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Synthesis and Surface Characterization of Hydrophilic–Hydrophobic Block Copolymers Containing Poly(2,3-dihydroxypropyl methacrylate)

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ABSTRACT: Block copolymers containing polystyrene, poly(4-octylstyrene), or polyisoprene as a hydrophobic segment and poly(2,3-dihydroxypropyl methacrylate) (poly(DIMA)) as a hydrophilic segment have been synthesized by anionic living polymerization. Microphase-separated structures of the block copolymers, poly(styrene-*b*-DIMA), poly(4-octylstyrene-*b*-DIMA), and poly(isoprene-*b*-DIMA), were confirmed by small-angle X-ray scattering and transmission electron microscopic (TEM) observation. Angle-dependent X-ray photoelectron spectroscopic (XPS) measurement of the as-cast film surfaces of the three block copolymers clearly indicated enrichment of the hydrophobic segments in the outermost surfaces. Furthermore, the XPS measurements revealed that the poly(DIMA) segment was enriched in the surface of poly(styrene-*b*-DIMA) soaked in water and that reconstruction of the surface occurred again by annealing the sample in air. The cross-sectional TEM view of poly(styrene-*b*-DIMA) film showed that the top surface was almost covered with a polystyrene layer for the as-cast film and that the spherical polystyrene domains were wrapped with a poly(DIMA) domain on the surface of the film soaked in water. Contact angle measurement indicated enrichment of the hydrophobic segment in the as-cast film surfaces of the three block copolymers and reconstruction of the surface structures according to dry and wet conditions.

Introduction

Much interest has been devoted to the surface structure and properties of block and graft copolymers, since the characteristic properties of surfaces have been applied to a broad spectrum of areas, including adhesives, membranes, chromatographic supports, composite materials, biomaterials, and drug delivery systems. The surface characterizations of block and graft copolymers have been studied by X-ray photoelectron spectroscopy (XPS),[1] attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR),[2] static secondary ion mass spectroscopy (static-SIMS),[3] ion scattering spectroscopy (ISS),[4] high-resolution electron energy loss spectroscopy (HREES),[5] transmission electron microscopic (TEM) observation,[6] and contact angle measurement.[7] Through these studies, it is generally recognized that the segments of lower surface energy, such as apolar and hydrophobic polymer chains, are enriched in the outermost surface region of block and graft copolymer films under dry conditions. When the surface is exposed to water, the reconstruction of the surface structure occurs to reduce the free energy of the water–polymer interface; *e.g.*, the outermost hydrophobic domain is exchanged by the hydrophilic domain. Such restructuring behaviors of the polymer surfaces have been followed by contact angle and XPS measurements. For a variety of block and graft copolymers, such as polyurethane-*b*-polysiloxane,[7] polyurethane-*g*-polysiloxane,[8] polyurethane-*g*-polyether,[9] polyurethane-*g*-polyamine,[9] poly(vinyl alcohol)-*g*-poly(dimethylsiloxane),[10] and poly(vinyl alcohol)-*g*-poly(tetrahydrofuran),[11] it was suggested that surface rearrangement took place along with the change of contacting medium from air to water. Furthermore, the wet surfaces of poly(acrylamide) or poly(2-hydroxyethyl methacrylate) grafted onto a silicone rubber substrate were characterized by Ratner *et al.* using XPS with a freeze-dry technique.[12] These grafts were observed on the hydrated surfaces and significantly decreased in surface concentration upon drying. The surface dynamics of plasma-fluorinated poly(ethylene terephthalate), polyethylene, Nylon 6, and PMMA samples were also observed by using similar techniques, indicating that the short-range rearrangement such as rotational migration of moieties, rather than large polymer segments, was the major mode of surface movement.[13] The surfaces of segmented poly(ether urethane urea)s with hydrophilic and hydrophobic polyether components[14] and poly[(styrene)-*b*-(ω-methoxyoligo(ethylene glycol methacrylate))]s[15,16] were analyzed by Kajiyama *et al.* They remarked that the surface chemical composition and surface molecular motion were affected by the chemical structure of the constitutional unit, the sequence content, the sequence length, the casting solvent, the end group of the side chain, and the side chain length. In principle, all these results indicated that the outermost surface of the as-cast films in dry conditions was rich in hydrophobic segment and the reconstruction of the surface occurred in response to the environment. The actual polymer surfaces are, however, more complicated, involving nonequilibrium structures of time, temperature, and environmental dependencies.

