Synthesis and Surface Characterization of Well-Defined Amphiphilic Block Copolymers Containing Poly[oligo(ethylene glycol) methacrylate] Segments

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ABSTRACT: A series of well-defined amphiphilic block copolymers containing poly[oligo(ethylene glycol) methacrylate] (POEGMA)) segments were synthesized by the sequential anionic copolymerization of styrene and trialkylsilyl-protected oligo(ethylene glycol) methacrylates followed by deprotection. OEGMA monomers possessed terminal OH groups on the pendant side chains and included the esters of ethylene glycol, di(ethylene glycol), and tri(ethylene glycol) to change the polarity of hydrophilic polymethacrylate segments. The corresponding methyl ethers of oligo(ethylene glycol) methacrylates (MOEGMA) were also employed to synthesize the amphiphilic block copolymers of polystyrene (PS) and PMOEGMA. Microphase separated structures of the block copolymers were analyzed by small-angle X-ray scattering (SAXS). The block copolymers containing POEGMA segments displayed strongly segregated lamellar structure with sharp interfaces; however, the PMOEGMA counterparts showed either weakly segregated lamellar or disorder structures. Angle-dependent X-ray photoelectron spectroscopic (XPS) measurement of the films of block copolymers with POEGMA segments revealed that hydrophobic polystyrene segments exclusively covered the outermost surfaces, as expected. By contrast, enrichment of oligo(ethylene glycol) units was unexpectedly observed in the block copolymers of PMOEGMA types. Contact angle measurement also indicated that the film surface was almost completely covered with hydrophilic PMOEGMA segments rather than polystyrene segments. The nature of the terminal moiety on the oligo(ethylene glycol) side chain, OH or OCH_3, played a very important role in determining the surface structure of the amphiphilic block copolymer films. The terminal moiety had a dominant influence either on the interaction parameter with PS or on the interaction with the surface, whereas the number of ethylene glycol units primarily determined the solubility of polymethacrylate segments in water.

Introduction

Amphiphilic (hydrophilic−hydrophobic) block copolymers have attracted a great deal of attention over the years for industrial and biomedical applications as well as for fundamental academic research.[1−14] Such copolymers can readily assemble into micelles or vesicles in selective solvents,[1−8] and they can also form a variety of heterophasic morphologies in bulk.[9−14] While block copolymers display multiphase patterns depending on the architecture, the surface is usually covered by low surface energy component and becomes homogeneous. A surface homogeneous layer can be formed in lamellar[15,16] or even in spherical domain structures.[17] By the same principle, the outermost surface of the as-cast film of various amphiphilic block copolymers under dry conditions is covered with hydrophobic segments, and the restructuring of the surface easily occurs in response to environment change.[7,11−14] These reconstructed surfaces sometimes induce several interesting properties. For example, Okano and co-workers have reported that amphiphilic block copolymer containing hydrophilic poly(2-hydroxyethyl methacrylate) (P1EGMA, conventionally called PHEMA) segment shows excellent nonthrombogenic activity.[18] The phase separation and surface rearrangement behavior of the copolymer having P1EGMA segment were extensively studied under either dry or wet conditions for a better understanding of its biological response.[13] This particular block copolymer was synthesized by the sequential anionic copolymerization of styrene and 2-[(*tert*-butyldimethylsilyl)oxy]ethyl methacrylate, **1**, and the subsequent deprotection of the resulting copolymer.[19]

We have recently succeeded in the living anionic polymerizations of *tert*-butyldimethylsilyl-protected oligo(ethylene glycol) methacrylates, **2** and **3** (Scheme 1),[20] similar to **1**. Polymethacrylates, poly[di(ethylene glycol) methacrylate], P2EGMA, and poly[tri(ethylene glycol) methacrylate], P3EGMA, having predictable M_n values and narrow molecular weight distributions ($M_w/M_n < 1.1$), were obtained after the quantitative deprotection of the trialkylsilyl groups of poly(**2**) and poly(**3**). Both the deprotected P2EGMA and P3EGMA showed good solubility in water at any temperature. It is noteworthy that hydrophilic P1EGMA, the ester of ethylene glycol, is not soluble in water, although it is extremely hygroscopic. On the other hand, a series of well-defined poly[oligo(ethylene glycol) methyl ether methacrylate]s, PM1EGMA, PM2EGMA, and PM3EGMA, were also formed via living anionic polymerization of the corresponding methyl ether monomers.[21] Both the PM2EGMA and PM3EGMA were readily soluble in water like their counterparts, P2EGMA and P3EGMA. More interestingly, aqueous solutions of PM2EGMA and PM3EGMA showed the reversible cloud points on either heating or cooling procedure, supporting their thermal sensitivities. These results demonstrate that both the

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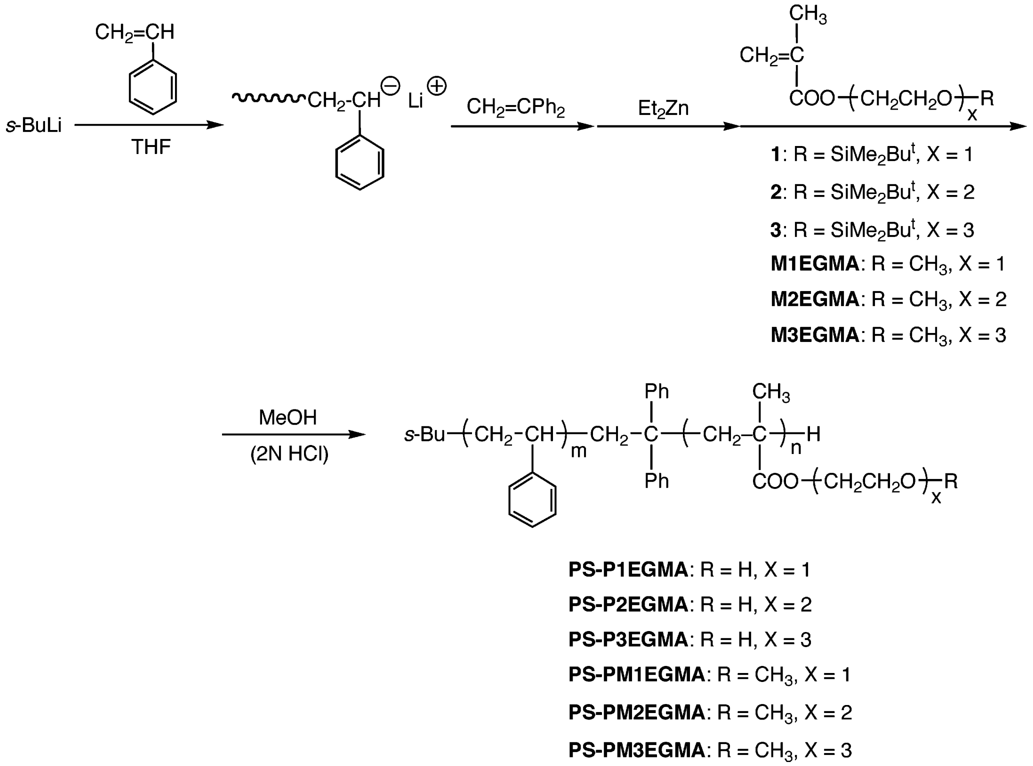
Scheme 1



side chain length and the ω-alkyl groups of the oligo(ethylene glycol) units are very important in determining the water solubility and thermosensitivity of these polymethacrylates.

