of the initiator solution to eliminate the impurities. The calculated volume of the initiator solution was then added, and tBA was distilled into the reaction vessel at −78 °C. To determine the molecular weight of PtBA in the block copolymer, a small amount of living PtBA solution was removed under a strong stream of high-purity argon before the addition of MMA and precipitated in a mixture of methanol and water (75%/25%). MMA was then distilled into the reaction solution at −78 °C. Polymerization was terminated with methanol followed by precipitation in a mixture of methanol and water (75%/25%). The resulting copolymers were dried under vacuum at 60 °C.

tert-Butyl groups were converted to short-chain poly(ethylene glycols), such as triethylene glycol monomethyl ether, by transesterification with 5 mol % *p*-toluenesulfonic acid and 5 mol % HCl (relative to *tert*-butyl groups) as catalysts. The PtBA, PMMA−PtBA, or PMMA−PtBA−PMMA block copolymers and catalysts were added into triethylene glycol monomethyl ether and stirred at approximately 100 °C for about 16 h. The converted polymers were precipitated from diethyl ether and dried under vacuum at 40 °C. Similar reactions were carried out with diethylene glycol methyl ether and 2-methoxyethanol. A PMMA−poly(acrylic acid)−PMMA triblock copolymer was converted from PMMA−PtBA−PMMA triblock copolymer by a similar method, using toluene as the solvent.

Characterization of Acrylic Polymers. Prior to the transesterification reactions, the molecular weights of the block copolymers and the molecular weight distributions (M_w/M_n) were determined from size exclusion chromatography (SEC) in THF referenced to polystyrene standards.[17] The composition of the copolymer was determined by proton nuclear magnetic resonance spectroscopy (^1H NMR, Gemini 300 MHz) using *d*-chloroform as the solvent and tetramethylsilane as an internal standard. The tBA content was calculated from the ratio of the t-$C(CH_3)_3$ signal (at 1.43 ppm) from PtBA to the OCH_3 signal (at 3.60 ppm) from PMMA. The percentage of the conversion reaction was also verified by ^1H NMR. During the conversion reaction, the t-$C(CH_3)_3$ peak (at 1.43 ppm) disappeared, and the OCH_2CH_2 peak appeared at 3.57−3.66 ppm. Differential scanning calorimetry (DSC) (Perkin-Elmer DSC 7) was used for the determination of thermal properties under an atmosphere of argon. A 5−10 mg sample of polymer was sealed into an aluminum sample pan. The sample was quickly heated above its glass transition temperature (T_g) to remove thermal history and quickly cooled to −80 °C. The sample was left to equilibrate and then was heated at a scan rate of 10 °C/min. The dynamic mechanical measurement was performed with a Bohlin rheometer equipped with a couette cell (coaxial cylinder). The polymer solution, preheated at 80 °C, was added between the coaxial cylinders. The solution was rapidly cooled to the desired temperature, at which point the measurement was made. The phase behavior of the triblock copolymer was examined by heating the mixture of polymer, ethanol, and water and then checking the gel formation at room temperature. Gelation was determined by a tilting method similar to that described by Deguchi et al.[18] If the homogeneous mixture did not flow appreciably over a period of several minutes when the vial was turned upside down, it was classified as a gel. If the solution flowed, it was considered to be a sol.

Wetting Behavior and Contact Angle Measurements. Samples for testing the wetting behavior of thin polymer films were prepared by spin-coating PMMA on precleaned silicon wafers. P(MMGA-*r*-AA), P(MDGA-*r*-AA), or P(MTGA-*r*-AA) PEG-acrylate/acrylic acid random copolymer was dissolved in methanol and spun-cast on top of the PMMA treated substrate. These samples were then annealed at 130 °C in a vacuum oven for at least 16 h. Contact angles for the resulting PEG-acrylate droplet on PMMA were measured by atomic force microscopy in the tapping mode using a NanoScope III manufactured by Digital Instruments. The interfacial tensions of various polymers were measured by Dr. Bryan Sauer, using a micro-Wilhelmy technique with a glass fiber as the vertical wetting probe.[19,20]

Substrates for water contact angle measurements were prepared by spin-coating a dilute solution of various copolymers in toluene/ethanol mixtures onto a precleaned silicon wafer. This process yielded uniform thin films about 100 nm thick as measured by a Sopra Moss ES4G/OMA ellipsometer. Some block copolymer films were prepared by floating copoly-

Table 1. Characterization of Poly(methyl methacrylate)−Poly(*tert*-butyl acrylate)−Poly(methyl methacrylate) (PMMA−PtBA−PMMA) Triblock or Poly(*tert*-butyl acrylate)−Poly(methyl methacrylate) (PtBA−PMMA) Diblock Parent Copolymers, Determined from Size Exclusion Chromatography and ^{1}H NMR Analysis

code	polymer	N^a	$M_w/M_n{}^b$
B138	PMMA−PtBA−PMMA	90−363−90	1.19
B141	PMMA−PtBA−PMMA	150−336−150	1.18
B145	PMMA−PtBA−PMMA	220−664−220	1.27
B207	PtBA−PMMA	164−140	1.06
C128	PtBA−PMMA	398−730	1.02