Several publications have described that the surface structure of some biomedical polymer systems may be correlated with blood interactions. Okano *et al.* demonstrated the excellent blood compatibility of the block copolymer of 2-hydroxyethyl methacrylate (HEMA) with styrene and discussed the relationship between the biomedical responses and the surface structure and properties such as microphase-separated domain size and wettability.[17–21] Using angle-dependent XPS and static-SIMS, Castner *et al.* investigated the surface compositions and structures of two types of amphiphilic block copolymers of HEMA with styrene.[3] They described that the

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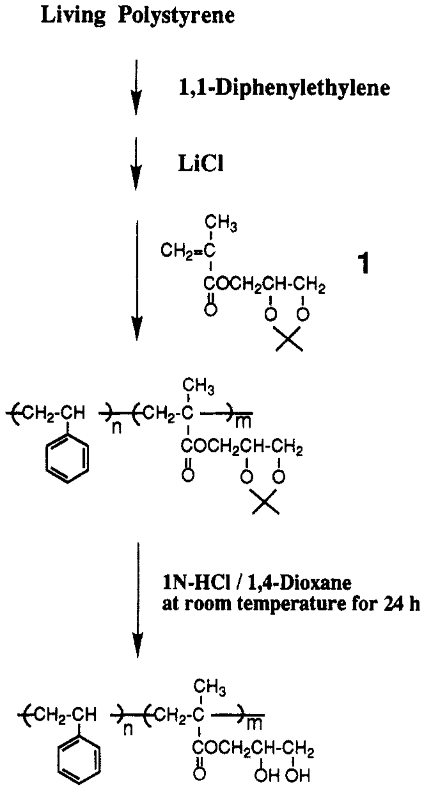
Scheme 1



DMF-cast film of the block copolymer prepared by anionic living polymerization showed significant surface enrichment of polystyrene component in the outermost surface. On the other hand, another block copolymer, where polystyrene and poly(HEMA) segments were connected with a urea linkage, exhibited very poor enrichment of the polystyrene segment in the surface region. This may be interpreted by the limited molecular motion due to hydrogen bonding between the urea linkages in the polymer chain.

Recently, we reported the synthesis of a well-defined block copolymer of 2,3-dihydroxypropyl methacrylate (DIMA) with styrene by using protection and anionic living polymerization techniques.[22] Since poly(DIMA) has two hydroxy groups per repeating unit, it is soluble in water, while poly(HEMA), having a constitutional unit with one hydroxy group analogous to that of poly(DIMA), only adsorbs water molecules. Thus, it is interesting to compare the surface behavior of poly(styrene-*b*-DIMA) with that of poly(styrene-*b*-HEMA).

In this paper, a series of new hydrophilic–hydrophobic block copolymers, poly(styrene-*b*-DIMA), poly(4-octylstyrene-*b*-DIMA), and poly(isoprene-*b*-DIMA), have been prepared and surface structures of the polymers are analyzed by TEM observation, angle-dependent XPS, and contact angle measurement. The combination of these complementary techniques is particularly effective for characterization of polymer surfaces in both dry and wet conditions.

