Synthesis and Surface Analysis of Siloxane-Containing Amphiphilic Graft Copolymers, Poly(2-hydroxyethyl methacrylate-*g*-dimethylsiloxane) and Poly(2,3-dihydroxypropyl methacrylate-*g*-dimethylsiloxane)

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Received March 1, 2002

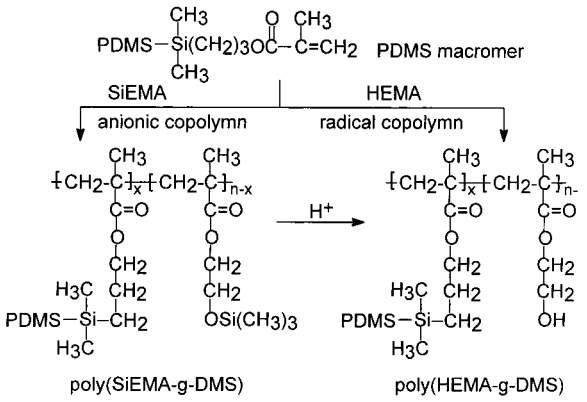
ABSTRACT: A series of novel amphiphilic graft copolymers having a hydrophilic poly(2-hydroxyethyl methacrylate) [poly(HEMA)] or water-soluble poly(2,3-dihydroxypropyl methacrylate) [poly(DHPMA)] backbone and hydrophobic poly(dimethylsiloxane) (PDMS) side chains have been synthesized to develop a model system to examine surface properties under dry and wet conditions. The direct radical copolymerization of PDMS macromer with HEMA generated graft copolymers poly(HEMA-*g*-DMS) with broad molecular weight distributions (MWD; $M_w/M_n = 2.85-3.55$). The anionic copolymerization of the same PDMS macromer with silyl-protected HEMA, namely, 2-(trimethylsiloxy)ethyl methacrylate (SiEMA), produced graft copolymers, poly(SiEMA-*g*-DMS). Successive hydrolysis eliminated the protecting trimethylsilyl groups in the backbone to afford amphiphilic graft copolymers poly(HEMA-*g*-DMS) with a narrow MWD ($M_w/M_n = 1.09-1.16$). For the well-defined graft copolymer with a water-soluble poly(DHPMA) backbone and hydrophobic PDMS side chains, anionic copolymerization of allyl methacrylate (AMA) with a PDMS macromer was carried out first, generating graft copolymers consisting of a poly(AMA) backbone and PDMS side chains. The unreacted allyl side groups of AMA units in the backbone were subsequently reacted with *N*-methylmorpholine *N*-oxide (NMO) in the presence of a trace amount of osmium tetroxide (OsO_4) to afford a new well-defined amphiphilic graft copolymer, poly(DHPMA-*g*-DMS). Using the angle-dependent X-ray photoelectron spectroscopy (XPS) technique, the surface compositions of solution-cast films of the graft copolymers were measured under both dry and wet (frozen) conditions. The effects of PDMS graft lengths, PDMS bulk content, and MWD on the surface composition were investigated. It was found that, for poly(HEMA-*g*-DMS) graft copolymers, the PDMS surface concentration increases with increasing PDMS bulk content. For a given PDMS bulk content, a longer PDMS graft gives a surface richer in siloxane. The effect of graft length is more significant than PDMS bulk content. Comparing radically to anionically prepared graft copolymers, the MWD has little effect on the dry air (free) surface composition but does affect the degree of reorganization upon exposure to water. In addition, the backbone hydrophilicity has a great effect on the PDMS segregation to the surface, and a significant surface composition difference between poly(HEMA-*g*-DMS) and poly(DHPMA-*g*-DMS) graft copolymers of similar PDMS graft length was found. Poly(DHPMA-*g*-DMS) with more hydrophilic backbone exhibited less PDMS concentration at the dry air (free) surface, even though its PDMS bulk content was higher than that of the poly(HEMA-*g*-DMS) graft copolymer. Furthermore, for poly(DHPMA-*g*-DMS), the effect of PDMS bulk content on its surface segregation was little even over a wide range of 9.0−26.0 wt %. However, as expected, upon exposure to water, poly(DHPMA-*g*-DMS) underwent a dramatic surface reorganization.

Introduction

Amphiphilic copolymers have been drawing great attention in recent years due to their special properties both in bulk and at the surface.[1] In particular, as biomaterials, they have been widely investigated and proved to possess many useful characteristics. For instance, Griffith and her colleagues conducted theoretical and experimental studies to elucidate the structure and properties of amphiphilic copolymer thin films as polymeric biomaterials.[2] Nakahama et al. reported that the triblock copolymer of styrene (St) and 2-hydroxyethyl methacrylate (HEMA), poly(HEMA-*b*-St-*b*-HEMA), exhibited excellent nonthrombogenic activity, which was evaluated by in vitro, ex vivo, and in vivo experiments.[3] Poly(HEMA)−PDMS hydrogels have been considered as potential contact lens materials.[4] Since biomaterials are in direct contact with the living body, the interfacial biocompatibility between a synthetic material and the living body is critical. A great number of studies have been performed to better understand the interaction between a synthetic polymer and the living body.[5] One conclusion that can be drawn from these studies is that the hydrophilicity of the biomedical polymer surface is of importance since a synthetic surface with a hydrophilic layer is lubricious, and in some applications this avoids serious damage to the living tissue surfaces. For instance, as a contact lens material, in addition to oxygen permeability and mechanical properties (material strength and stability), wettability is also important. If the lens is not sufficiently wettable, it would not be worn comfortably in the eye because of the lack of the lubrication.[4] To render the synthetic surface hydrophilic, many technologies have been employed, such as coating the surface with a hydrophilic layer[6] to make it lubricious, but this is not effective for long-term applications because of short life span of the coated layer. Plasma treatment is another method to create a hydrophilic surface on which the protein adsorption as well as platelet adhesion was found to be significantly reduced. By the covalent immobilization of water-soluble polymers on the material surface, a lubricated surface can be produced.[6]

10.1021/ma020323a CCC: $22.00
Published on Web 06/18/2002

Scheme 1



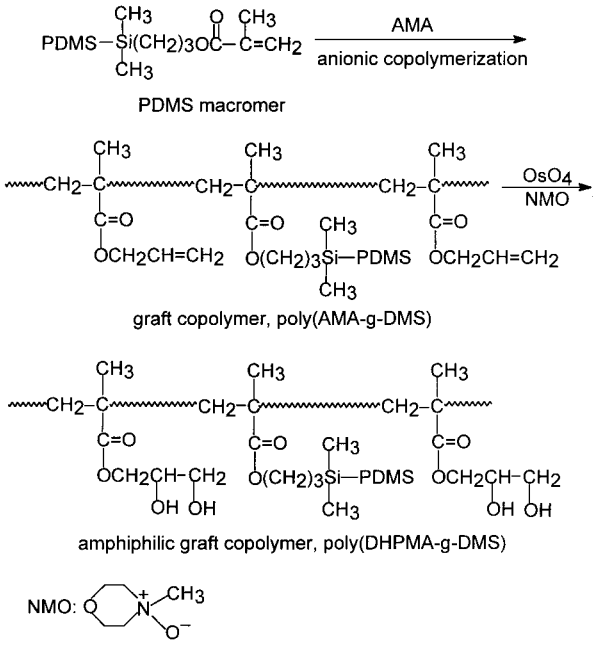
Poly(HEMA) possesses many valuable properties, such as transparency, high mechanical strength, biocompatibility, and hydrophilicity. In comparison with poly(HEMA), poly(2,3-dihydroxypropyl methacrylate) [poly(DHPMA)] is more hydrophilic and even soluble in water since it contains two hydroxyl groups in each of its repeat units. As a specialty polymeric material, poly(dimethylsiloxane) (PDMS) has received widespread attention due to its unique properties, such as excellent thermal and oxidative stability, high chain flexibility, low glass transition temperature, low surface energy, good biocompatibility, and excellent oxygen permeability. Utilizing the useful properties of PDMS, a wide variety of PDMS containing copolymers have been synthesized and characterized.[7]

In the present paper, we report the preparation of novel amphiphilic graft copolymers with a range of compositions and architectures as model systems to evaluate surface structure and water-induced surface reorganization. These copolymers contain a hydrophilic or water-soluble backbone, such as poly(HEMA) or poly(DHPMA), and hydrophobic PDMS side chains. By manipulating the bulk composition ratio, the PDMS chain length, the hydrophilicity of the backbone, and the molecular weight distribution, a series of amphiphilic graft copolymers with different architectures have been synthesized. This approach allows to combine the unique properties of poly(HEMA) or poly(DHPMA) with those of PDMS and to obtain useful polymeric materials with special bulk and surface properties and to test hypotheses relating surface structure to polymer architecture and composition.