In the present study, we introduce these water-soluble and thermally sensitive poly[oligo(ethylene glycol) methacrylate] segments into new amphiphilic polystyrene-based block copolymers through sequential anionic copolymerization as shown in Scheme 1. The polymethacrylate segments included P1EGMA, P2EGMA, and P3EGMA (POEGMA), and the corresponding methyl ethers, PM1EGMA, PM2EGMA, and PM3EGMA (PMOEGMA), to compare their phase separation behavior. The chemical structures of the polymethacrylate segments such as side chain length and terminal moiety of the oligo(ethylene glycol) units should play very important roles not only on the above-mentioned solubility of the homopolymers but also on the phase separation behavior and surface structure of the amphiphilic block copolymers. Very recently, we found that a diblock copolymer of deuterated styrene (C_8D_8)[22] and M3EGMA, dPS-M3EGMA, exclusively exposes the "*water-soluble*" PM3EGMA segment to the outermost surface even under dry conditions.[23] Furthermore, even in blends of dPS−PM3EGMA and PS, a small amount of dPS−PM3EGMA segregates at the surface of the blends and effectively covers the surface. We now consider that the hydrophobic terminal methyl groups of the hydrophilic tri(ethylene glycol) side chain of PM3EGMA segment predominantly cover the surface to reduce the free energy of the system by the increased configurational entropy by exposing many chain ends to the surface. The present study will address the effects of side chain length and terminal moiety of hydrophilic segments for a series of amphiphilic block copolymers on their bulk morphologies using small-angle X-ray scattering (SAXS) and on their surface structures and properties using X-ray photoelectron spectroscopy (XPS) and contact angle measurements.

Experimental Section

Materials. M1EGMA (Aldrich) and M2EGMA (Nippon Oils and Fats) were purified by column chromatography (silica gel, hexane/ethyl acetate) followed by fractional distillation from CaH_2 in vacuo. M3EGMA and **1**−**3** were synthesized and purified according to previous reports.[20,21] Et_2Zn (Tosoh-Akzo) was distilled under the reduced pressure and diluted with dry THF. Trioctylaluminum (Sumitomo Chemical Industry) was diluted with dry *n*-heptane. 1,1-Diphenylethylene (Tokyo Kasei) was distilled from CaH_2 in vacuo and then distilled in the presence of 1,1-diphenylhexyllithium on a vacuum line. THF was refluxed over sodium wire, distilled over $LiAlH_4$ under nitrogen, and finally distilled from sodium naphthalenide solution on a vacuum line. *n*-Heptane was washed with concentrated H_2SO_4 and dried over anhydrous $MgSO_4$, and it was dried over P_2O_5 for 1 day under reflux. It was then distilled in the presence of *n*-BuLi under nitrogen. Commercially available *sec*-BuLi (1.3 M in cyclohexane, Nacalai Tesque Inc.) was used without purification and diluted with dry *n*-heptane. After reaction with 1,1-diphenylethylene, the concentration of *sec*-BuLi was determined by colorimetric titration using standardized 1-octanol in THF in a sealed reactor in vacuo as previously reported.[24]

Purification of Monomers. After careful fractional distillation, methacrylate monomers were degassed and sealed off in an apparatus equipped with a break-seal in the presence of CaH_2 and diluted with dry *n*-heptane. The monomer solution in heptane was stirred for 10 h at room temperature and distilled from CaH_2 on a vacuum line into ampules fitted with break-seals. The distilled methacrylates were treated with 1−2 mol % of trioctylaluminum in *n*-heptane for 10 min and again distilled under high vacuum conditions. The purified monomers were finally distilled in vacuo into an ampule fitted with a break-seal and diluted with dry THF. The resulting monomer solutions (0.2−0.3 M) in THF were stored at −30 °C until ready to use for the anionic polymerization. Styrene was washed with 10% aqueous NaOH solution and water and dried over anhydrous $MgSO_4$. It was then dried and distilled over CaH_2 in vacuo and finally distilled from a THF solution of benzylmagnesium chloride on a vacuum line.

Polymerization Procedures. All polymerizations were carried out at −78 °C in an all-glass apparatus equipped with break-seals under high vacuum conditions as previously reported.[24] A typical polymerization procedure of styrene and M3EGMA was as follows. Styrene (9.85 mmol) in THF (12 mL) was rapidly added to a *n*-heptane solution (2 mL) of *sec*-BuLi (0.108 mmol) through the break-seal at −78 °C with vigorous shaking of the apparatus. After 20 min, a THF solution (3 mL) of 1,1-diphenylethylene (0.200 mmol) and a THF solution (3 mL) of Et_2Zn (1.20 mmol) were successively added to the living polystyrene to cap the propagating carbanion at −78 °C. The resulting solution was allowed to stand at −78 °C for 20 min. Then, M3EGMA (3.96 mmol) in THF (12 mL) was added to the polymerization system at −78 °C. After the reaction was allowed to stand at −78 °C for 2 h, the polymerization was terminated with degassed methanol. The sequential copolymerizations of styrene and other methacrylates were similarly performed. After concentration of the reaction mixture in vacuo, the residue was poured into a large excess of *n*-hexane to precipitate a polymer. In the cases using **1**−**3**, the polymerization solution was treated with 2 M HCl (1 mL) at 0 °C for 2 h to remove the *tert*-butyldimethylsilyl protecting groups prior to precipitation. The resulting block copolymers were further purified by reprecipitations in a THF/*n*-hexane system and by freeze-drying from benzene solution. Polymers thus obtained were characterized by ^1H and ^{13}C NMR spectroscopy.

Polymer Characterization. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX300 spectrometer (300 MHz for ^1H and 75 MHz for ^{13}C) in either $CDCl_3$ or d_6-DMSO to determine the block copolymer compositions. SEC chromatograms for determination of molecular weight distribution were obtained in THF at 40 °C at a flow rate of 1.0 mL min^{-1} with a TOSOH HLC-8020 instrument equipped with three polystyrene gel columns (TOSOH G5000H_{XL}, G4000H_{XL}, and G3000H_{XL}, measurable molecular weight range: 2×10^3 to 4×10^6) with either ultraviolet (254 nm) absorption or refractive index detection. SEC measurement was also performed in DMF containing 0.01 M LiBr at 40 °C at a flow rate of 1.0 mL min^{-1} with a TOSOH HLC-8120 instrument equipped with three polystyrene gel columns (TOSOH GMH_{XL} × 2 and G2000H_{XL}, measurable molecular weight range: 10^3 to 4×10^8) with either ultraviolet (270 nm) absorption or refractive index detection.