Experimental Section

Preparation of the Block Copolymers. The block copolymer of styrene and DIMA was synthesized according to the method described in the previous paper.[22] Prior to the polymerization, the two hydroxy groups of DIMA were protected in the form of a cyclic acetal, (2,2-dimethyl-1,3-dioxolan-4-yl)methyl methacrylate (1), as shown in Scheme 1. The polymerization was carried out in an all-glass apparatus equipped with breakseals under high-vacuum conditions. The living polystyrene was prepared by the reaction of styrene (10.6 mmol) with *n*-butyllithium (0.137 mmol) in THF (14.7 mL) at −78 °C for 30 min and was end-capped with 1,1-diphenylethylene (0.233 mmol), and then LiCl (0.317 mmol) was added to the resulting solution. An aliquot of the living polystyrene solution was divided for molecular weight measurement. After sampling, a THF solution of the second monomer, 1 (5.34 mmol), was added to the remaining living polystyrene solution (0.78 equiv mmol) at −78 °C, and the mixture was allowed to stand at −78 °C for 1 h to complete the polymerization of 1. The propagating end was quenched with a small amount of methanol, and the reaction mixture was concentrated under reduced pressure. The residue was dissolved in a small amount of THF and was poured into MeOH to precipitate the polymer. The polymer was purified by repeating precipitation from THF solution into MeOH two times and by freeze-drying from 1,4-dioxane. The yield of the polymer was almost quantitative. ^{1}H NMR (90 MHz, $CDCl_3$) δ 6.3–7.3 (br d, Ar), 3.6–4.6 (br m, OCH_2, OCH), 0.6–2.4 (br m, CH_2CH and CH_2, α-CH_3), 1.43, 1.38 (two s, $C(CH_3)_2$); IR (KBr) 1730 (C=O), 1370 cm^{-1} ($C(CH_3)_2$).

The composition of each segment determined by ^{1}H NMR was found to be almost equal to the calculated one based on the molar ratio of the monomers in the feed. The SEC profile showed that the peak of the block copolymer shifted to the higher molecular weight side without a shoulder at the peak position of the starting polystyrene and that the molecular weight distribution of the block copolymer was unimodal and fairly narrow ($\bar{M}_w/\bar{M}_n$ = 1.06 calibrated with standardized polystyrene). The molecular weight of the block copolymer estimated by the composition and the $\bar{M}_n$ of the starting polystyrene agreed well with the calculated one from the molar ratio of total monomer to initiator as shown in Table 1.

To the 1,4-dioxane solution (9 mL) of poly(styrene-*b*-1) (0.30 g) was added aqueous 1 N HCl (3 mL) dropwise at 0 °C, and the mixture was stirred at room temperature for 24 h to become transparent in the progress of the reaction. The resulting solution was poured into hexane–EtOH (1:1) to precipitate the polymer, which was again reprecipitated from THF–MeOH (4:1) to hexane–EtOH (1:1) and freeze-dried from 1,4-dioxane containing a small amount of MeOH. Yield of the polymer was quantitative: (90 MHz, DMSO-d_6) δ 6.3–7.3 (br d, Ar), 3.4–4.6 (br m, OCH_2, OCH), 0.5–2.0 (br m, CH_2CH and CH_2, α-CH_3); IR (KBr) 1717 (C=O), 3000–3800 cm^{-1} (OH). From the IR and ^{1}H NMR spectra, it was confirmed that hydrolysis of the dioxolane ring in the poly(1) segment proceeded completely, resulting in poly(styrene-*b*-DIMA).

The living polymers were prepared by the reaction of 4-octylstyrene with *n*-BuLi at −78 °C for 30 min in THF and by the reaction of isoprene with *n*-BuLi in heptane at room temperature for 6 h. Poly(4-octylstyrene-*b*-1) and poly(isoprene-*b*-1) were similarly synthesized by the subsequent propagation reaction of 1 with the living poly(4-octylstyrene) and with the living polyisoprene, respectively. The deprotections of the block copolymers produced were performed in a similar manner to afford poly(4-octylstyrene-*b*-DIMA) and poly(isoprene-*b*-DIMA).

Poly(styrene-*b*-DIMA) and poly(4-octylstyrene-*b*-DIMA) obtained are soluble in *N*,*N*-dimethylformamide (DMF), pyridine, benzene/methanol (4/1, v/v), and THF/methanol (5/1, v/v), while poly(isoprene-*b*-DIMA) is only soluble in pyridine and THF/methanol (5/1, v/v). Thus, to cast the sample film for SAXS, XPS, TEM, and contact angle measurement, poly(styrene-*b*-DIMA) and poly(4-octylstyrene-*b*-DIMA) were dissolved in DMF or benzene/methanol (4/1, v/v), and poly(isoprene-*b*-DIMA) was dissolved in THF/methanol (5/1, v/v).