Poly(HEMA-*g*-DMS) amphiphilic graft copolymers were prepared via both radical and anionic polymerization techniques. As shown in Scheme 1, the direct radical copolymerization of PDMS macromer with HEMA generated an amphiphilic graft copolymer with poly(HEMA) backbone and PDMS side chains. Anionic copolymerization of this macromer with the silyl-protected HEMA, namely, 2-(trimethylsiloxy)ethyl methacrylate (SiEMA), produced a graft copolymer with a poly(SiEMA) backbone and PDMS side chains (Scheme 1). Successive hydrolysis eliminated the silyl-protecting groups to afford an amphiphilic graft copolymer poly(HEMA-*g*-DMS) with a narrow MWD.

Additionally, as shown in Scheme 2, the anionic copolymerization of allyl methacrylate (AMA) with the PDMS macromer was carried out to afford a graft copolymer consisting of a poly(AMA) backbone and PDMS side chains. During this copolymerization process, the allyl side groups of AMA units in the backbone

Scheme 2



remained unchanged, which were further reacted with *N*-methylmorpholine *N*-oxide (NMO) in the presence of a trace amount of osmium tetroxide (OsO_4). This osmylation process changed the poly(AMA) backbone to poly(DHPMA), and a well-defined amphiphilic graft copolymer, poly(DHPMA-*g*-DMS), was obtained.

Since the characterization of polymer surfaces is crucial in a broad spectrum of applications, such as adhesion, biomedical materials, coatings, surfactant, and wear resistance, numerous analytical techniques have been utilized to establish a fundamental understanding of polymer interfaces.[8] XPS has developed into one of the more useful spectroscopic techniques to provide quantitative information about surface composition from 20 to 100 Å sampling depth. Therefore, by using angle-dependent XPS with low-temperature sample handling,[9] the effects of the hydrophilicity of the backbone, the graft length, the molecular weight distribution, and the composition in bulk on the surface properties of the graft copolymers were investigated under dry and wet conditions.

Experimental Section

Materials. Tetrahydrofuran (THF) was dried with CaH_2 under reflux for more than 10 h, distilled, and distilled again from a solution of 1,1-diphenylhexyllithium (DPHL) just before use. Hexane was first dried and distilled over CaH_2 and then distilled from a solution of *n*-BuLi. Hexamethylcyclotrisiloxane (D_3) was purified as follows. In a well-dried and nitrogen-protected flask containing a magnetic stirring bar, an aliquot of sublimated D_3 was added. Then, the purified THF was introduced into this flask to obtain a 30 wt % solution, to which CaH_2 was added. In this way, this THF solution was dried with magnetic stirring at room temperature for about 4 h. Subsequently, CaH_2 was removed by filtration using a glass tube filter with two reduced ends in a completely sealed apparatus. HEMA (Aldrich, 97%) was distilled under reduced pressure. SiEMA was prepared through the reaction of HEMA with an equal molar amount of 1,1,1,3,3,3-hexamethydisilazane.[10] Before polymerization, SiEMA was twice distilled under reduced pressure in the presence of calcium hydride. AMA (Aldrich, 98%) was dried over CaH_2 with magnetic stirring under reduced pressure, vacuum-distilled over CaH_2, and finally distilled in the presence of Al(*sec*-Bu)$_3$.[11] 1,1-

Diphenylethylene (DPE, Aldrich, 97%) was distilled over CaH_2 and then distilled in the presence of DPHL under reduced pressure. Lithium chloride (Aldrich, 99.99%) was dried at 120 °C for 24 h and dissolved in THF.[12] *n*-BuLi (Aldrich, 1.6 M solution in hexane) was diluted with purified hexane. 3-(Methacryloyloxy)propyldimethylchlorosilane (AMASiCl), 2,2-dimethoxy-2-phenylacetophenone (DPA; photoinitiator; Aldrich, 99.9%), osmium tetroxide (Aldrich, 4 wt % in water), *N*-methylmorpholine *N*-oxide (NMO; Aldrich; 97%), and benzoic anhydride (Aldrich, 90%) were used as received.

Photoinduced Radical Copolymerization of HEMA with PDMS Macromer. PDMS macromer with a methacryloyl end group was synthesized by using a reported method.[13] The photopolymerization was carried out under an overpressure of nitrogen at room temperature. To a round-bottom flask, an appropriate amount of photoinitiator (DPA) was first added, and this was followed by the addition of THF. After the initiator dissolved completely, HEMA, a THF solution of PDMS macromer and propanol ($V_{THF}/V_{propanol} = 3:1$) were sequentially added. The system was degassed and replaced with nitrogen for three times. Then, this flask was illuminated under a 15 W fluorescent lamp for 12 h. The copolymer thus obtained was purified by pouring the polymerization solution into hexane, washed with hexane for several times to remove the unreacted PDMS-macromer, and finally vacuum-dried at 50 °C for 24 h.

Anionic Synthesis of Poly(HEMA-*g*-DMS). The hydroxyl group of HEMA was first reacted with 1,1,1,3,3,3-hexamethydisilazane to obtain a silyl-protected monomer, SiEMA.[10] Its anionic copolymerization with PDMS macromer were carried out in a round-bottom flask under an overpressure of argon with magnetic stirring. A well-dried 100 mL round-bottom flask containing a magnetic stirring bar was degassed and replaced with argon for three times, and the addition of solvent, monomer, or initiator was carried out with dried syringes.

The vacuum-dried PDMS-macromer was further purified according to the following procedure before use. First, the macromer was freeze-dried from its benzene solution (ca. 5 wt %) for 12 h at room temperature. Then, in a well-dried and nitrogen-protected flask, a certain amount of PDMS macromer was added and dissolved in purified THF. This solution was dried by adding a small amount of CaH_2 with stirring at room temperature for about 3 h. Prior to polymerization, CaH_2 was removed by filtration with a completely sealed filter, and the filtrate was directly used in the anionic copolymerization.

Before copolymerization, the initiator, 1,1-diphenylhexyllithium (DPHL), was first prepared in situ through the reaction between 1,1-diphenylethylene (DPE) and *n*-BuLi. After THF, DPE ($mol_{DPE}/mol_{n-BuLi} = 1.2$), and a THF solution of LiCl ($mol_{LiCl}/mol_{n-BuLi} = 2$) were added with dry syringes, the flask was cooled to −40 °C, and *n*-BuLi (in hexane) was added. The deep red color of DPHL appeared at once, and the reaction was allowed to last 20 min. Then, the system was cooled to −60 °C, and the copolymerization reaction was induced by introducing a mixture of SiEMA and the THF solution of PDMS macromer into the above initiator system. About 60 min later, a small amount of polymerization solution (ca. 0.2 mL) was taken out with a dry syringe for the GPC measurement. Subsequently, an aqueous solution of hydrochloric acid (2.0 M, 2.0 mL) was added to the polymerization system, and the stirring was continued for about 1.5 h. In this manner, the termination of the copolymerization and the elimination of trimethylsilyl-protecting groups were accomplished simultaneously. Then, the graft copolymer thus prepared was precipitated into a mixture of water and methanol (9/1 by volume), washed with water, vacuum-dried overnight at 40 °C, and finally freeze-dried from a 1,4-dioxane solution containing a small amount of methanol.