[a] Values given for N are the number-average degrees of polymerization for each block.

mer films onto a water bath and then transferring the films onto a silicon wafer that had been coated with PMMA layers. The substrates were dried in a vacuum oven at 40 °C. The water contact angles were measured by a NRL C. A. model 100-00-115 goniometer telemicroscope manufactured by Ramé Hart Inc., equipped with a video camera and monitor. The relative humidity in the sample chamber was controlled by equilibrating with a reservoir of water for 15 min prior to taking measurements. A drop of water with an approximate volume of 1 μL was placed into contact with the flat surface using a microsyringe. While the drop was still in contact with the syringe tip, additional water was added to the drop to advance the drop edge as slowly as possible. When the three phase contact line had stopped moving (after about 30 s), the advancing contact angle was measured. Receding contact angles were measured following the same procedure after withdrawing water from the drop. All measurements were performed at room temperature.

Adhesion Measurements. Adhesion measurements were performed as described previously.[21] An acrylic elastomer lens of cross-linked poly(*n*-butyl acrylate) was attached to a spacer which enabled us to immerse the lens in water while bringing it into contact with a flat substrate. The substrate was a polished silicon wafer with a thin film of either PMMA or a PMMA−P(MTGA-*r*-AA)−PMMA triblock copolymer. The substrate itself was mounted to the bottom of a polystyrene tissue culture dish which was filled with water.

Results and Discussion

Polymer Synthesis and Modification. Block copolymers are obtained by first using anionic polymerization to synthesize a precursor polymer, where one of the blocks is poly(*tert*-butyl acrylate) (PtBA). The procedures used are similar to those described by Varshney et al.[16] Prior to the transesterification reactions, the molecular weight distributions of the precursor polymers were determined by size exclusion chromatography (SEC). Results of these measurements are listed in Table 1. While we were not able to conduct SEC measurements on the converted polymers, similar transesterification reactions have been shown to have no effect on the molecular weight distributions between precursor polymers and converted polymers.[22] These reactions do not appear to affect the PMMA portions of the polymers.[16,23]

Block copolymers containing hydrophilic blocks were obtained from the precursor polymers by exchanging the *tert*-butyl groups with short-chain poly(ethylene glycols), as shown schematically in Figure 2. As shown by the data in Table 2, a substantial fraction of the *tert*-butyl groups were converted to acrylic acid rather than PEG-acrylate side chains, either by hydrolysis or by the elimination of isobutylene.[24] The converted polymers are actually copolymers with a relatively narrow distribution of chain lengths, but with an assumed random distribution of acrylic acid. While the presence of these acrylic acid groups provides a route for further functionalization of these polymers,[25] their presence may introduce undesirable acid/base or electrostatic interactions with biological macromolecules. The net effect of these acid groups on the performance of the polymers as antifouling coatings is still unclear, however. For example, Kulik et al. found that the introduction of poly(acrylic acid) moieties into polyacrylamide slightly reduced platelet adhesion to these materials.[26]

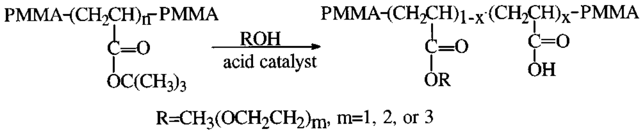

Figure 2. Transalcoholysis reaction for producing block copolymers of interest from precursor block copolymers containing poly(*tert*-butyl acrylate).

Acrylic polymers based on poly(methoxy monoethylene glycol acrylate-*r*-acrylic acid) (P(MMGA-*r*-AA), $m = 1$), poly(methoxy diethylene glycol acrylate-*r*-acrylic acid) (P(MDGA-*r*-AA), $m = 2$), and poly(methoxy triethylene glycol acrylate-*r*-acrylic acid) (P(MTGA-*r*-AA), $m = 3$) have been synthesized as part of this work. All three PEG-acrylate/acrylic acid random copolymers can be dissolved in water or methanol. The block copolymers containing shorter PEG-acrylates dissolve easily in toluene. A combination of toluene with a small amount of ethanol is used to dissolve copolymers for spin-coating. Methanol can be used as a solvent for spin-coating PEG-acrylate/acrylic acid random copolymers, although the films produced have nonuniform thicknesses due to the high volatility of methanol. A spun-cast P(MTGA-*r*-AA) layer can be washed away by water or methanol. After annealing in a vacuum at 120 °C for 1 h, it still can be washed away by water or methanol. However, after vacuum annealing at 120 °C for 16 h, the film cannot be dissolved in either solvent. In addition, some of the polymers become cross-linked after storage in room temperature for 1 year. Storage of these polymers in gel form in a solvent such as ethanol alleviates this cross-linking problem. Similar cross-linking phenomena have been observed previously in polymers prepared by free radical polymerization of PEG-acrylate macromonomers.[27,28] These effects were attributed to chain transfer reactions during the polymerization process. Side reactions might occur in our case during the acid-catalyzed transesterification reaction. The presence of acrylic acid groups might play a role in the thermal stability of our polymers as well. For example, anhydride formation at elevated temperatures is a well-known phenomenon in these types of polymers.