Measurements. IR spectra were recorded on a JEOL JIR-AQS20M FT-IR spectrometer. ^{1}H NMR spectra were recorded on a JEOL FX-90Q in ppm downfield relative to $(CH_3)_4Si$ (δ 0) and DMSO-d_6 (δ 2.50) for ^{1}H NMR. SECs were obtained at 40 °C with a TOSOH HLC-8020 with three polystyrene gel columns (TOSOH G5000H$_{XL}$, G4000H$_{XL}$, and G3000H$_{XL}$) using THF as an eluent at a flow rate of 1.0 mL/min. Vapor-pressure osmometric (VPO) measurement was made in benzene with a Corona 117. The glass transition temperatures of the homopolymers were measured by differential scanning calorimetry at a heating rate of 20 °C/min using a Seiko Instruments SSC/5200.

Table 1. Characterization of Block Copolymers Containing Poly(DIMA) as a Hydrophilic Segment

	$\bar{M}_n$(calcd)		$\bar{M}_n$(obsd)			
hydrophobic segment	hydrophobic segment	poly(DIMA) segment	hydrophobic segment[a]	poly(DIMA) segment[b]	poly(DIMA) wt %[c]	$\bar{M}_w/\bar{M}_n$[a]
polystyrene	8100	8000	8400	7800	48	1.06
poly(4-octylstyrene)	8500	7500	8600	6900	45	1.08
polyisoprene	8400	7800	8500	9400	53	1.06

[a] $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ were obtained by SEC, using standardized polystyrene for calibration. [b] $\bar{M}_n$ was estimated from the compositions and $\bar{M}_n$'s of the starting polymers. [c] The composition was determined by ^{1}H NMR.

Evaluation of Hygroscopic Property. After complete purification of poly(HEMA) and poly(DIMA) by freeze-drying *in vacuo* (0.1 Torr) for 24 h, the polymers in small vials were allowed to stand in a desiccator almost saturated with water vapor (ca. 90% relative humidity) for several days at room temperature (ca. 20 °C). The weight of water absorbed in the polymer was gravimetrically determined.

SAXS Measurement. SAXS measurement was performed with a Rikagaku Denki Co., Ltd., R-AXIS with an imaging plate situated 400 mm from the samples. Ni-filtered Cu Kα radiation (40 kV and 100 mA) was used. A pinhole (0.5-mm diameter) collimation system was used for SAXS. The observed intensities were correlated for the linearity with length from the sample to the detecting point on the imaging plate. Specimens were mounted into a sample holder with poly(ethylene terephthalate) thin film as window.

TEM Observation. Ultrathin cross sections of specimens for TEM observation were made from the dry film stained with OsO_4 vapor and from the wet film stained with aqueous OsO_4 solution. The dry film was prepared by casting the polymer solution (3 wt %) onto a clean glass disk or a polyurethane film. After evaporating the solvent gradually overnight, the film was dried at 40 °C for 12 h in vacuum and stained by OsO_4 vapor in air for 1–3 days. For the wet sample, the as-cast film was soaked in water at room temperature for 1 h and then stained with aqueous OsO_4 solution for 2 days to fix the surface structure under wet conditions. The stained film was rinsed with distilled water and air-dried at room temperature overnight. The films stained under dry and wet conditions were embedded in epoxy resin (Quetol-812 (Nisshin EM Ltd.)) and cut into ultrathin sections (600–800 Å thick) with an ultramicrotome with a diamond knife. TEMs were obtained with a JEM 1200-Ex (JEOL Ltd., Japan) electron microscope at an accelerating voltage of 80–100 kV.