Film Preparation and Treatment. A polymer solution (3 wt %) in toluene was filtered through a Teflon filter (0.45 μm pore size) and then spun-cast (4000 rpm, 20 s) onto a clean glass disk (18 mm diameter). In the case of PS−P1EGMA, DMF was used for the casting solvent. The solvents on the films were allowed to evaporate overnight on a clean bench. The prepared films on the glass were 100−200 nm thick and optically transparent. This as-cast specimen was used for the following measurements. For the contact angle measurement, the film was treated under various environments such as soaking in water at either 20 or 85 °C, air-drying at room temperature, and annealing at 100 °C as well as the as-cast film. Thick films for small-angle X-ray scattering were prepared by casting from the solutions. The films were annealed at 140 °C for 8 h and then quenched to room temperature.

X-ray Photoelectron Spectroscopy (XPS). A PHI Quantum 2000 spectrometer equipped with a hemispherical capacitor analyzer using a monochromated X-ray from Al Kα was employed for angular dependent XPS analysis. A chamber pressure during the measurements was maintained at ca. 1×10^{-7} Pa. Au $4f_{7/2}$ (84.0 eV), Cu $2p_{3/2}$ (932.6 eV), and Ag $3d_{5/2}$ (368.3 eV) photoelectrons calibrated the binding energy scale of the instrument. A 100 μm-diameter X-ray beam at 20 W was scanned over a 500 μm by 500 μm square area. C 1s and O 1s peaks without neutralization were fairly sharp and were shifted by setting the C 1s peak to 284.8 eV. High-resolution scans of C 1s and O 1s regions were acquired with a pass energy of 35.8 eV at θ, which was defined as the angle between the surface plane and the direction toward the analyzer. θ of 10, 15, 20, 25, 30, 35, 40, 45, 55, 65, and 85 ° were chosen for the angular dependence measurements. An analyzer aperture limited the range of takeoff angle within ±4°.

Contact Angle Measurements. Contact angles of water were measured using a Contact Angle Meter CA-A (Kyowa Interface Science Co., Ltd.). A water droplet of 5 μL was placed on the as-cast films and static measurements were carried out after 1 min. The measurements were repeated at least four times on other positions of the same specimen. For water-soaked specimen, excess water on the specimen was removed off centrifugally prior to the measurements.

Small Angle X-ray Scattering (SAXS). An X-ray diffractometer (Rigaku Ultrax 4153A 172B) equipped with an imaging plate measured the SAXS profiles of the copolymers. A Cu Kα radiation ($\lambda = 1.54$ Å) was used as an incident X-ray beam. A scattered X-ray detected with the imaging plate placed approximately 600 mm behind the specimen was azimuthally averaged to obtain the plots of the intensity vs the scattering angle, 2θ. Wave vector, q, is defined as $q = (4\pi/\lambda) \sin \theta$. All SAXS measurements were performed at room temperature.

Results and Discussion

Synthesis of Amphiphilic Block Copolymers. The OH groups of oligo(ethylene glycol) methacrylates (OEGMA) were masked with bulky *tert*-butyldimethylsilyl protecting groups, and the resulting silyl ethers, **1**−**3**,[20] were employed for the sequential copolymerization. On the other hand, the methyl ether counterparts (MOEGMA), M1EGMA, M2EGMA, and M3EGMA,[21] were directly used for the copolymerization.

The first-stage polymerization of styrene was carried out with *sec*-BuLi in THF at −78 °C for 20 min, and the resulting living anionic polystyrene was used as a macroinitiator to synthesize the amphiphilic block copolymers. Prior to the addition of methacrylate monomers, the propagating chain end of the living polystyrene was capped with 1,1-diphenylethylene to suppress the side reaction of carbonyl attack,[25] and a 15-fold Et_2Zn was then added to the reaction mixture to narrow the molecular weight distribution of the resulting polymethacrylates.[26] The methacrylate monomers, **1**−**3**, M1EGMA, M2EGMA, and M3EGMA, were finally added to the reaction mixture at −78 °C, and the second-stage polymerizations were performed for 2−3 h to achieve complete monomer conversion. After the reaction was quenched with methanol, the block copolymers were obtained quantitatively.

The results of these block copolymerizations are summarized in Table 1. The size exclusion chromatography (SEC) data revealed that each copolymer possessed a unimodal and narrow molecular weight distribution, indicating very high block efficiency. The polydispersity index, M_w/M_n, was always less than 1.1. The total molecular weights estimated from the segmental ratios measured by ^1H NMR agreed with the calculated values based on the monomer/initiator molar ratios. The compositions of the copolymers were also consistent with the theoretical values.

The *tert*-butyldimethylsilyl groups of poly(**1**), poly(**2**), and poly(**3**) segments in the block copolymers were quantitatively deprotected with 2 M HCl in THF at 0 °C. The complete removal of this protecting group was confirmed by the disappearance of ^1H NMR signals at 0.9 ($SiCH_3$) and 0.1 ppm ($SiC(CH_3)_3$). The SEC curves of the deprotected copolymers had unimodal narrow molecular weight distributions ($M_w/M_n < 1.1$) after acid hydrolysis.

We then attempted to estimate the stereoregularity of the polymethacrylate segments in the block copolymers from ^1H NMR spectroscopy, as previously reported.[20,21] However, the α-methyl proton signal overlapped with the signals due to the polystyrene main chain at 1−2 ppm. The tacticity was therefore evaluated using the α-methyl carbon signals which appeared at 18−24 ppm in the ^{13}C NMR spectra of block copolymers, as previously reported.[20,21] The stereoregularity of polymethacrylate segment always showed syndiotactic-rich configuration (*rr*

Table 1. Block Copolymerization of 1−3, M1EGMA, M2EGMA, and M3EGMA with Styrene in THF at −78 °C[a]

block copolymer code	styrene[b] [A]/[initiator]	second monomer, [B]/[initiator]	M_n(PS)	M_n(B segment)[c]	M_n(total)[d]	M_w/M_n[e]	B segment, wt %[f]
PS−P1EGMA	106	**1**, 64.5	11 000	8200[g]	19 000	1.05	43
PS−P2EGMA	92.1	**2**, 48.5	9600	8400[g]	18 000	1.07	47
PS−P3EGMA	92.8	**3**, 35.1	9700	7400[g]	17 000	1.09	43
PS−PM1EGMA	121	M1EGMA, 84.5	12 600	11 400	24 000	1.05	48
PS−PM2EGMA	89.4	M2EGMA, 54.1	9300	9700	19 000	1.07	51
PS−PM3EGMA	91.2	M3EGMA, 36.7	9500	8200	18 000	1.06	46

[a] Polymerization time: 2−3 h for **1**−**3**, M1EGMA, M2EGMA, and M3EGMA; 20 min for styrene. [b] A 2-fold excess of 1,1-diphenylethylene and 15-fold excess of Et_2Zn were subsequently added to the living anionic polystyrene before the addition of second monomer. [c] Polymethacrylate segment. [d] M_ns of the block copolymers were determined by using the M_ns of the homopolystyrenes and the molar ratios of monomer units in the block copolymer analyzed by ^{1}H NMR. [e] Determined by SEC in DMF containing 0.01 M of LiCl. [f] Weight percent of polymethacrylate segment in the block copolymer. [g] After deprotection of *tert*-butyldimethylsilyl groups of the copolymer.