The miscibility of PMMA with the PEG-acrylate polymers we have synthesized is an issue of obvious importance with respect to the phase behavior of the block copolymers. Poly(ethylene glycol) forms a complex with poly(acrylic acid)[29] and is miscible with PMMA.[30] One expects that PEG-acrylate graft copolymers with sufficiently long PEG degrees of polymerization would also be miscible with PMMA. Complicating factors in our case include the presence of the acrylic acid groups, the very low degrees of polymerization of the PEG side chains, and the fact that acrylic and methacrylic polymers with similar or identical ester groups are generally not miscible with one another. As discussed in the following three subsections, we have used three comple-

Table 2. Characterization of Converted PEG-Acrylate Containing Polymers

code	polymer	N	M_w/M_n	x^a	$w_{aa}{}^b$	$w_{pmma}{}^c$	T_g (°C)
B126	P(MMGA-*r*-AA)	547	1.41	0.20	0.10	0	−37
B124	P(MDGA-*r*-AA)	469	1.39	0.43	0.20	0	−28
C187	P(MTGA-*r*-AA)	398	1.04	0.46	0.18	0	−62
C97	P(MTGA-*r*-AA)	363	1.15			0	−43
C2	P(MDGA-*r*-AA)-PMMA	164−136	1.06	0.48	0.23	0.41	−2
C6	P(MTGA-*r*-AA)-PMMA	164−136	1.06	0.23	0.07	0.31	−32
B155	PMMA−P(MMGA-*r*-AA)−PMMA	220−664−220	1.27	0.26	0.13	0.37	−28
B149	PMMA−P(MDGA-*r*-AA)−PMMA	220−664−220	1.27	0.16	0.06	0.30	−56
B147	PMMA−P(MTGA-*r*-AA)−PMMA	220−664−220	1.27	0.48	0.19	0.32	−41
B169	PMMA−P(MTGA-*r*-AA)−PMMA	150−336−150	1.18	0.31	0.10	0.35	−48
C15	PMMA−P(MTGA-*r*-AA)−PMMA	90−363−90	1.19				
C201	PMMA−PAA−PMMA	220−664−220	1.27				100
C117	PMMA	760	1.04			1	132
PMMA^d	5000	1.09	1	123			
P(MTGA-*r*-AA)(C97)/PMMA^d blend	0.5	−31					

[a] Acrylic acid mole fraction in PEG-acrylate portion of the polymer. [b] Acrylic acid weight fraction in PEG-acrylate portion of the polymer. [c] Overall PMMA weight fraction in the polymer.

mentary methods to understand the nature of the PMMA/PEG-acrylate interactions. These methods include measurements of the glass transition temperatures of various copolymers and blends, measurements of the wetting behavior of PEG-acrylate/acrylic acid statistical copolymers on various substrates (including PMMA), and measurements of the rheological properties of block copolymer solutions in water/ethanol mixtures.

Thermal Analysis. Because it has the longest PEG-acrylate side chain, our expectation is that the P(MTGA-*r*-AA) statistical copolymer has the highest probability of being miscible with PMMA homopolymer. As a test of the miscibility of one of the P(MTGA-*r*-AA) polymers with PMMA, we dissolved a 50/50 mixture (by weight) of these polymers in a toluene/ethanol mixture, which is a common solvent for both polymers. The blend formed by slow evaporation of the solvent shows a broad glass transition at a temperature of −31 °C, which is about 12° higher than the glass transition temperature of the P(MTGA-*r*-AA) statistical copolymer itself. The proximity of this glass transition to the glass transition of the P(MTGA-*r*-AA) indicates that at least some phase separation has occurred, an interpretation that is also consistent with the thermal analysis of the block copolymers. An estimate of the glass transition that would be obtained for a completely miscible system is obtained from the Fox equation, which in our case can be written in the following form:

$$\frac{1}{T_g} = \frac{w_{pmma}}{T_{g,pmma}} + \frac{1 - w_{pmma}}{T_{g,acryate}} \tag{1}$$

where T_g is the absolute glass transition temperature of the blend, w_{pmma} is the weight fraction of PMMA in the system, $T_{g,pmma}$ is the glass transition temperature of PMMA, and $T_{g,acrylate}$ is the glass transition temperature for the appropriate PEG-acrylate. The glass transition behavior of homogeneous blends of PMMA and poly(ethylene oxide) is in good agreement with this equation.[31] As listed in Table 2, observed glass transitions for the PEG-acrylate/acrylic acid statistical polymers range from −28 to −62 °C, depending on the length of the side chain and the acrylic acid content. The lowest glass transitions are close to −60 °C. Taking $w_{pmma} = 0.3$, $T_{g,pmma} = 120$ °C, and $T_{g,acrylate} = -60$ °C gives a predicted T_g of −16 °C for a homogeneous blend. The measured glass transition temperature for the PMMA/P(MTGA-*r*-AA)/PMMA triblock copolymer with $w_{pmma} = 0.3$ is much lower (−58 °C), close to the expected glass transition for the PEG-acrylate midblock. From this information we conclude that this polymer forms an ordered domain morphology, with glass transition behavior that is dominated by the matrix component of the block copolymer morphology.