XPS Measurement. The polymer solution (3 wt %) was filtered through a Teflon filter (0.45-μm pore size) and then centrifugally (4000 rpm, 20 s) cast onto a clean glass disk (18-mm diameter). The solvent was allowed to evaporate overnight on a clean bench. The prepared films were typically 200–800 Å thick and optically transparent. The angle-dependent XPS data were collected by using a 5500MT X-ray photoelectron spectrometer with a monochromatic Al Kα X-ray source (Perkin-Elmer Co., Ltd.). The takeoff angle (TOA) was defined as the angle between the horizontal axis of the surface and the axis of the analyzer lens system. The TOAs of 10, 20, 45, and 80° employed lead approximately to sampling depths of 15, 35, 70, and 100 Å, respectively. A low-energy (5–20 eV) electron flood gun was used to minimize sample charging on the nonconducting polymers. All binding energies (BEs) were referenced by setting the CH_x peak maximum in the C_{1s} spectrum to 285.0 eV. Two types of spectra were recorded for each sample. Survey scans (0–1200 eV BE) were acquired at an analyzer pass energy of 187.85 eV, and an X-ray spot size of 0.4 mm at four TOAs to determine the surface composition at each TOA. High-resolution scans of the C_{1s} region at each TOA were performed with an analyzer pass energy of 23.5 eV. The acquisition time of the data at all four TOAs was ~3 h. The stability of poly(DIMA) homopolymer over this time period was examined. The small increase in the carbon concentration observed for poly(DIMA) (<0.5 atomic %/h) was within typical XPS experimental error limits. Experimental uncertainties are approximately ±0.5 atomic % in the elemental composition.

Contact Angle Measurement. Contact angle measurements were carried out with a CA-A contact angle meter (Kyowa Kaimen Kagaku Co., Ltd.). The water in air system measurement was performed by a sessile droplet technique, where a water droplet was placed on the film surface. The specimen was made by centrifugal casting (4000 rpm, 20 s) of the polymer solution (3 wt %) onto a clean glass disk. After spin-coating, the specimen was placed under various environments, *i.e.*, as-cast, soaking in water, and air-drying at room temperature and annealing at 100 °C. Water on the sample film once immersed in water was blown off centrifugally before the contact angle measurement. Measurements were carried out within 30 s after placing a water droplet on the film and were repeated at least 4 times on the other positions of the same specimen.

Results and Discussion

We have synthesized the block copolymer of DIMA with styrene by the sequential polymerization of styrene and (2,2-dimethyl-1,3-dioxolan-4-yl)methyl methacrylate (**1**), as a protected form of DIMA, with the anionic initiator followed by complete deprotection of the resulting polymer. To avoid undesirable side reactions, the anionic propagating end of polystyrene was capped with 1,1-diphenylethylene, and ca. 3 equiv of LiCl was added to the reaction mixture before the addition of **1** to the living polystyrene (Scheme 1). The detailed reaction conditions were previously described.[22] Poly(4-octylstyrene-*b*-DIMA) and poly(isoprene-*b*-DIMA) were similarly prepared. As summarized in Table 1, block copolymers having very narrow molecular weight distributions and predictable block lengths were produced owing to the living nature of the polymerizations of the monomers used. The poly(styrene-*b*-DIMA), poly(4-octylstyrene-*b*-DIMA), and poly(isoprene-*b*-DIMA) prepared here contain almost the same weight fraction of hydrophobic and hydrophilic segments and are expected to have characteristic surface structures, which may be reconstructed by an environmental change from dry to wet conditions.

The surface behavior of block copolymer films is affected by the chemical structure, glass transition temperature (T_g), surface energy, and composition of each segment.[7-16] Thus, before discussion of the surface analyses, the T_g, solubility, hygroscopic property, and contact angle of each segment are evaluated. In expectation of the effect of T_g on the surface movement of the block copolymer film, polystyrene, poly(4-octylstyrene), and polyisoprene having different T_g's were used as a hydrophobic segment linked with poly(DIMA). The T_g's of polystyrene and poly(4-octylstyrene) produced by anionic polymerization were determined by DSC to be 95 °C (lit.[23] 100 °C) and −42 °C (lit.[23] −45 °C), respectively, and the T_g of polyisoprene (cis-1,4 microstructure, 92%) obtained by anionic polymerization with a lithio initiator in heptane was −69 °C (lit.[23] −73 °C). The T_g of freeze-dried poly(DIMA) was observed to be 69 °C, which is close to that of poly(HEMA) (67 °C). Measurement of the contact angle of a water drop on the polymer film was performed at room temperature. The low contact angles for poly(HEMA) (θ = 17°) and poly(DIMA) (θ = 15°) compared to those for polystyrene (θ = 98°), poly(4-octylstyrene) (θ = 105°), and polyisoprene (θ = 94°) suggest the hydrophilicity of poly(HEMA) and poly-