~71−77%), as previously observed for polymerizations initiated with the organolithiums in THF.[20,21,26a]

These results indicate that the sequential copolymerizations of styrene and oligo(ethylene glycol) methacrylates proceeded well to give well-defined block copolymers having narrow molecular weight distributions and the predicted M_ns and compositions. Table 1 presents the molecular characteristics of a series of amphiphilic block copolymers. The data for deprotected block copolymers containing P1EGMA, P2EGMA, and P3EGMA segments are shown. Total molecular weights of the amphiphilic block copolymers were around 20000, and their weight compositions were designed to be almost 1:1. In the following sections, we employed six block copolymers to compare the effects of hydrophilic/water-soluble polymethacrylate segments.

Solubility of Block Copolymers. The solubilities of block copolymers containing poly[oligo(ethylene glycol) methacrylate]s are shown in Table 2 with those of the corresponding homopolymer and also polystyrene as references. Di(ethylene glycol) and tri(ethylene glycol) esters of poly(methacrylic acid), P2EGMA, P3EGMA, PM2EGMA, and PM3EGMA, were water-soluble, while the ethylene glycol counterparts, P1EGMA and PM1EGMA, were not soluble in water, as described in the Introduction. The ω-methyl ethers presented remarkably wide solubility in various organic solvents, compared to the corresponding polymethacrylates bearing OH termini on the side chains.

The amphiphilic block copolymers except for PS−P1EGMA were soluble in a fairly wide range of solvents but not in methanol and ethanol. Their solubility apparently reflects those of hydrophobic PS and hydrophilic polymethacrylate segments, as expected. Interestingly, they were soluble in dimethyl sulfoxide (DMSO), nonsolvent of PS segment, indicating the effects of polar polymethacrylate segments. Both PS−P2EGMA and PS−P3EGMA possessing water-soluble segments were soluble in nonpolar benzene, suggesting the large dissolving effect of PS segment. Among the block copolymers, PS−P1EGMA had the most limited solubility similar to the case of homopolymer of 1EGMA. PS−P1EGMA became soluble in THF and 1,4-dioxane and insoluble in methanol and ethanol because of the effect of the PS block.

Bulk Structures: Lamellar Thickness. Small angle scattering (SAXS) experiments were performed on PS−P1EGMA, PS−P2EGMA, and PS−P3EGMA, and the profiles are plotted in Figure 1. The samples were all annealed in a vacuum at 140 °C for 8 h and quenched to room temperature. They all showed characteristic peaks of integer values of q/q^*, where q^* is the wavenumber of the first-order peak, indicating lamellar structures in those copolymers. PS−P1EGMA and PS−P2EGMA, in particular, showed very clear higher harmonics, which indicated the presence of a step-function like lamellae with sharp interfaces. PS−P3EGMA displays only weak second and third-order peaks; PS−P3EGMA still shows lamellae but with less sharp interfaces. It should also be noted that the q^* of PS−P1EGMA is the smallest, followed by that of q^*s of PS−P2EGMA and then PS−P3EGMA. The q^* difference of those copolymers is significant given that the molecular weights of those copolymers are nearly equivalent. The spacing, D ($=2\pi/q^*$), of PS−P1EGMA lamellae is estimated from the first-order peaks to be 40.7 nm, while those of PS−P2EGMA and PS−P3EGMA are 22.8 and 19.0 nm, respectively. The difference of monomer structures in those hydrophilic methacrylates may have some minor impacts on D's due to the slightly different statistical segment lengths. Nevertheless, PS−P1EGMA must be highly stretched perpendicular to the lamellae to have such a large value of D. The high degree of stretching in the PS−P1EGMA block copolymer clearly leads to stronger repulsive interactions between the PS and P1EGMA blocks than those between PS and P2EGMA or PS and P3EGMA.

Let us first estimate the χ parameter of PS and P1EGMA from the domain spacing D using Semenov's theory.[27] In the strong segregation regime, the lamellar spacing D is given by

$$D = 4(3/\pi^2)^{1/2} a N^{2/3} \chi^{1/6} \tag{1}$$

where a, N and χ are the segment length, number of segments, and interaction parameter. It should be noted that the lamellar period is independent of block fraction f, unless f significantly deviates from 0.5 and the morphology changes to cylinders or spheres. $N^{2/3}$ dependence of D has been experimentally confirmed.[28] While segment length a of PS is 0.67 nm, no values for P1EGMA, P2EGMA and P3EGMA are available. Since the unperturbed end-to-end distance divided by molecular weight, $r_0/M^{1/2}$, does not vary much, we assume $r_0/M^{1/2}$ to be a reasonable value for POEGMA. As a reference, $r_0/M^{1/2}$ for PS is 0.0660. Assuming that $r_0/M^{1/2}$ of P1EGMA takes a value between 0.0500 and 0.0900, which is the value for most of the methacrylates tabulated in the literature,[29] segment lengths are in the range 0.57−1.07 and χ is estimated to be 20−3.5 using eq 1. The repulsion between P1EGMA and PS is thus extremely strong even for the lowest value of χ. Another estimate of χ parameter using solubility parameters is given in eq 2.

$$\chi = V_{\mathrm{ref}}\, (\delta_{\mathrm{PS}} - \delta_{\mathrm{P1EGMA}})^2/(RT) \tag{2}$$

The solubility parameters found in the literature for PS[30] were $\delta_{\mathrm{PS}} = 17.5$, and for P1EGMA,[31] $\delta_{\mathrm{P1EGMA}} = 26.9$ (MPa)$^{1/2}$. The V_{PS} and V_{P1EGMA} are being 9.8 and is 12.3×10^{-5} m^3/mol, respectively and the average reference volume is given by $V_{\mathrm{ref}} = (V_{\mathrm{PS}}\ V_{\mathrm{P1EGMA}})^{0.5}$. The χ between PS and P1EGMA is calculated to be 2.8 at 150 °C, which indicates very strong repulsion and reasonably agrees with the value determined from lamellar spacings. The value of the χ parameter for P1EGMA and PS indicates that the repulsive interaction is an order of

Table 2. Solubility of Polymers (I = Insoluble; S = Soluble)

solvent	PS−P1EGMA	PS−P2EGMA	PS−P3EGMA	PS−PM1EGMA	PS−PM2EGMA	PS−PM3EGMA	P1EGMA	P2EGMA	P3EGMA	PM1EGMA	PM2EGMA	PM3EGMA	PS
hexane	I	I	I	I	I	I	I	I	I	I	I	I	I
benzene	I	S	S	S	S	S	I	I	I	S	S	S	S
$CHCl_3$	I	S	S	S	S	S	I	S	S	S	S	S	S
acetone	I	I	S	S	S	S	I	I	S	S	S	S	S
ethyl acetate	I	I	I	S	S	S	I	I	S	S	S	S	S
Et_2O	I	I	I	I	I	I	I	I	I	I	I	I	S
1,4-dioxane	S	S	S	S	S	S	I	S	S	S	S	S	S
THF	S	S	S	S	S	S	I	I	I	S	S	S	S
DMF	S	S	S	S	S	S	S	S	S	S	S	S	S
DMSO	S	S	S	S	S	S	S	S	S	S	S	S	I
EtOH	I	I	I	I	I	I	S	S	S	I	S	S	I
MeOH	I	I	I	I	I	I	S	S	S	I	S	S	I
water	I	I	I	I	I	I	I	S	S	I	S[a]	S[b]	I

[a] Cloud point around 26 °C. [b] Cloud point around 52 °C.