Wetting Behavior of Polymers. To more thoroughly characterize the thermodynamic interactions between PMMA and PEG-acrylate/acrylic acid statistical copolymers, we used atomic force microscopy to study the wetting properties of the PEG-acrylate/acrylic acid copolymers on PMMA substrates. This information is important, because it provides further information on the thermodynamic interactions between PMMA and the various PEG-acrylate/acrylic acid random copolymers, complementing the qualitative information from the thermal analysis described above. As an example, the phase behavior of a PMMA−P(MTGA-*r*-AA)−PMMA triblock copolymer will depend on the net interaction parameter between PMMA and P(MTGA-*r*-AA), which is in turn related to the interfacial energy between these two polymers. These interfacial energies are obtained from measurements of the relevant polymer/polymer contact angle.

Polymer/polymer contact angles were obtained by coating thin PMMA films onto polished silicon wafers. Thin films of P(MMGA-*r*-AA), P(MDGA-*r*-AA), or P(MTGA-*r*-AA) were then spun-cast onto the PMMA films from solutions in methanol. Methanol is a good solvent for the PEG-acrylates, but a nonsolvent for PMMA, so that this procedure results in a sandwich consisting of a thin film of the PEG-acrylate supported on a thin film of PMMA, as illustrated in Figure 3a. These samples were then annealed in a vacuum at elevated temperatures in order to enhance the approach toward equilibrium. In nonwetting situations, the PEG-acrylates form isolated droplets, exposing the underlying PMMA substrate as illustrated in Figure 3b. Dewetting was observed for the P(MMGA-*r*-AA) and P(MDGA-*r*-AA) films, but not for the P(MTGA-*r*-AA) films. For situations where dewetting was observed, the contact angles of the droplets were measured by atomic force microscopy (AFM). The contact angles were calculated by measuring both the heights and lateral dimensions of the drops as described previously.[32] Contact angles of approximately 30° were obtained for P(MMGA-*r*-AA) on PMMA and for P(MDGA-*r*-AA) on PMMA.

If we assume that the measured contact angles, θ_p, characterizing the polymer/polymer interfaces are the equilibrium contact angles, then these angles can be

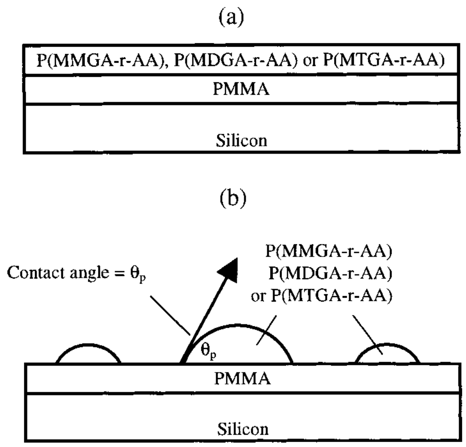

Figure 3. Schematic representation of samples for contact angle determinations for polymer/polymer interfaces: (a) as-prepared samples; (b) after dewetting.

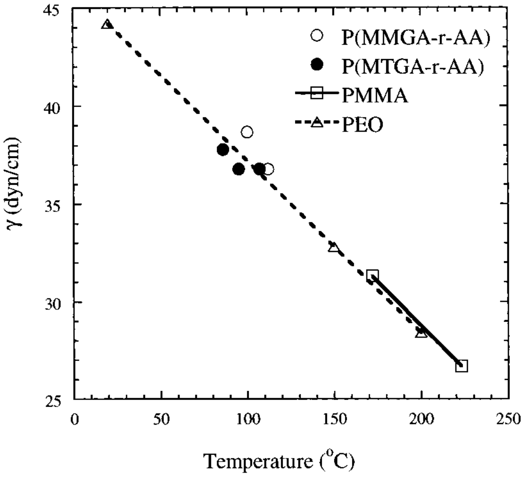

Figure 4. Temperature dependence of the surface tension of various PEG-acrylates.

related to the surface energy of the substrate (γ_s), the surface energy of the dewetting liquid (γ_l), and the interfacial energy between the liquid and the substrate (γ_{sl}) in the following manner:

$$\gamma_s = \gamma_{sl} + \gamma_l \cos \theta_p \tag{2}$$

We have obtained data on the surface energies of P(MMGA-*r*-AA) and P(MTGA-*r*-AA) by the Wilhelmy fiber method.[19] As shown in Figure 4, the surface energies of both polymers are within about 1 dyn/cm of the surface energies of high molecular weight PMMA or poly(ethylene oxide) (PEO). The extrapolated value for these surface energies at room temperature is 44 dyn/cm. Using this value for γ_s and γ_l in eq 2 with $\theta_p = 30°$ gives a value of 6 dyn/cm for the interfacial tension between PMMA and P(MMGA-*r*-AA). The error in this number is determined by the error in the PMMA and PEG-acrylate surface tensions, i.e., ±2 dyn/cm. Regardless of the specific value of this interfacial energy, its value is clear that its magnitude is characteristic of a polymer interface between highly immiscible polymers.