Copolymerization of AMA with PDMS Macromer. The copolymerization of AMA with PDMS macromer was induced by introducing a mixture of AMA and the THF solution of PDMS macromer into the same DPHL initiator system as prepared above. About 90 min later, the system was quenched by adding a small amount of methanol (ca. 1 mL), and the graft copolymer thus prepared was precipitated into a mixture of water and methanol (9/1 by volume), then washed with water, and vacuum-dried overnight at 40 °C.

Osmylation. The osmylation reaction of the backbone of the graft copolymer, poly(AMA-*g*-DMS), was carried out with magnetic stirring, under nitrogen, at room temperature, for 24 h. A mixture of THF, acetone, methanol, and water was used as the solvent. Compared to the molar amount of C=C bonds in the backbone, an excess amount of NMO and a trace amount of OsO_4 (2 mol %) were employed.

Poly(AMA-*g*-DMS) (1.0 g) and an aliquot of NMO were added to a round-bottom flask containing a magnetic stirring bar. This flask was degassed and protected with nitrogen. First, THF and acetone were introduced into the flask to dissolve the graft copolymer, while NMO remained insoluble. Then, a small amount of methanol was added, and the system became homogeneous and transparent. The reaction was started by adding an aqueous solution of osmium tetroxide (4 wt %) with a syringe. As the reaction was proceeding, the system gradually became turbid. To keep the reaction proceeding homogeneously, a small amount of methanol was added. After 24 h, the resulting copolymer was precipitated by pouring the reaction solution into a mixture of hexane and ethanol (1:1 by volume). The copolymer was kept in this mixture overnight, washed carefully with ethanol, vacuum-dried at 40 °C for 24 h, and finally freeze-dried from a 1,4-dioxane solution containing a small amount of methanol.

Measurements. ^1H NMR spectra were recorded in $CDCl_3$ or a mixture of CD_3OD with THF-d_8 on an INOVA-500 spectrometer. FT-IR spectra were recorded using KBr pellets on a Perkin-Elmer 1760-X spectrometer. M_n and M_w/M_n of the (co)polymer were determined by gel permeation chromatography (GPC) on the basis of a polystyrene calibration curve. The GPC measurements were carried out using THF as eluent, at 35 °C, with a Waters 410 RI detector. The flow rate and chart speed were 1.0 mL/min and 1.0 cm/min, respectively. Three polystyrene gel columns (10^5, 10^3, and 500 Å) were connected to a Waters precision pump.

Surface Analysis. All graft copolymer samples for XPS measurements were cast as films in clean aluminum weighing pans from ca. 1% (w/v) solutions in a mixture of THF and methanol (2/1 by volume), while PDMS in THF and poly(HEMA) in methanol, respectively. The films were first allowed to air-dry at room temperature for 72 h and further vacuum-dried at ambient temperature overnight to obtain as-cast films.

XPS data were obtained using a Physical Electronics (PHI) model 5100 spectrometer equipped with an Mg/Ti dual anode source and an Al/Be window. The system uses a hemispherical analyzer with a single-channel channeltron detector. An achromatic Mg Kα X-ray (1253.6 eV) source was used and operated at 300 W, 15 kV, and 20 nA. The base pressure of the system was no higher than 2×10^{-8} Torr, with an operating pressure no higher than 1×10^{-7} Torr. A pass energy of 89.45 eV was used when obtaining the survey spectra, and 35.75 eV was used for the high-resolution scans. The instrument was calibrated using Mg Kα X-radiation such that the Ag $3d_{5/2}$ peak of sputtered-clean Ag had a binding energy of 367.9 ± 0.1 eV, and the binding energy difference between the Cu $2p_{3/2}$ and Au $4f_{7/2}$ was 848.7 ± 0.1 eV. The full width at half-maximum for Ag $3d_{5/2}$ was measured to be 0.80 eV at a rate of 30 000 counts. A survey spectrum of each sample was first acquired to detect all elements present except hydrogen. High-resolution spectra of each element in a sample were collected with an energy window of 20 eV and sufficient scans to achieve an acceptable signal-to-noise ratio. Spectra for PDMS macromer, homopoly(HEMA), poly(HEMA-*g*-DMA), and poly(DHPMA-*g*-DMS) graft copolymer films were obtained at the following takeoff angles (TOAs): 15°, 30°, 45°, 60°, and 90°, which leads to various sampling depths from 28 to 103 Å. Data manipulation was performed using a PC running RBD Auger scan version 2.0 software.

For the water exposure, the coated slides where placed in a glass Petri dish and submerged in distilled water (Barnstead Mega-Pure MA-6) for 24 h. Prior to analysis, a Dewar flask was filled with liquid nitrogen, and the sample puck was placed in a holding clamp used for introduction. A small

Table 1. Preparation of PDMS Macromer via Ring-Opening Anionic Polymerization of D_3[a]

run	[*n*-BuLi]$_0$ (M)	time (h)	[AMASiCl][b] (M)	M_n	M_w/M_n[d]	functionality[c]
PDMS-1	0.333	4.0	0.40	1340[c]	1.17	100
PDMS-2	0.158	3.0	0.39	2170[d]	1.13	100
PDMS-3	0.166	4.5	0.20	2430[d]	1.16	100
PDMS-4	0.114	3.0	0.30	3170[d]	1.14	100
PDMS-5	0.102	5.0	0.13	3820[d]	1.12	100

[a] The anionic polymerization was started by adding a hexane solution of *n*-BuLi to the THF solution of D_3 ($[D_3]_0 = 1.50$ M) at room temperature. [b] An excess amount of terminator, 3-(methacryloyloxy)propyldimethylchlorosilane (AMASiCl), was introduced into the reaction system after the polymerization, and this termination reaction was allowed to last more than 6 h at room temperature. [c] Determined by ^{1}H NMR. [d] Determined by GPC.

droplet of water was placed on the sample puck surface. The coated slide was removed from the water and immediately placed on the sample puck surface, spreading the droplet of water uniformly and adhering the glass slide to the puck surface. This was immediately followed by submerging the sample-mounted puck into the liquid nitrogen until the rapid boiling ceased to ensure that the sample was completely frozen. The sample was placed into the cold-probe introduction chamber over nitrogen and pumped on 20−30 s. The sample is then transferred to the precooled finger (−130 °C) under ultrahigh-vacuum conditions. Varying the nitrogen flow to the finger can regulate the temperature of the coldfinger. Thus, the nitrogen flow was decreased to allow the temperature of the coldfinger and sample to increase slightly, to about −100 °C, to allow for rapid sublimation of the water. The sample is held at this temperature for 30−40 min followed by cooling it back to −130 °C before analysis. The sublimation of ice on the surface was followed visually and by the pressure gauge in the main chamber. The cryogenic sample handling technique used in this study was developed in this laboratory and discussed in a previous paper.[9]

Results and Discussion

Synthesis of PDMS Macromer. The rapid advances in living anionic polymerization have made it possible to accurately control the primary structure of (co)polymers, such as the molecular weight, molecular weight distribution (MWD), side and/or end groups, monomer sequence, composition, geometrical shape, etc.[14] In the present paper, the living anionic polymerization technique was applied to the synthesis of both poly(HEMA-*g*-DMS) and poly(DHPMA-*g*-DMS) amphiphilic graft copolymers.

The macromer synthesis technique has been a powerful tool for preparing block and graft copolymers via the copolymerization with the common monomers.[13] PDMS with a methacryloyl end group is a popular macromer and constitutes the grafting component after the copolymerization.[13] The PDMS macromers were prepared via the anionic ring-opening polymerization of D_3 (Table 1), followed by the termination with AMASiCl as described previously.[13] The quantitative end-functionality was confirmed by ^{1}H NMR.