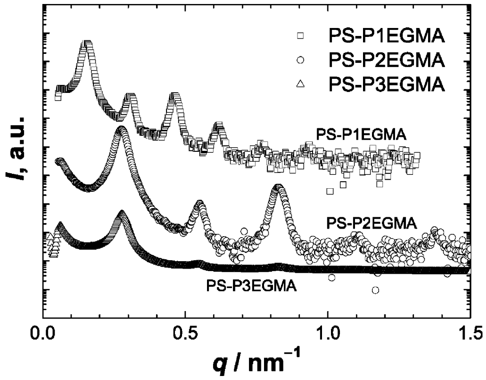


Figure 1. Logarithmic SAXS intensities of PS−P1EGMA, PS−P2EGMA, and PS−P3EGMA plotted against $q = (4\pi/\lambda) \sin \theta$, where λ is the wavelength of incident X-ray and 2θ is the scattering angle. The intensities are vertically shifted for clarity.

magnitude stronger than a typical strongly segregating pair such as PS and poly(2-vinylpyridine), where χ is approximately 0.1.[32]

Let us compare the interaction parameters of P1EGMA, P2EGMA, and P3EGMA with PS based on an educated guess of monomeric dimensions since neither dimensional parameters nor solubility parameters for those methacrylates are available besides P1EGMA. Let us assume $r_0/M^{1/2}$ to be 0.060 and that the values of a for P1EGMA, P2EGMA, and P3EGMA take 0.68, 0.78, and 0.89, respectively. Using eq 1, one can estimate the χ's of PS−P1EGMA, PS−P2EGMA, and PS−P3EGMA to be 11, 0.7, and 0.3, respectively. It should be pointed out that the interaction parameters of those PMOEGMA with PS are significantly reduced by the insertion of ethylene oxide (EO) units into the side chains. The choice of the segmental lengths has only a minor influence on the χ parameter. The interaction parameter of PS−P1EGMA is at least an order of magnitude stronger than those of PS−P2EGMA and PS−P3EGMA. As already discussed, the water solubility of the series of POEGMAs is enhanced with increasing number of EO groups in the side chains. P1EGMA is not even water-soluble, while it appears to have the strongest repulsive interaction with hydrophobic PS. P2EGMA, and P3EGMA show complete water solubility without any indication of phase separation at temperatures from 0 to 100 °C. Why do EO units inserted into the side chains of POEGMA reduce the repulsive interaction with PS, while enhancing the solubility in water? P1EGMA has only one EO unit connecting ester and OH groups; therefore, there are a limited number of possible conformations to avoid the contact between the OH group and the surrounding hydrophobic PS. The side chains of P2EGMA and P3EGMA are longer and appear to be more flexible than those of P1EGMA: the number of allowed conformations increases with increasing number of EO units. It is reasonable to speculate that the OH terminal groups prefer to avoid contact with the hydrophobic polystyrene chains by bending the side chains inward. The OH group may form an intramolecular hydrogen bond in the case of P2EGMA and P3EGMA. However, water can penetrate into the interior of the side chains to interact or to form hydrogen bonds with EO units by breaking the intramolecular hydrogen bond. Therefore, adding EO units in the interior of the side chains effectively increase the solubility of POEGMA, whereas the repulsive interaction with PS decreases.

SAXS profiles of another series of block copolymers containing PMOEGMA segments are shown in Figure 2. Note that the scattering profiles in Figure 2 are on a linear scale. PS−PM1EGMA shows evidence of lamellae with the higher order harmonics while PS−PM2EGMA and PS−PM3EGMA show single broad peaks, which represent compositional fluctuation

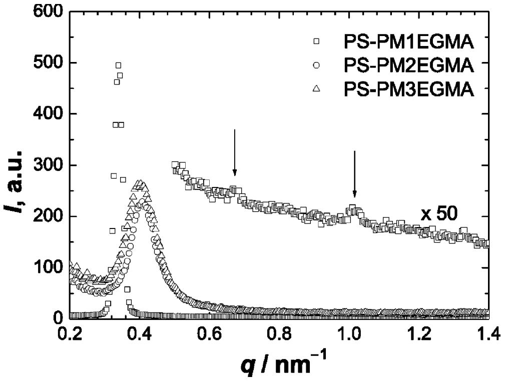


Figure 2. SAXS profiles of PS−PM1EGMA, PS−PM2EGMA, and PS−PM3EGMA. PS−PM1EGMA shows Bragg peaks of lamellae. PS−PM2EGMA and PS−PM3EGMA show fluctuation peaks.

in disordered melts. We obtain a χ parameter of 0.07 for PS−PM1EGMA using Semenov's theory based on the same assumption for OH terminal series as described earlier. Since Semenov's theory is valid only for strong segregation, the resultant χN indicating weak segregation is suspicious. Nevertheless, the repulsive interaction between PS and PM1EGMA is much smaller than that of PS with POEGMA with OH termini. Especially comparing PS−P1EGMA and PS−PM1EGMA, both of which have the same number of EO units, the repulsive interaction is different by a few orders of magnitude. Adding methyl terminal groups to the side chains changes the interaction with hydrophobic polymers tremendously. For PS−PM2EGMA and PS−PM3EGMA in disorder states, we can estimate the upper limits of χ using $(\chi N)_t = 10.495 + 41.002(Na^6\rho^2)^{-1/3}$, which is the Fredrickson and Helfand prediction of order−disorder transition $(\chi N)_t$ as a finite molecular weight correction of Leibler's order−disorder transition (ODT).[33] Again, the monomer dimension of the polymethacrylate block is not available and we use the parameters of PS, $\rho = 6$ nm^{-3} and $a = 0.67$ nm, for the whole block copolymers as a rough estimate. We obtain only the upper limits of $\chi < 0.11$ for PM2EGMA and < 0.13 for PM3EGMA. It should be, however, pointed out that χ's are reduced with added methyl termini, at most, to around 0.1 irrespective of the number of EO units in the side chains. The methyl termini effectively screen the repulsive interaction with hydrophobic polymers. This effect is most significant when the side chains have only one EO unit. The difference in the χ parameters of PS−P1EGMA and PS−PM1EGMA illustrates the importance of methyl termini.