As described in the Appendix, an approximate relationship can be obtained between the polymer/polymer interfacial tension and the ability of a block copolymer to form an ordered morphology. This relationship is expressed in terms of the minimum molecular weight of the minority block for which microphase separation will occur. For flexible polymers such as polystyrene, poly(methyl methacrylate), poly(2-vinylpyridine), and the PEG-acrylates with relatively short side chains, the critical molecular weight of the minority block for polymer pairs with an interfacial energy of 3 dyn/cm is 6000 g/mol. Using this length as a guideline, we come to the conclusion that microphase separated morphologies are expected for the block copolymers containing P(MMGA-*r*-AA) bocks. This is the only system for which we were able to determine both the polymer surface energy and the appropriate polymer/polymer contact angle. However, one expects that the surface energy of P(MDGA-*r*-AA) would be similar to those of P(PMMGA-*r*-AA) and P(MTGA-*r*-AA), in which case we arrive at the conclusion from the contact angle data that P(MDGA-*r*-AA) is also highly immiscible with PMMA. Dewetting was not observed for the P(MTGA-*r*-AA) films on PMMA substrates. Either the contact angle is quite low in this case (indicating a low interfacial energy), or the dewetting process for this polymer was kinetically hindered.

Gel Formation of Triblock Copolymer. The results from the previous two sections provide useful information about the thermodynamic interactions between the polymer blocks in the bulk, undiluted state. Application of these materials as surface coatings, however, requires that their solution behavior be understood in more detail. These coatings are applied by solution-casting or spin-coating, and polymer/solvent interactions will clearly play a role in the development of the microstructure. In addition, the presence of water during use of the coatings may induce the formation of a microphase separated morphology, even if such a morphology is not favored in the dry state. Swelling measurements of spun-cast PMMA/P(MTGA-*r*-AA) thin films in controlled humidity environments are, in fact, consistent with the formation of a microphase separated morphology.[33]

The detailed structure of a triblock copolymer thin film will clearly depend on the copolymer structure and on the deposition conditions, including temperature, casting solvent, etc. One of the issues that we have addressed directly involves the effect of solvent on the properties of a bulk triblock copolymer solution. We are particularly interested in the phase behavior and mechanical properties of triblock copolymer solutions in water/ethanol mixtures. To illustrate some important general features of these types of systems, we have created a phase diagram characterizing the solution behavior of a triblock copolymer with relatively short PMMA end blocks ($N = 90$) and a longer P(MTGA-*r*-AA) midblock ($N = 336$). Different mixtures were heated to about 85 °C, where a one-phase liquid is generally formed. The properties of these mixtures after cooling to room temperature are illustrated by the ternary phase diagram shown Figure 5. The triblock copolymer forms a gel in pure ethanol, because pure ethanol is a nonsolvent for PMMA. For our purposes a gel is defined as a solution that does not flow appreciably over a period of about 1 min when the sample vial is turned upside down. A sol is defined as a solution that does flow under these conditions. Because PMMA dissolves in ethanol/water mixtures, a sol is formed when water is added to the ethanol. Water itself is a nonsolvent for PMMA, so a gel is again formed as the ratio of water in the solvent mixture is increased further. For intermediate polymer concentrations, separate polymer-rich and solvent-rich phases are observed, and for high polymer concentra-

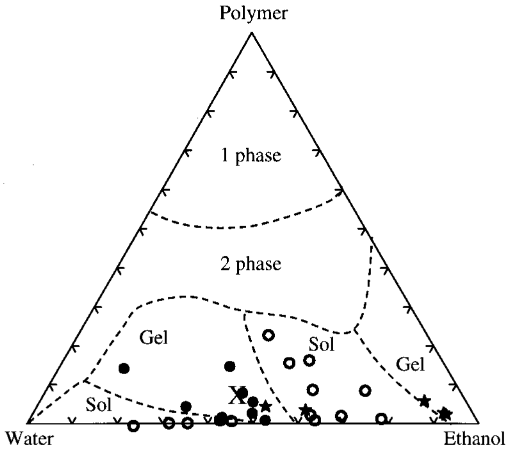

Figure 5. Phase diagram for a PMMA−P(MTGA-*r*-AA)−PMMA triblock copolymer (C15) in ethanol/water mixtures at room temperatures. Freely flowing "sols" are indicated by open circles. Gels are indicated by filled circles, and stars represent samples with intermediate properties. Approximate phase borders are indicated by the dashed lines. The "X" corresponds to the composition of the sample for which more detailed rheological data were obtained (Figure 6).