Anionic Copolymerization of PDMS Macromer and SiEMA. Anionic polymerization techniques have not been widely employed in the synthesis of the graft copolymers via the macromer method,[15] since a macromer pure enough for the anionic polymerization is difficult to obtain. For this reason, radical polymerization methods are used more frequently.[7]

In the present paper, PDMS macromers were thoroughly purified and used for the anionic copolymerization with silyl-protected HEMA (See Experimental Section). The GPC measurements indicated that a single and sharp peak appeared at the higher molecular weight side after the copolymerization, and the peak corresponding to its macromer precursor was no longer present. Consequently, the PDMS macromer was completely incorporated into the graft copolymer. After the copolymerization, as confirmed by ^{1}H NMR and FT-IR, the protecting trimethylsilyl groups in the backbone were completely eliminated by the reaction with hydrochloric acid. The composition of the two components calculated according to the intensity ratios was close to that designed (Table 2). As shown in Table 2, by changing the feed ratios of HEMA and PDMS macromer, several groups of amphiphilic graft copolymers with various compositions and different graft lengths were obtained.

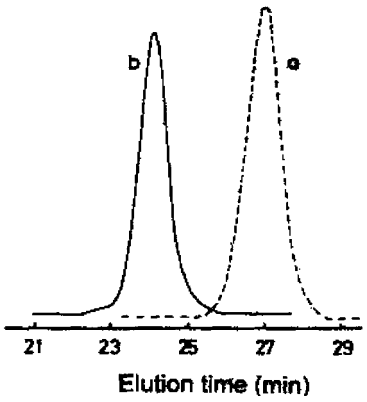


Figure 1. GPC traces of the graft copolymer, poly(AMA-*g*-DMS) (peak b, AD-1 in Table 3, $M_n = 20\,500$, $M_w/M_n = 1.10$), and of its precursor, PDMS macromer (peak a, PDMS-2 in Table 1, $M_n = 2170$, $M_w/M_n = 1.13$).

Anionic Copolymerization of AMA with PDMS Macromer. The anionic copolymerization was induced by adding a mixture of AMA and PDMS macromer to DPHL initiator solution. As shown in Table 3, the polymer yield was 100% in each case and the MWD of the graft copolymer was narrow ($M_w/M_n = 1.08-1.19$). As illustrated in Figure 1, the GPC chromatogram exhibits a single and sharp peak (peak b; AD-1 in Table 3; $M_n = 20\,500$, $M_w/M_n = 1.10$), and the peak of its macromer precursor (peak a; PDMS-2 in Table 1; $M_n = 2170$, $M_w/M_n = 1.13$) no longer exists, indicating that the PDMS macromer was completely incorporated into the graft copolymer. In the ^{1}H NMR spectrum of the graft copolymer, the peaks corresponding to the allyl groups [4.52 ppm ($-CH_2$), 5.20−5.51 ppm (CH═), and 5.91 ppm (═CH_2)] in the backbone of the graft copolymer are present quantitatively. Therefore, the methacryloyl C═C bond of AMA was selectively polymerized, while the allyl C═C bond remained unreacted. In addition, besides the peaks of poly(AMA) component, the resonance (0.05 ppm) due to the DMS repeating units in the side chains of the graft copolymer also appears in this spectrum, and the weight ratio of the two components calculated according to the peak intensity ratio coincides with the feed amount ratio (Table 3). Thus, the composition of the graft copolymer can be well controlled.

Osmylation of the Graft Copolymers. The reaction of the C═C bond with NMO in the presence of osmium tetroxide has been a reliable method for cis-dihydroxylation.[16] In the present paper, to obtain amphiphilic graft copolymers consisting of a hydrophilic poly-

Table 2. Synthesis of the Graft Copolymer, Poly(HEMA-*g*-DMS), via the Anionic Copolymerization of PDMS Macromer with Protected HEMA[a]

run	DPHL[b] (mmol)	macromer[c] (g)	SiEMA[d] (g)	$10^{-4}M_n$[e]	M_w/M_n[e]	wt % (PDMS)[f] calcd	wt % (PDMS)[f] obsd[g]
HD-1	0.17	PDMS-1/0.016	4.98	2.98	1.15	0.5	1.2
HD-2	0.17	PDMS-1/0.049	4.95	3.04	1.15	1.5	2.1
HD-3	0.17	PDMS-1/0.11	4.89	2.93	1.16	3.4	4.5
HD-4	0.17	PDMS-1/0.16	4.84	2.38	1.11	4.9	5.1
HD-5	0.17	PDMS-1/0.39	4.61	3.19	1.16	11.6	13.4
HD-6	0.17	PDMS-1/0.64	4.36	2.49	1.13	18.6	21.6
HD-7	0.17	PDMS-1/0.97	4.03	2.98	1.16	27.2	22.8
HD-8	0.18	PDMS-3/0.16	4.84	2.52	1.12	4.9	5.5
HD-9	0.18	PDMS-3/0.39	4.61	2.27	1.12	11.6	11.3
HD-10	0.18	PDMS-3/0.64	4.36	2.63	1.14	18.6	15.4
HD-11	0.18	PDMS-3/0.97	4.03	3.13	1.16	27.2	21.3
HD-12	0.20	PDMS-5/0.16	4.84	2.24	1.09	4.9	7.0
HD-13	0.20	PDMS-5/0.48	4.52	2.46	1.11	14.2	17.8
HD-14	0.20	PDMS-5/0.81	4.19	2.41	1.11	23.1	22.6

[a] The anionic copolymerization was carried out in THF in the presence of LiCl ([LiCl]/[*n*-BuLi]$_0$ = 3) at −78 °C for 50−60 min. The total volume of the polymerization system was 60 mL. The termination and the elimination of trimethylsilyl-protecting groups were performed simultaneously by adding a small amount of hydrochloric acid (ca. 2.0 mL, 1.5 M) after the copolymerization. [b] The initiator, DPHL, was prepared in situ before the addition of the mixture of PDMS macromer and the protected HEMA, through the reaction between *n*-BuLi and DPE ([DPE]/[*n*-BuLi]$_0$ = 1.2) at −40 °C for 20 min. [c] See Table 1. [d] Protected HEMA: 2-(trimethylsilyl)ethyl methacrylate. [e] Determined by GPC. [f] The weight content of DMS units in the graft copolymer. [g] Determined by ^{1}H NMR.

Table 3. Preparation of the Graft Copolymer, Poly(AMA-*g*-DMS), via the Anionic Copolymerization of PDMS Macromer with AMA[a]

no.	*n*-BuLi (mmol)	macromer[b] wt (g)	AMA wt (g)	$10^{-4}M_n$ calcd[c]	$10^{-4}M_n$ GPC[d]	M_w/M_n[d]	W_{DMS}/W_{AMA}[e] designed	W_{DMS}/W_{AMA}[e] obsd[f]
AD-1	0.333	PDMS-2/0.50	4.50	1.53	2.05	1.10	9/91	9/91
AD-2	0.333	PDMS-2/1.00	4.00	1.53	1.92	1.16	18/82	16/84
AD-3	0.333	PDMS-2/1.50	3.50	1.53	1.81	1.17	27/73	26/74
AD-4	0.180	PDMS-4/0.20	3.80	2.25	2.72	1.08	5/95	5/95
AD-5	0.620	PDMS-4/0.60	3.40	0.67	0.79	1.19	14/86	13/87
AD-6	0.167	PDMS-4/1.00	3.00	2.42	3.02	1.11	23/77	21/79
AD-7	0.100	PDMS-4/1.50	2.50	4.02	5.09	1.19	35/65	33/67

[a] The initiator, DPHL, was first prepared in situ through the reaction between *n*-BuLi and DPE ([DPE]/[*n*-BuLi]$_0$ = 1.4), in THF, in the presence of LiCl ([LiCl]/[*n*-BuLi]$_0$ = 2], at −40 °C, for 20 min. The anionic copolymerization was started by adding a mixture of PDMS macromer and AMA to the above initiator solution, and the reaction was allowed to last 1.5 h at −60 °C. The total volume of the polymerization system was 50 mL. The yield of the graft copolymer was 100% in each case. [b] See Table 1. [c] M_n(calcd) = [W_{PDMS} + W_{AMA}]/mol$_{n-BuLi}$ + 238 (initiator). [d] Determined by GPC. [e] The weight ratio of DMS and AMA units in the graft copolymer. [f] Determined by ^{1}H NMR.