Surface Structures of Homo Polymethacrylates and Block Copolymers. Surface compositions of multicomponent systems are not always the same as bulk compositions but can be completely dominated by the component with the lower surface energy. Block copolymers are a typical example of a multicomponent system, and the lower surface energy block, in general, covers the surface exclusively and reduces the surface energy of the system. Such segregation is sensitively monitored by X-ray photoelectron spectroscopy (XPS).[34] We evaluated the surface compositions of polymers using XPS at various takeoff angles. Examples of spectra obtained from PS−P2EGMA and PS−PM2EGMA are shown in Figure 3. Since P2EGMA and PM2EGMA are both hydrophilic polymers, we expected that the hydrophobic PS would cover the surface of the copolymers to reduce the surface energy. In Figure 3a, we find fairly sharp C 1s peaks at various takeoff angles. Hydrocarbon peaks at 285 eV dominated the spectra at all takeoff angles. The dominant sharp C 1s peak is evidence of PS covering the surface of PS−P2EGMA exclusively. The $\pi-\pi^*$ shake-up peaks indicate the presence of aromatic rings near the surface, which is additional evidence of PS at the surface. The weak C−O and O−C═O peaks are barely visible even at higher takeoff angles suggesting that the oxygen atoms lie below the film surface. Thus, PS completely covers the surface of the block copolymer, and hence P2EGMA is excluded from the surface and embedded within the bulk. Figure 3b, however, displays completely different spectra. Contributions of C−O and O═C−O are evident in the spectra of PS−PM2EGMA, especially at lower takeoff angles. The difference between PS−P2EGMA and PS−PM2EGMA is only the addition of CH_3 group at the termini of the pendant side groups, but such a subtle difference in structure completely changes the surface composition. The $\pi-\pi^*$ shake-up satellites, which are fingerprints of PS, are not observed. It is obvious

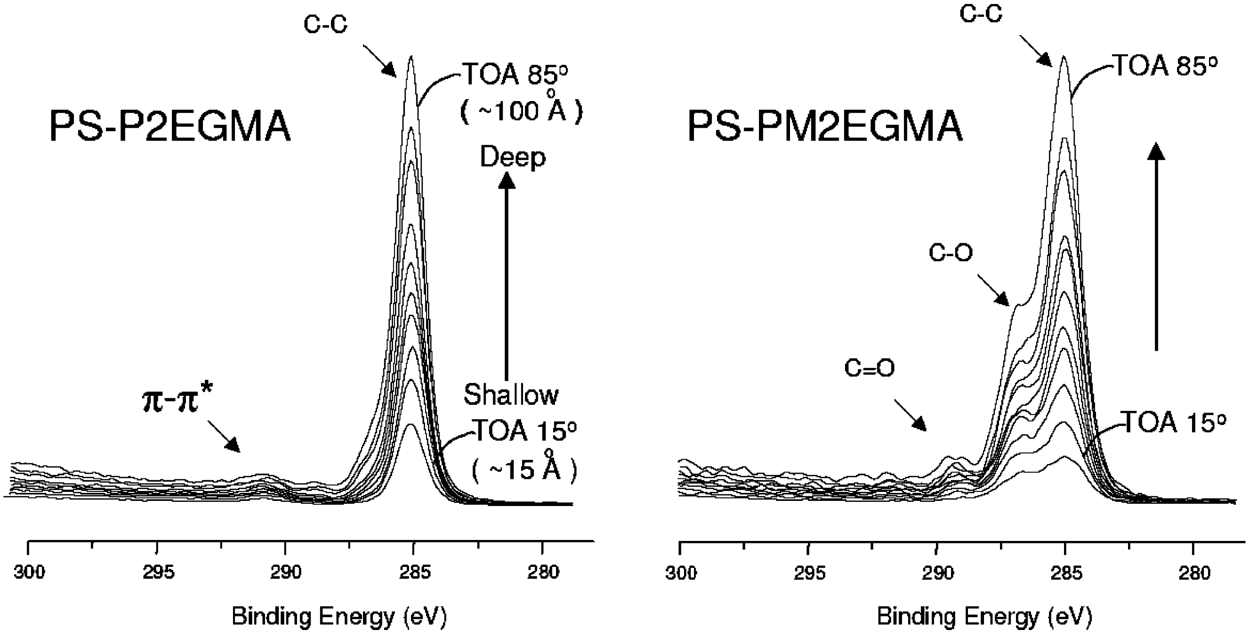


Figure 3. C 1s photoelectron intensities of PS−P2EGMA (a) and PS−PM2EGMA (b). The intensities increase monotonically with increasing takeoff angle (TOA). Hydrocarbon (C−C), carbon next to oxygen (C−O), and ester carbonyl carbon (O═C−O) peaks appear at 285, 287, and 289 eV, respectively.

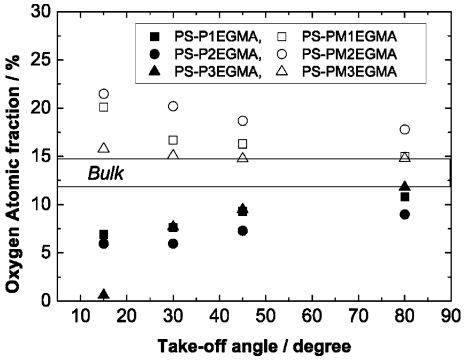


Figure 4. Oxygen atomic fraction estimated from O 1s/C 1s peak areas from XPS measurements as a function of takeoff angles. Filled and open symbols are corresponding to the block copolymers having polymethacrylate segments with OH and CH_3 termini, respectively. Bulk oxygen atomic percent is in the range 12−15 for the samples.

that PM2EGMA excludes PS from the surface. Our group has previously reported this type of behavior for dPS−PM3EGMA, which has a deuterated polystyrene (C_8D_8) block instead to utilize nuclei sensitive techniques for surface characterizations.[23] The conclusion from the previous study is that the methyl termini of the side chains cover the surface and reduce the apparent surface energy. The methyl termini are just barely covering the EO layers underneath them. Such surface structure becomes immediately unstable upon contact with a hydrophilic environment like water and undergoes reconstruction. Therefore, the surface of dPS−PM3EGMA becomes practically hydrophilic. Even in the mixture with homo PS, dPS−PM3EGMA segregates to the surface and spontaneously changes the surface of PS to “hydrophilic”.

We show the angular dependence of oxygen atomic fraction of the surfaces of the block copolymers in Figure 4. The range of atomic fraction of oxygen between 12 and 15 at. % indicates the range of bulk compositions of those block copolymers. Higher values of oxygen atomic fractions of PS−PM1EGMA, PM2EGMA, and PM3EGMA are evidence of segregation of PMOEGMA and exclusion of PS from the surface. With decreasing takeoff angle and hence sampling depth, the oxygen signals of methyl terminated series increase, but POEGMA show opposite trends. It is a general trend that the methyl termini of the side chains cover the surface, while OH termini avoid contact with air and expose PS to the surface, irrespective of the number of EO units.