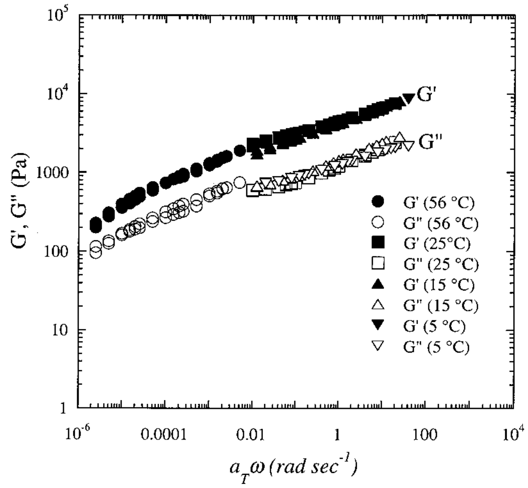

Figure 6. Master curve of frequency sweep of the storage and the loss moduli for a triblock copolymer gels in a 47/53 ethanol/water mixture. The overall weight fraction of polymer in the gel is 0.072. Empirically determined temperature shift factors were as follows: $a_T = 2$ at 5 °C, $a_T = 1.25$ at 15 °C, $a_T = 0.000\,25$ at 56 °C.

tion, a single-phase, swollen polymer gel is observed.

The more detailed rheological properties of one of the gels are illustrated by the data in Figure 6. This gel was formed from a 7.2 wt % solution of a triblock copolymer in an ethanol/water mixture containing 47 wt % ethanol. This gel has a predominantly elastic character, with the storage modulus in shear (G') exceeding the loss modulus (G'') over a wide range of frequencies and for temperatures ranging from 5 to 56 °C. Empirical horizontal shift factors, a_T, have been used in order to plot the data obtained at different temperatures on a single master curve. The structure of this thermoreversible gel is presumed to be physically cross-linked network of spherical PMMA junctions bridged by PEG-acrylate midblocks, as has been observed in other triblock copolymer systems.[34] The materials are not completely elastic in water/ethanol mixtures, because this solvent mixture is able to swell the PMMA blocks of the associating polymers. As illustrated by Figure 5, this particular sample has a composition that places it inside the region of the phase diagram which we characterize as a "gel".

Table 3. Advancing (θ_a) and Receding (θ_r) Contact Angles (in deg) of Water on Various Polymer-Coated Silicon Surfaces at 25 °C

polymer layers	N^a	θ_a	θ_r
PMMA (Polymer Lab.)	5000	80	78
PMMA−PAA−PMMA(C201)	220−664−220	37	20
PMMA−P(MMGA-*r*-AA)−PMMA (B163)	150−336−150	51	23
PMMA−(PMDGA-*r*-AA)−PMMA (B149)	220−664−220	59	44
PMMA−(PMTGA-*r*-AA)−PMMA (B169)	150−336−150	70	29

Hydrophilicity of Polymeric Films. The next step in our characterization of these polymers was to study the hydrophilicity of thin films of block copolymers which had been cast onto silicon substrates. One of the simplest available methods for probing the surface properties of a material involves the measurement of the contact angles of water on these surfaces. Baier et al. have found empirically that minimal fouling of hydrophobic polymer surfaces is obtained for intermediate values of the critical surface tension, obtained from the contact angles of a series of different liquids.[35] In the contrasting case of grafted, water-soluble polymers, low contact angles are preferred, simply because low contact angles provide an indication that the water-soluble polymer is present at the surface of the material. In our case advancing and receding contact angles for water droplets were measured. The results of the contact angle measurements are shown in Table 3, along with the structural characterization of the different block copolymers which were used. Significant decreases in the contact angles are obtained with triblock copolymers with PMMA end blocks and hydrophilic midblocks such as P(MTGA-*r*-AA). The advancing contact angle of water on PMMA is reduced from 80° to 70° by the addition of a 600 Å triblock copolymer layer with a P(MTGA-*r*-AA) midblock. More significantly, the receding contact angle is reduced from 78° to about 29°. The difference between advancing and receding contact angles on the block copolymer layers is also much larger than the difference between these angles on PMMA. The large contact angle hysteresis in these measurements can be attributed to the fact that the receding drops probe a fully hydrated layer, whereas advancing drops probe a "dry" layer. If the droplet is forced back over a triblock copolymer film immediately after the receding contact angle is measured, the properties of the hydrated layer are probed, and the measured advancing contact angle is very close to the receding contact angle.