(DHPMA) backbone and hydrophobic PDMS side chains, this osmylation process was applied to the dihydroxylation of poly(AMA) backbone of the graft copolymer poly(AMA-*g*-DMS).

In the ^{1}H NMR spectrum of the osmylated product, the peaks [4.52 ppm (−CH_2), 5.20−5.51 ppm (CH═), and 5.91 ppm(═CH_2)] corresponding to the allyl side groups of poly(AMA) backbone disappeared completely, and those due to the formed dihydroxypropyl groups [3.62 ppm, −CH(OH)CH_2OH; 3.92 ppm, −OCH_2CH(OH)−; and 4.03 ppm, −CH_2*CH*(OH)−] emerged quantitatively. In addition, similar to its precursor, the resonance (0.05 ppm) corresponding to the PDMS side chains remained unchanged, and the weight ratio of the two components calculated on the basis of the spectrum is close to the theoretical value. The ^{1}H NMR results are also supported by the FT-IR measurements. After osmylation, the typical peak (1620 cm^{-1}) of the C═C double bond in poly(AMA) backbone disappeared completely, and a strong broad band (3200−3600 cm^{-1}) corresponding to the formed hydroxyl groups emerged. The above results indicate that the osmylation procedure hydrolyzed the poly(AMA) backbone to poly(DHPMA), creating amphiphilic graft copolymers.

The graft copolymers before and after osmylation exhibit different solubilities. As shown in Table 5, before osmylation, the graft copolymers are soluble in benzene, chloroform, DMF, pyridine, 1,4-dioxane, THF, and acetone but insoluble in ethanol, methanol, and water. However, their osmylated products are soluble in methanol and swollen by water but insoluble in benzene, chloroform, 1,4-dioxane, THF, and acetone.

Photoinduced Radical Copolymerization of HEMA with PDMS Macromer. To explore the effect of MWD on surface segregation, the direct photoinduced copolymerization of PDMS macromer with HEMA was carried out, and amphiphilic graft copolymers with broad MWDs were synthesized (Table 6). To investigate the effect of the graft copolymer length on the surface properties of the resulting copolymer, three PDMS macromers with different molecular weights (M_n = 1340, 3820, and 10 000) were employed. The GPC chromatogram of the obtained graft copolymer exhibits a single and symmetrical peak, and its ^{1}H NMR and FT-IR spectra (not shown) are similar to those of the graft copolymers prepared anionically.

Surface Analysis via XPS under Dry Conditions. In the air (free) surface region of multicomponent copolymers, the thermodynamic driving force for minimizing the total free energy of the system results in preferential surface segregation of the lower surface energy constituent in the copolymers. This has been quantified with angle-dependent XPS. The results demonstrate a gradient in concentration of PDMS over the

Table 4. Synthesis of Amphiphilic Graft Copolymer, Poly(DHPMA-*g*-DMS), via the Osmylation of the Backbone of Poly(AMA-*g*-DMS)[a]

no.	polymer[b]	C=C[c] (mmol)	OsO_4[d] (mmol)	NMO[e] (mmol)	THF/acetone/CH_3OH/H_2O[f] by volume (mL)	CH_3O[g] (mL)	functionality[h]
ADOH-1	AD-1	7.21	0.144	9.01	8/10/1/0.5	6.0	100
ADOH-2	AD-2	6.66	0.133	8.33	9/9/1/0.5	4.0	100
ADOH-3	AD-3	5.86	0.117	7.33	10/7/1/0.5	1.5	100
ADOH-4	AD-4	7.52	0.150	9.02	7/10/1/0.5	5.0	100
ADOH-5	AD-5	6.92	0.138	8.30	8/9/1/0.5	4.0	100
ADOH-6	AD-6	6.24	0.125	8.11	10/7/1/0.5	3.0	100
ADOH-7	AD-7	5.36	0.107	7.50	12/6/1/0.5	2.5	100

[a] The reaction was carried out at room temperature under the protection of N_2 with magnetic stirring for 24 h. [b] The weight of the graft copolymer employed was 1.00 g. [c] Molar amount of allyl groups in the backbone of poly(AMA-*g*-DMS). [d] 4 wt % solution in water. [e] *N*-Methylmorpholine *N*-oxide. [f] Mixed solvent employed at the beginning of the reaction. [g] Added gradually during the osmylation process to keep the reaction proceeding homogeneously. [h] Determined by ^{1}H NMR.

Table 5. Solubility Comparison before and after Dihydroxylation of the Backbone[a]

no.[b]	hexane	Bz	$CHCl_3$	DMF	pyridine	1,4-dioxane	THF	acetone	C_2H_5OH	CH_3OH	H_2O
AD-1	I	S	S	S	S	S	S	S	I	I	I
ADOH-1	I	I	I	S	S	I	I	I	I	S	W
AD-2	W	S	S	S	S	S	S	S	I	I	I
ADOH-2	I	I	I	S	S	I	I	I	W	S	W
AD-3	S	S	S	S	S	S	S	S	I	I	I
ADOH-3	I	I	I	S	S	I	I	I	S	S	W

[a] The experiment was carried out at room temperature. The amounts of polymer and the solvent were 0.03 g and 1.0 mL, respectively. S = soluble; W = wetting; I = insoluble. [b] OH: the (co)polymers after dihydroxylation.

Table 6. Synthesis of Graft Copolymer, Poly(HEMA-*g*-DMS), via Photoinduced Radical Copolymerization[a]

run	macromer/M_n[b]	M_n (copolymer)[c]	M_w/M_n (copolymer)[c]	wt % (DMS)[d]
R-HD-1	PDMS-1/1340	29 800	3.55	0.8
R-HD-2	PDMS-1/1340	26 900	2.88	1.5
R-HD-3	PDMS-1/1340	31 700	3.15	2.3
R-HD-4	PDMS-1/1340	32 900	3.22	2.7
R-HD-5	PDMS-1/1340	27 800	2.85	7.0
R-HD-6	PDMS-1/1340	27 700	3.10	10.9
R-HD-7	PDMS-5/3820	47 000	3.21	6.5
R-HD-8	PDMS-5/3820	52 000	3.15	7.9
R-HD-9	PDMS-6/10000	62 000	3.30	1.5
R-HD-10	PDMS-6/10000	64 500	3.40	6.7
R-HD-11	PDMS-6/10000	92 000	3.26	9.8
R-HD-12	PDMS-6/10000	76 000	3.10	16.3

[a] The radical copolymerization was carried out in a mixed solvent of THF and propanol (3:1 by volume) at room temperature. HEMA, PDMS macromer, and the photoinitiator 2,2-dimethoxy-2-phenylacetophenone were dissolved in above mixture. The reaction was started by irritating the system with an UV lamp, and the irritation was allowed to last 24 h. [b] PDMS-1 and PDMS-5: see Table 1; PDMS-6: purchased from Aldrich (average M_n ca. 9000−12 000; viscosity 100−200 cps). [c] Estimated by GPC. [d] The weight percent of DMS units in the graft copolymer, which was determined by ^{1}H NMR.

surface region. Higher takeoff angles (TOAs) yield results from deeper region from the surface; for example, a 90° TOA leads to corresponding sampling depth of approximately 103 Å, while a 15° TOA decreases the sampling depth to 28 Å.