POEGMA blocks connected to the PS block can avoid contact with air by exposing PS to the surface, but POEGMA homopolymer must be in contact with air. Figure 5 shows the XPS spectra of POEGMA and PMOEGMA. For POEGMA, the strongest peaks are hydrocarbon peaks at binding energy of 285 eV irrespective of the number of EO units in the side chains. The C−O at 287 eV and O═C−O peaks at 289 eV become relatively strong as the takeoff angle increases. This is a clear indication that EO side chains are embedded and the backbone of POEGMA is exposed to the surface. The surface energy increment for exposing OH groups is so large that POEGMA has to accept the backbone exposed to the surface, although such conformation may lose conformational entropy: the backbone has less available conformations to accommodate the planar surface. On the other hand, PMOEGMA has primary peaks of C−O at 287 eV instead of the hydrocarbon peak at 285 eV, while PM1EGMA shows comparable hydrocarbon and C−O peaks due to the small number of C−O carbons. Comparisons of P1EGMA/PM1EGMA, P2EGMA/PM2EGMA,

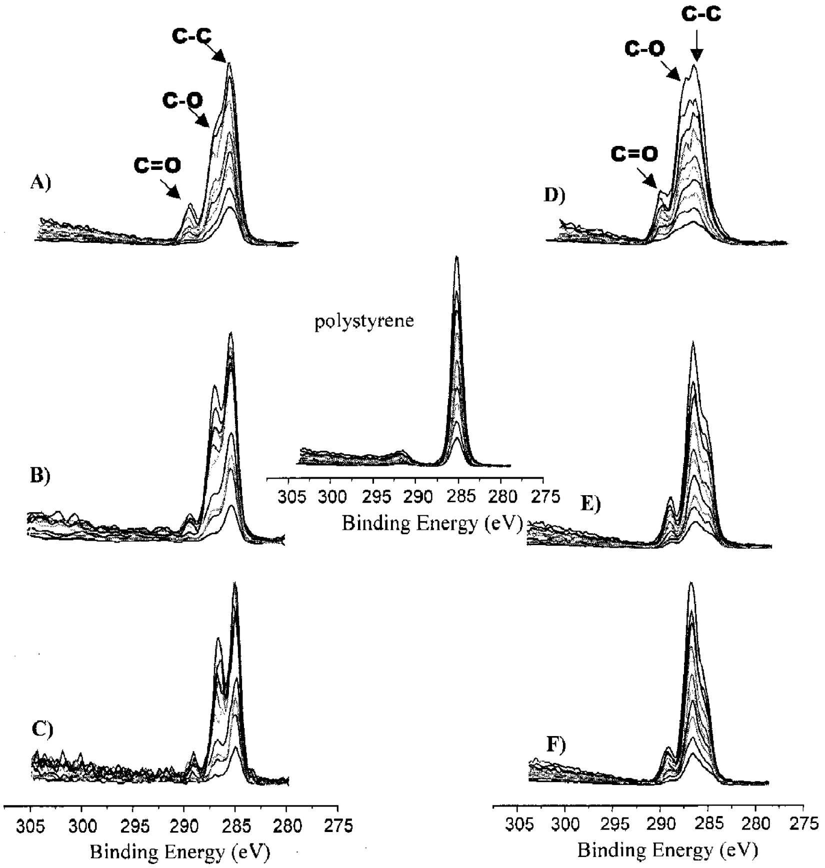


Figure 5. C 1s peaks with various takeoff angles of homopolymers of 1EGMA (A), 2EGMA (B), 3EGMA (C), M1EGMA (D), M2EGMA (E), M3EGMA (F), and styrene. The peak intensities increase with increasing takeoff angles. Takeoff angles: 15, 20, 25, 30, 35, 45, 55, 65, and 85°. The smallest and largest peaks correspond to 15 and 85°, respectively.

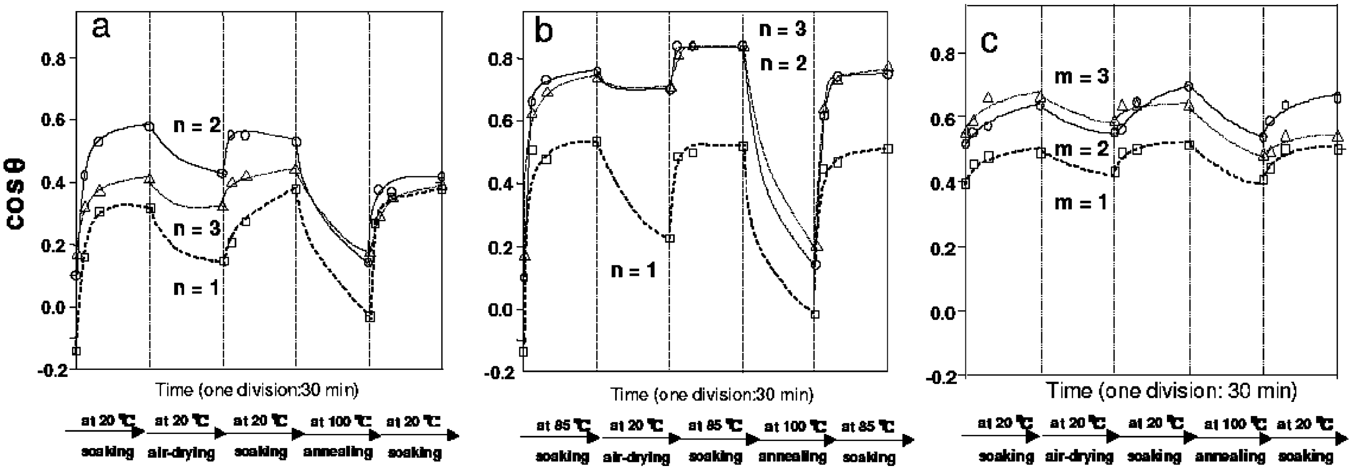


Figure 6. Cosine of contact angles of the surfaces of PS−P(M)OEGMA block copolymers with OH (a, b) and CH_3 termini (c) on the side chains. *n* and m are defined as the numbers of EO units in a side chain with an OH terminal and with a CH_3 terminal, respectively. Static contact angles were measured through the course of soaking and annealing processes. Soaking temperatures of 20 (a) and 85 °C (b) are compared while maintaining the other parameters. Cosines of static contact angles of the surfaces of PS−P(M)OEGMA block copolymers with OH (a) and CH_3 (c) termini on the side chains show significant difference of the response to the environmental changes.

and P3EGMA/PM3EGMA clearly indicate the presence of EO side chains near the surface for PMOEGMA. The surfaces of PMOEGMA are the same as those of the corresponding block copolymers with PS. However, POEGMA exposes the backbone, while the corresponding block copolymers with PS leads to partitioning of the hydrophobic block at the surface to reduce the surface energy.