Adhesion Measurements. Because the purpose of the coatings is to affect adhesion, it is important to have an appropriate method for quantifying the adhesive interactions. The adhesion measurements are based on the contact of a hemispherical elastomer with a flat surface, as described initially by Johnson, Kendall and Roberts,[36] and later by Maugis and Barquins,[37] and many others. The model system we have employed involves a hemispherical poly(*n*-butyl acrylate) (PnBA) elastomer, adhering to flat substrate in an aqueous environment, as illustrated in Figure 7. The measurements are in some ways similar to the contact angle measurements, in that hysteresis is generally observed for the results obtained for increasing compressive loads (corresponding to an advancing contact line) and decreasing loads (corresponding to a receding contact line). Instead of measuring a contact angle, we record a, the radius of the circular area between the PnBA lens and

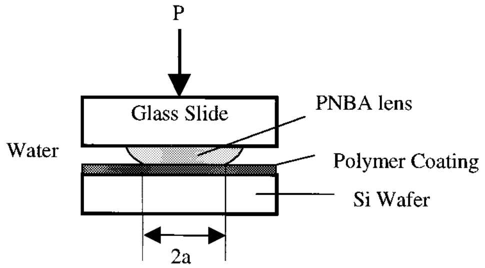

Figure 7. Experimental apparatus for measurements of the adhesion energy of a poly(*n*-butyl acrylate) elastomer against coated polymer substrates in water.

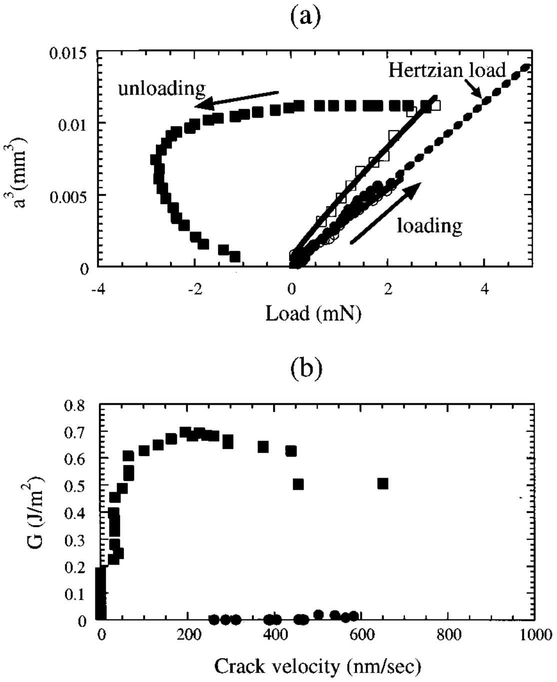

Figure 8. (a) Relationship between the cube of the contact radius and the applied load for a poly(*n*-butyl acrylate) lens pressed against PMMA (squares) or a PMMA–P(MTGA-*r*-AA)–PMMA triblock copolymer (C15, circles) in water. Loading data (increasing contact radius) are represented by the open symbols, and unloading data (decreasing contact radius) are represented by the filled symbols. (b) Adhesion energies obtained from the data in part a, plotted as a function of the crack velocity, given by the rate of change of the contact radius.

the coated substrate, as a function of P, the applied load. Typically, the cube of the contact radius is plotted as a function of P, as illustrated in Figure 8a. Note that substantial adhesion hysteresis is observed for the PMMA coating. A negative (tensile) load of almost 3 mN is required to separate the PnBA and PMMA surfaces during the unloading portion of the experiment. A very different result is obtained for the adhesion to the PMMA–P(MTGA-*r*-AA)–PMMA triblock copolymer coating. In this case adhesion hysteresis is not observed, indicating that the work of adhesion is equal to the thermodynamic work of adhesion.

To quantify the adhesion energy determined from these experiments, we use a linear elastic fracture mechanics analysis. The adhesion energy, G, is obtained from the following expression:[37]

$$G = \frac{3\left(\frac{16Ea^3}{9R} - P\right)^2}{32\pi E a^3} \tag{3}$$

where E is Young's modulus for the hemispherical lens and R is its radius of curvature. We have assumed here that the lens is incompressible with a Poisson's ratio equal to 0.5. The lens used in our experiments has $R = 0.85$ mm and $E = 1.7 \times 10^5$ Pa. If G is equal to zero, then a plot of a^3 as a function of P gives a straight line with a slope of $16E/9R$. The data for the triblock copolymer layer do indeed fall on a straight line, with a slope in agreement with the actual values of E and R. This value corresponds to the actual elastic modulus for the lens, which can be obtained independently from simultaneous measurements of the load, displacement, and contact radius during a loading/unloading cycle.[38,39] Within the resolution of our experiment, the adhesion energy of the PnBA lens to the triblock copolymer layer is indeed equal to zero. The adhesion energy of the PnBA lens to PMMA is much larger, as illustrated in Figure 8b. The data obtained in this figure were obtained by applying eq 3 to the unloading data shown in Figure 8a, using $R = 0.85$ mm and $E = 1.7 \times 10^5$ Pa. The adhesion energies are plotted as a function of the crack velocity, v, equal to the time derivative of the contact radius. Separation of the PnBA lens from the PMMA layer requires a significant amount of energy, even at very low crack velocities. In contrast, no energy is required to separate the PnBA lens from the triblock copolymer layer, for all of the crack velocities probed in this experiment.