In the present paper, both poly(HEMA-*g*-DMS) and poly(DHPMA-*g*-DMS) graft copolymers contain the same hydrophobic PDMS side chains which preferentially segregate to the air (free) surface region. Results from the extent of segregation and in-depth distribution of PDMS are studied as a function of PDMS bulk content, PDMS graft length, and, more interestingly, the hydrophilicity of the backbone.

In the XPS survey spectra of the as-cast films of homopoly(HEMA), only carbon and oxygen peaks were detected, which is consistent with its composition,

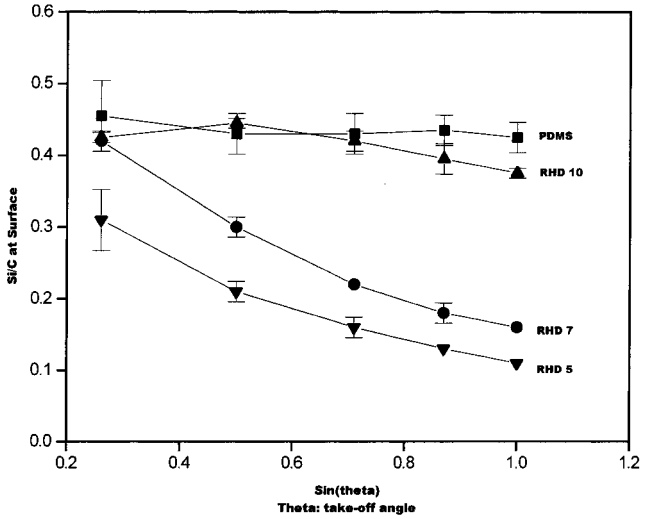


Figure 2. Angle-dependent XPS data of Si/C atomic ratios for the PDMS macromer, poly(HEMA-*g*-DMS) graft copolymers of R-HD-10, R-HD-7, and R-HD-5 with PDMS graft length of 132, 45, and 14 DMS repeat units, respectively. The PDMS bulk contents for all the graft copolymers are about 6.5 wt %.

indicating that the sample was free from surface contamination within the XPS detection limit of about 1% atomic. On the other hand, for both the PDMS macromers and the graft copolymers, signals from carbon, oxygen, and silicon atoms were observed in the survey spectra.

High-resolution spectra of carbon 1s, oxygen 1s, and silicon 2p were recorded for the quantitative XPS analysis. Si was selected to quantify the PDMS component in the copolymer by measurement of atomic ratios of Si/C, which range from 0 (if the surface is completely comprised of poly(HEMA) component) to 0.5 (if the surface is completely comprised of PDMS component).

Figure 2 shows the angle-dependent XPS data, in particular Si/C atomic ratios for the PDMS macromer and a selected group of poly(HEMA-*g*-DMS) graft copolymers. The copolymer designed R-HD-10, R-HD-7, and R-HD-5 have nearly the same PDMS bulk content

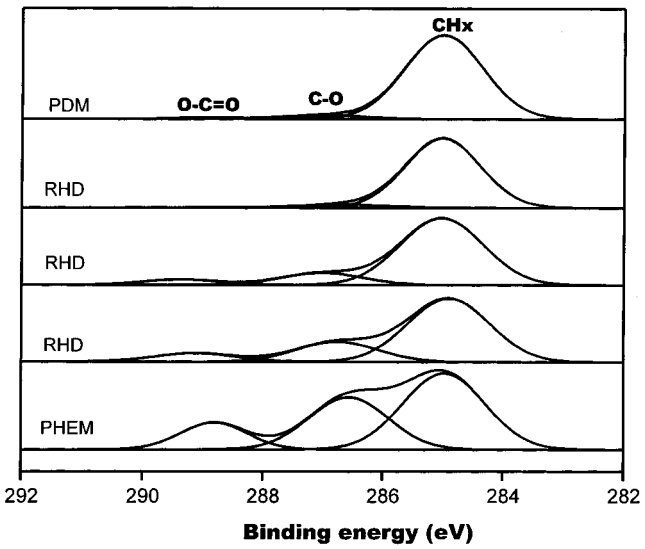


Figure 3. C 1s high-resolution XPS spectra of PDMS macromer, homopoly(HEMA), and poly(HEMA-*g*-DMS) graft copolymers, namely R-HD-10, R-HD-7, and R-HD-5 with a PDMS graft length of 132, 45, and 14 siloxane repeat units, respectively. The PDMS bulk content for all the graft copolymers is about 6.5 wt %.

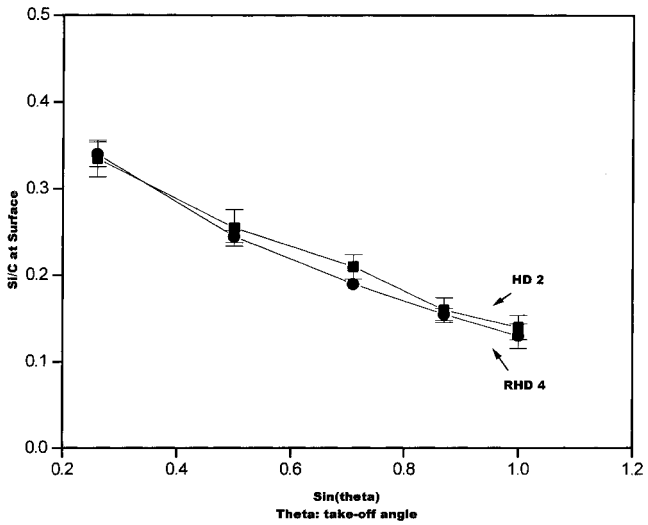


Figure 4. Angle-dependent XPS data of Si/C atomic ratios for poly(HEMA-*g*-DMS) graft copolymers of HD-2 and R-HD-4 with different MWDs of 1.15 and 3.22, respectively. The PDMS bulk contents for both HD-2 and HD-4 are around 2.5 wt %.

(ca. 6.5 wt %) but different PDMS graft lengths of about 132, 45, and 14 siloxane repeat units, respectively. Results in Figure 2 show that the increase of the PDMS graft length leads to an major change in the PDMS concentration at the air surface. Furthermore, a thicker PDMS surface layer was detected for the graft copolymer with longer PDMS graft length, as evidenced by the angle-dependent XPS data. In comparison with the data of PDMS macromer, it is clear that the surface region over 100 Å of the sample R-HD-15 with PDMS graft of 132 siloxane repeat units was nearly completely dominated by the PDMS component. The high-resolution XPS spectra of C 1s regions of pure poly(HEMA), PDMS macromer, and the group of poly(HEMA-*g*-DMS) graft copolymers of R-HD-10, R-HD-7, and R-HD-5, shown in Figure 3, confirm that with increasing the PDMS graft length, the intensities of the O═C−O (at 289.0) and C−O (at 286.7 eV) peaks from the poly(HEMA) component decrease gradually; that is, the concentration of PDMS component at the surface increases. In particular, for the sample R-HD-10 with the longest PDMS graft length of 132 siloxane repeating units, the C 1s region is similar to that of PDMS macromer, composed of a main peak (at 285.0 eV) contributed from C−H groups and negligible O═C−O and C−O peaks, suggesting that the surface region was covered by the PDMS component completely.

The effects of the chemical structure, glass transition temperature, surface energy, and composition of each segment of block and graft copolymer films on their surface properties have been widely studied.[18] However, the effect of the molecular weight distribution (MWD) on surface properties remains uninvestigated. In this study, a group of poly(HEMA-*g*-DMS) graft copolymers with the same PDMS bulk content but different MWDs was selected, and their surface compositions were compared. As shown in Figure 4, there is no significant difference in surface composition between these two copolymers for the dry surface. From a kinetics point of view, the graft copolymers with low molecular weights and high PDMS content are expected to have higher possibility of segregation to the air free surface, yielding a higher PDMS content than narrow MWD samples. However, since the graft copolymers with broad MWDs were purified by precipitating in hexane several times, the graft copolymer fraction with high PDMS content and low molecular weight could have been removed along with the unreacted PDMS macromer by dissolution in hexane. This would result in less or even no PDMS-rich component existing in the lower molecular weight portion of this system. Consequently, the graft copolymers with high PDMS component remain in either the most abundant average or larger molecular weight portions of the system. We hypothesize that for these reasons, under dry conditions, no difference in surface segregation was detected between the graft copolymers with broad and narrow MWDs. This is contrasted with the results from comparing results of the surface compositions of samples with different polydispersities upon exposure to water (see below).