Surface Wetting Properties. Water-soluble hydrophilic polymers are of great interest for biomedical applications to prevent protein adsorption and induce blood compatibilities. For such applications, surface-wetting properties is very important. Multicomponent systems including block copolymers show preferential segregation of a particular component and dominate the surface properties. As we have already shown in the XPS analysis, the surfaces of POEGMA are exclusively covered with hydrophobic PS segments. This spontaneous enrichment of PS is technologically problematic, since the surface of these block copolymers is essentially pure PS, which has poor antifouling properties and blood compatibilities. It has been reported that PS−P1EGMA has good blood compatibilities, while neither PS nor P1EGMA alone provides sufficient blood compatibilities.[18] No conclusive reason for the antifouling mechanism of PS−P1EGMA has been given other than the statement that microdomain structures somehow reduce the activity of cells. Through this study, we have shown that PS covers the surface of PS−P1EGMA as anticipated. Microdomains are not directly exposed to the surface similar to many other block copolymers. However, once the block copolymer is exposed to water, surface structures may change. To address this issue, we investigated water contact angles on the block copolymers. The response to environmental change was probed by measuring water contact angles during the following sequential process: (1) as-cast, (2) soaking into water at a particular soaking temperature (T_s) for 30 min, (3) air-drying at 20 °C, (4) soaking into water at T_s for 30 min, (5) annealing in a vacuum at 100 °C, and (6) soaking into water at T_s for 30 min. Cosines of the contact angle as a function of time are presented in Figure 6. Parts a and b of Figure 6 compare the effect of T_s on the response of contact angles. Even at 20 °C, which is 80 °C below the glass transition temperature of PS, water contact angles change during the soaking process and then recover imperfectly in air. The maximum soaking time of 30 min does not seem to be enough for full response of the block copolymers. By exposing the surfaces to hydrophilic (water) environment, the surface becomes more hydrophilic on time scales of tens of minutes or longer. Additionally, $n = 2$ (PS−P2EGMA) and 3 (PS−P3EGMA) show larger cos θ, i.e. more hydrophilic, than $n = 1$ (PS−P1EGMA).

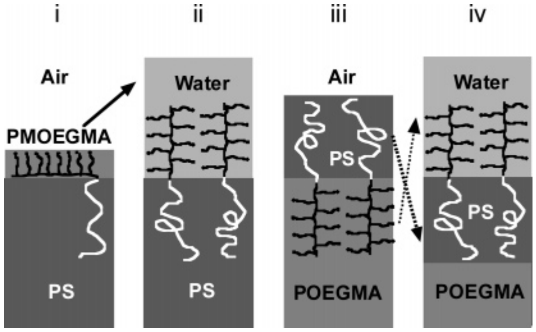


Figure 7. Schematic representation of phase separations before and after soaking in water. The rapid response of PS−PMOEGMA and slow temperature dependent response of PS−POEGMA are shown as i to ii) and iii to ii, respectively. White and black chains represent PS and POEGMA or PMOEGMA chains, respectively. ● represent OH or CH_3 terminal group of side chain in the polymethacrylate domain.

At an elevated T_s of 85 °C, we find a similar but stronger response of water contact angles after soaking. Since the air-drying process is the same as (a), the recovery of cos θ is still small: full recovery is not observed. Because of that, we find much larger cos θ during the second soaking. The effect of soaking seems to be additive. Annealing at 100 °C in a vacuum, however, re-forms the surface to its original hydrophobic characters. P1EGMA seems to be less effective in rendering the PS surface hydrophilic, since it is not a water-soluble polymer. It should be noted that P1EGMA has the strongest interaction with PS among these polymethacrylates, while it is the least effective for modifying the surface and switching it to hydrophilic. Conclusively, we observed surface reconstruction of PS−POEGMA. The surface domain that is preferred in a hydrophobic environment (PS domain) has to swap with the POEGMA domain that is embedded initially. The PS−POEGMA required surface reconstruction of the PS and POEGMA blocks, which may be completely hindered by the layered lamellae parallel to the surface and glassy PS. We schematically draw pictures of two different plausible reconstructions in Figure 7. Because of the lamellar structure parallel to the surface, simple swapping, i.e. Figure 7, parts iii to iv, between the top PS domain and the adjacent POEGMA domain is not allowed. Such reconstruction results in creating an additional interface as indicated in Figure 7, part iv, which is not favored thermodynamically. A mechanism of such reconstruction was speculated that the surface PS layer would peeled off and expose the internal hydrophilic domains.[13c] Consequently, the surface of PS−POEGMA strongly depends on the environment change and thermal history; therefore, the surface may not be reproducible and may limit the use of such surfaces for industrial applications.

PS−PMOEGMA shows a completely different response: $\cos\theta$ does not change much during the course of environmental stimuli, as clearly displayed in Figure 6c. From the initial as-cast state, $\cos\theta$ is fairly large and lies between 0.4 and 0.6. After soaking, $\cos\theta$ does not vary much; therefore, very little surface reconstruction is displayed. Our XPS study has shown that the PMOEGMA domains cover the surfaces of PS−PMOEGMA. Thus, PMOEGMA block is always partitioned at the surface either in air or water as illustrated in Figure 7, parts i and ii. Note, however, that the reconstruction within PMOEGMA has been observed in the hysteresis between advancing and receding contact angles.[23] Therefore, surface reconstruction of PS−PMOEGMA is considered to be through the relaxation of side chains followed by the PMOEGMA blocks, and it should be very fast.

Conclusions. Well-defined amphiphilic block copolymers of oligo(ethylene glycol) methacrylates and styrene were successfully synthesized via sequential anionic copolymerization. The numbers of oligo(ethylene glycol) units of polymethacrylate segment were varied from one to three to tune the hydrophilicity. The resulting block copolymers possessed narrow molecular weight distributions and predictable block lengths and compositions. They were categorized into two groups depending solely on the type of termini in the side chains of polymethacrylate segments: OH (POEGMA) and OCH_3 (PMOEGMA) terminated series. The interaction between the POEGMA block and PS is very strong and displays distinct sharp interfaces of lamellae, whereas the PMOEGMA series of copolymers barely form lamellar structures. The surfaces of PS−POEGMA are fully covered by the lower surface energy PS block, as expected. PS−PMOEGMA, nevertheless, enriches the EO side chains at the surface, irrespective of the number of EO units. The weak interaction with PS and the general tendency to segregate to the surface are clearly indicative of the termini of side chains dominating the bulk and surface properties. Solubility in water, on the other hand, is strongly affected by the number of EO units in the side chains and is less sensitive to the type of termini: water apparently interacts with the interior of the side chains. This comprehensive study of the series of block copolymers with oligo(ethylene glycol) units leads to the design rule that the surface properties and interaction with hydrophobic polymers can be selectively controlled by replacing the termini of the side chains, whereas the solubility (or interaction with liquid) can be tuned by inserting appropriate units into the interior of the side chains. Consequently, we can deliver a water-soluble block to the surface even in hydrophobic environments, and selectively control the surface properties for biomedical applications.[35]

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