Summary

We have developed hydrophilic coatings to minimize adhesion in aqueous environments. These coatings are based on block copolymers consisting of water-insoluble PMMA blocks coupled to water-soluble PEG-acrylate blocks. The characterization of these polymers can be summarized in terms of structural characterization, which is somewhat indirect, and a more direct characterization of surface properties related to the interactions of thin films of these polymers with water. Our primary conclusions are listed below.

Structural Characterization. (1) Thermal analysis indicates that block copolymers with PMMA blocks coupled to PEG-acrylate blocks form microphase separated morphologies. (2) Interfacial free energies were determined from measurements of the polymer surface energies and from AFM measurements of polymer/polymer contact angles. These measurements indicate that P(MTGA-*r*-AA) and P(MMGA-*r*-AA) are both highly immiscible with PMMA. (3) Rheological measurements on bulk gels formed by diluting triblock copolymers with a solvent mixture that is selective for the midblock of the copolymers confirm our expectation that these triblock copolymers form thermally reversible gels under appropriate conditions. The ternary phase diagram for a triblock copolymer in an ethanol/water mixture can be understood in terms of the net interaction between the solvent mixture and the associating, PMMA end blocks.

Surface Characterization. (1) Triblock copolymers with PMMA end blocks and a PEG-acrylate midblock can be easily applied to a variety of surfaces. The coatings do not dissolve in water and result in a very hydrophilic surface, as determined by measurements of water contact angles. (2) The adhesion of a hydrophobic, poly(*n*-butyl acrylate) elastomer to PMMA is actually greater in water than it is in air. This adhesion energy is reduced to zero, however, when the triblock copolymer layers are cast onto a surface of interest. The block copolymer layers are very effective at eliminating hydrophobic interactions that are often responsible for adhesive interactions in aqueous environments.

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Appendix

An approach for determining the tendency of an asymmetric diblock copolymer to form an ordered spherical morphology can be understood by calculating μ_{cmc}, the chemical potential for copolymer chains in an isolated micelle, as described initially by Semenov.[40] The following expression for this chemical potential can be obtained by considering the balance between interfacial and chain-stretching free energies:[41,42]

$$\mu_{\mathrm{cmc}}/k_{\mathrm{B}}T = 1.72(f\chi N)^{1/3}f^{1/9}(1.74f^{-1/3} - 1)^{1/3} \qquad (4)$$

where f is the volume fraction corresponding to the minority block, and χ is the Flory interaction parameter characterizing the thermodynamic interactions between the different blocks. The copolymer chemical potential in the disordered state is $\chi Nf(1 - f)k_{\mathrm{B}}T$, which we equate with the expression above to give the following expression for χ at the order/disorder transition:

$$f\chi N = 2.26f^{1/6}(1.74f^{-1/3} - 1)^{1/3}/(1 - f) \qquad (5)$$

For all values of f less than 0.25, the right-hand side of eq 5 is approximately equal to 3. Comparisons to experiments and to more detailed self-consistent-field calculations have shown that the scaling treatment underestimates $\mu_{\mathrm{cmc}}/k_{\mathrm{B}}T$ (and hence the critical value of $f\chi N$) by an additive factor of approximately 1.5.[43] We use 4.5 as a general approximation for $\mu_{\mathrm{cmc}}/k_{\mathrm{B}}T$, which will be valid for diblock copolymers with $f < 0.25$. For larger values of f, the possibility of cylindrical, lamellar, or more complicated geometries needs to be considered.[42] The characteristic value of $f\chi N$ at the order/disorder transition does not vary substantially, however. For example, the mean-field order/disorder transition for a symmetric system ($f = 0.5$) occurs at $f\chi N = 5.25$.[44] For all possible values of f ($0 < f < 0.5$), the following condition adequately approximates the location of the order/disorder transition:

$$f\chi N \approx 5 \qquad (6)$$

Because of the underlying symmetry of triblock copolymer molecules, eq 6 is roughly valid in these situations as well, provided that the molecular weights of the two end blocks of the triblock copolymer are identical and that one uses half the overall degree of polymerization of the triblock copolymer for N in eq 6.[45] This expression can be written in terms of the interfacial energy, γ_{ab}, by using the following expression:[46]

$$\gamma = ak_{\mathrm{B}}T(\chi/6)^{1/2}/v_0 \qquad (7)$$

where a is the statistical segment length and v_0 is the segmental volume. Solving for χ and substituting into eq 6 gives the following expression for fN, the degree of polymerization of the minority component of the block copolymer at the order/disorder transition:

$$fN \approx 0.8\left(\frac{ak_{\mathrm{B}}T}{v_0\gamma}\right)^2 \qquad (8)$$

An estimate of fN can be made by using the appropriate parameters for polystyrene at 178 °C, for which accurate values exist for a (6.7 Å)[47] and $v_0 = (165\ \text{Å}^3)$.[48] Using these values, with $\gamma = 3$ dyn/cm ($\chi \approx 0.1$), we obtain $fN = 57$, corresponding to a molecular weight for the minority block of about 6000 g/mol.

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