The effect of PDMS bulk content on the surface composition of poly(HEMA-*g*-DMS) graft copolymers with relatively short PDMS graft length of 14 siloxane repeat units was also investigated. As shown in Figure 5, the topmost surface of the graft copolymer films consists of a siloxane-rich layer, even for the graft copolymer containing only 1.2 wt % of PDMS in the bulk (sample HD1). However, along with the increase of PDMS bulk content, the PDMS concentration at the air surface slightly increases. Even when the PDMS content was increased to 21.6 wt % (sample HD6), the surface was still not covered completely with PDMS, indicating that there was still detectable poly(HEMA) component existing at the surface. This result is consistent with the observation of previous work[17] on PDMS-containing block copolymers with short PDMS segments. The dominant factor in defining the surface composition of short segment PDMS copolymers is not bulk composition, but in fact siloxane segment length.[17]

Figure 6 presents the angle-dependent XPS data; to compare the effects of the two different backbones, Si/C atomic ratios are reported for the PDMS macromer, poly(HEMA-*g*-DMS) (HD-9, PDMS bulk content: 11.3 wt %) and poly(DHPMA-*g*-DMS) (ADOH-2, PDMS bulk content: 16.0 wt %). Both graft copolymers, HD-9 and ADOH-2, possess PDMS side chains with the same

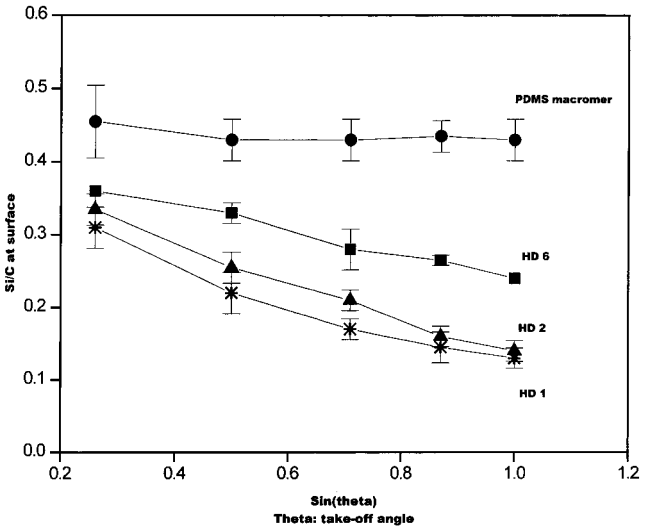


Figure 5. Angle-dependent XPS data of Si/C atomic ratios for PDMS macromer and poly(HEMA-*g*-DMS) graft copolymers of HD-6, HD-2, and HD-1 with different PDMS bulk contents of 21.6, 2.1, and 1.2 wt %, respectively. The PDMS graft length for all the graft copolymers is about 14 DMS repeat units.

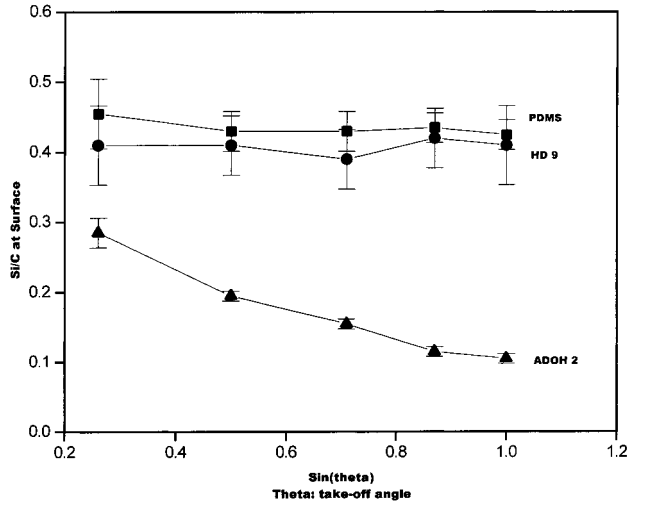


Figure 6. Angle-dependent XPS data of Si/C atomic ratios for PDMS macromer, poly(HEMA-*g*-DMS) (HD-9, PDMS bulk content: 11.3 wt %), and poly(DHPMA-*g*-DMS) (ADOH-2, PDMS bulk content: 16.0 wt %) graft copolymers. The graft length for both HD-9 and ADOH-2 is about 30 DMS repeat units.

chain length of about 30 repeat units but different hydrophilicity in their backbones; that is, ADOH-2 contains one more hydroxy group than HD-9 in each backbone repeat unit. Interestingly, even though HD-9 has a lower DMS bulk content than ADOH-2, its PDMS surface composition is much higher than that of ADOH-2, which possesses the more hydrophilic backbone. This observation can be explained by considering that more hydroxyl groups in poly(DHPMA-*g*-DMS) result in the formation of more hydrogen bonds which might restrict the mobility of the PDMS side chains, consequently decreasing the segregation of the PDMS component to the air (free) surface.

From the investigation of the effect of PDMS bulk content on the surface composition of poly(DHPMA-*g*-DMS) graft copolymers via the angle-dependent XPS technique, another interesting phenomenon has been observed. As shown in Figure 7, a group of poly(DHPMA-*g*-DMS) graft copolymers, ADOH-1, ADOH-2, and ADOH-3, with the same PDMS graft length of 30 DMS repeat units, contain different PDMS bulk contents of 26.0, 16.0, and 9.0 wt %, respectively. It is clear that no significant differences in the PDMS surface composition were detected among these three samples regardless of their different PDMS bulk content. Furthermore, in comparison with pure PDMS, all these three graft copolymers show much lower PDMS composition at the air free surface, confirming that more hydrophilic backbones of the graft copolymers restrict the segregation of the hydrophobic PDMS side chains to the air (free) surface region and indicating a promising surface hydrophilicity which is desired for biomedical applications.

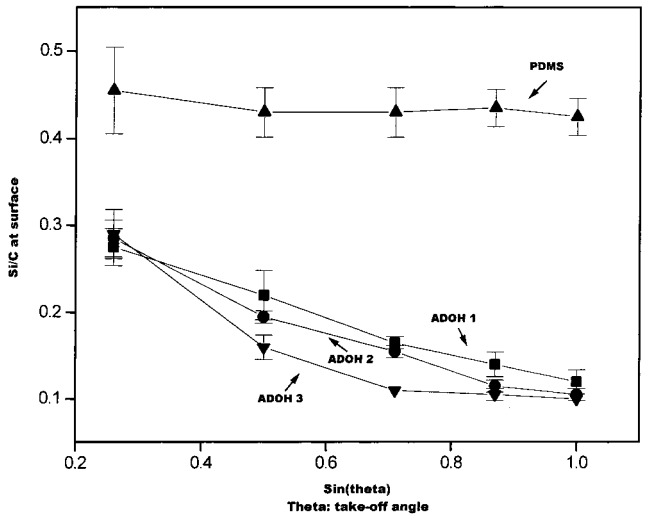


Figure 7. Angle-dependent XPS data of Si/C atomic ratios for PDMS macromer, poly(DHPMA-*g*-DMS) graft copolymers of ADOH-1, ADOH-2, and ADOH-3, with different PDMS bulk contents of 26.0, 16.0, and 9.0 wt %, respectively. The PDMS graft length for all the three copolymers is about 30 DMS repeat units.

Surface Analysis via XPS under Wet (Frozen) Conditions. It has been reported by several research groups that when multicomponent copolymers or hydrogels are exposed to water, the polymer surface undergoes an interesting structure reorganization.[18] The change in surface composition and the surface molecular motion are affected by the chemical structure of the constitutional units, the sequence content, the sequence length, the end group of the side chains, and the side chain length.[18]

The angle-dependent XPS data of Si/C atomic ratio for sample HD-2 under both dry and wet conditions are shown in Figure 8. The differences were not statistically significant at the 95% confidence level (2.63 standard deviations), leading to the conclusion that reorganization is not occurring at the topmost surface layer. The lack of deviation continues at deeper sampling depths.

To examine the effects of MWD on the reorganization, the radically polymerized poly(HEMA-*g*-DMS) graft copolymer, the sample R-HD-5 with broad MWD, was chosen. Figure 8 also includes the angle-dependent data of the Si/C atomic ratio for both the dry and frozen sample of R-HD-5. These results show a change in the Si/C at the surface between the dry and frozen polymer systems. The change in the Si/C was observed in only the topmost layer of the graft copolymer system. The deviation is due to the shorter chain segments being able to reorganize to create a more favorable energetic conformation at the surface.

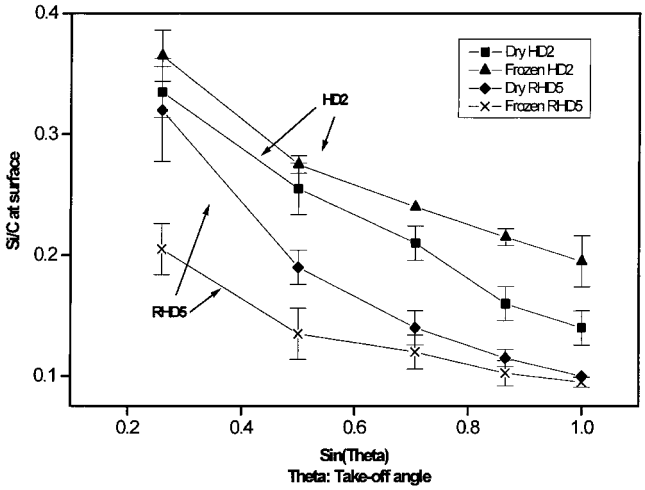


Figure 8. Angle-dependent XPS data of Si/C atomic ratios of HD-2 and R-HD-5 for both the dry and frozen, 24 h water exposure, samples.

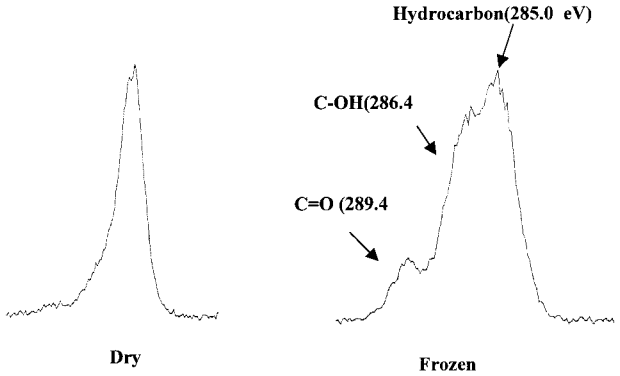


Figure 9. C_{1s} spectra of ADOH2 taken at a 15° takeoff angle for both the dry and frozen, upon 24 h water exposure, samples.

For the poly(DHPMA-*g*-DMS) system, the sample ADOH2 was investigated. As shown in Figure 9, by comparing the C 1s region of the dry and frozen (upon 24 h water exposure) samples of poly(DHPMA-*g*-DMS) graft copolymer at a 15° takeoff angle corresponding to a sampling depth of about 28 Å, a dramatic increase in the hydrophilic DHPMA portion of the graft copolymer system under the frozen condition was observed. The C−OH region of the spectra from the frozen sample is much larger than that from the dry counterpart. The carbonyl region is also more pronounced in the spectra from the frozen sample, corresponding to a higher concentration of poly(DHPMA) backbone at the surface of the system that was exposed to water. The spectra suggest that upon exposure to water the poly(DHPMA) backbone of the copolymer migrates toward the water−polymer interface to create a more energetically favorable surface composition.

Figure 10 shows the angle-dependent XPS data of Si/C atomic ratio for sample ADOH-2 under both the dry and frozen conditions. A large deviation is observed in the Si/C between the dry and frozen samples and continues throughout all of the depths sampled, up to a 90° takeoff angle corresponding to a sampling depth of 103 Å. The deviation is most pronounced at shallower takeoff angles. The dramatic decrease of the Si/C corresponds to a reorganization of the PDMS grafts away from the interface and into the bulk of the system to minimize the interfacial tension.

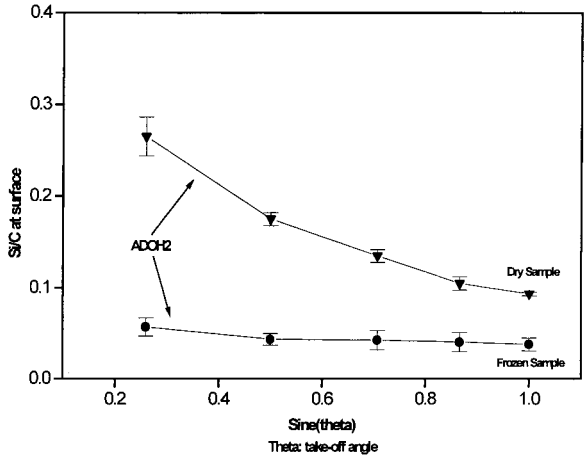


Figure 10. Angle-dependent XPS data of Si/C ratios of ADOH2 of the dry sample vs the frozen sample.

Conclusions

Well-defined amphiphilic graft copolymers, poly(HEMA-*g*-DMS), and poly(DHPMA-*g*-DMS) with controlled molecular weights, narrow molecular weight distributions ($M_w/M_n = 1.08-1.19$), and designed compositions were prepared via living anionic polymerization technique. The photoinduced radical copolymerization of HEMA and PDMS macromergenerated an amphiphilic graft copolymer poly(HEMA-*g*-DMS) with a relatively broad molecular weight distribution. Using different PDMS macromers and changing the feed amount ratios of comonomers and PDMS macromer, a series of amphiphilic graft copolymers with various graft lengths and different compositions were obtained.

Angle-dependent XPS analysis of these graft copolymers reveals that the PDMS concentration at the air surface increases slightly with increasing the PDMS bulk content. For a particular PDMS bulk content, as the PDMS graft becomes longer, the PDMS concentration at the air (free) surface of the graft copolymer film increases, and a thicker PDMS layer was detected for a graft copolymer with longer PDMS graft length. However, the MWD has little effect on the air surface composition.

Poly(DHPMA-*g*-DMS) has a more hydrophilic backbone than poly(HEMA-*g*-DMS). Angle-dependent XPS analysis revealed that the PDMS concentration at the air surface of the former graft copolymer was much lower than that of the latter graft copolymer. The effect of PDMS bulk content on the surface segregation of PDMS graft was also investigated, and no significant difference was observed over a range of 9.0−26.0 wt % of PDMS content in bulk.

As evident from XPS data obtained via the cryogenic sample handling technique to observe the water-induced reorganization, it was observed that the radically synthesized poly(HEMA-*g*-DMS) reorganized to a larger extent than the anionically synthesized poly(HEMA-*g*-DMS). The increase in reorganization can be attributed to the broader MWD of the radically prepared poly(HEMA-*g*-DMS) graft copolymer. For the poly(DHPMA-*g*-DMS) system, it was found that the graft copolymer undergoes surface reorganization as water is absorbed into the polymer system. The cryogenic sample handling technique yielded results in agreement with a reorganization of the hydrophilic poly(DHPMA) backbone migrating toward the surface upon water exposure to minimize the system's interfacial tension.

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MA020323A