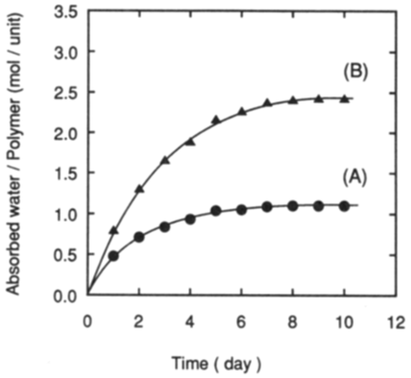


Figure 1. Absorbed water content in poly(HEMA) (A) and poly(DIMA) (B) as a function of time.

(DIMA). Poly(DIMA) is soluble in methanol and water and insoluble in ethanol, while poly(HEMA) is soluble in methanol and ethanol and insoluble in water. The amount of absorbed water in poly(DIMA) and poly(HEMA) placed in a desiccator saturated with water vapor was determined. As shown in Figure 1, poly(DIMA) adsorbed water more rapidly than poly(HEMA). These results indicate that the two hydroxy groups on the repeating unit of poly(DIMA) markedly enhance the hygroscopic property.

The microphase-separated structures of the block copolymers in the bulk region were investigated by SAXS measurement and TEM observation. The SAXS peaks were observed for poly(styrene-*b*-DIMA), poly(4-octylstyrene-*b*-DIMA), and poly(isoprene-*b*-DIMA), and the Bragg spacings were calculated from the scattering angles of the respective peak maxima to be 235, 260, and 220 Å. Figure 2 shows cross-sectional TEM views of the three block copolymer films in the bulk region. The dark area corresponds to the poly(DIMA) domain for poly(styrene-*b*-DIMA) and poly(4-octylstyrene-*b*-DIMA), whereas the polyisoprene domain is deeply stained with OsO_4 for poly(isoprene-*b*-DIMA). As shown in Figure 2A, the poly(styrene-*b*-DIMA) film exhibits a microphase-separated structure including polystyrene cylinders in a poly(DIMA) matrix with a period of 230 Å. Although the weight fraction of polystyrene segment is virtually equal to that of poly(DIMA), the cylindrical structure predominates over the lamellar one. This is reasonable considering that DMF used for casting the specimen is a good solvent for poly(DIMA) and a poor one for polystyrene. The morphologies of poly(4-octylstyrene-*b*-DIMA) and poly(isoprene-*b*-DIMA) are lamellar with periods of 230 and 225 Å, respectively (Figure 2B,C).

A cross-sectional TEM view in the near-surface region of the poly(styrene-*b*-DIMA) film cast from DMF and stained with OsO_4 vapor in air is shown in Figure 3. The upper part is embedding epoxy resin, corresponding to the air side of the sample film. In the picture, the outermost surface of the poly(styrene-*b*-DIMA) film is clearly observed to be covered predominantly with a continuous polystyrene layer (light gray part), whereas the polystyrene microdomain in the bulk is mainly cylindrical. In contrast to the dry surface, the structure of the wet top surface must be entirely changed due to the hydrophilicity of the poly(DIMA) segment. A cross-sectional view of the wet surface of the poly(styrene-*b*-DIMA) film was successfully observed by TEM in this study. The film cast from DMF was soaked in water for 1 h at room temperature and then stained with aqueous OsO_4 solution for 2 days. The wet surface structure may be fixed by staining and is unchanged during the subsequent sampling process. As shown in Figure 4, polystyrene cylinders still dominate in the bulk region of the wet film, similar to the case of the dry sample. Interestingly, the significant change of the wet top surface structure was clearly observed compared with the dry surface. The outermost layer of polystyrene observed for the as-cast film (Figure 3) completely disappeared by hydration. Alternatively, polystyrene spheres with different sizes, which seem to be covered with poly(DIMA) domains and contain poly(DIMA) domains (dark gray part) inside in some cases, were seen on the surface. During soaking the

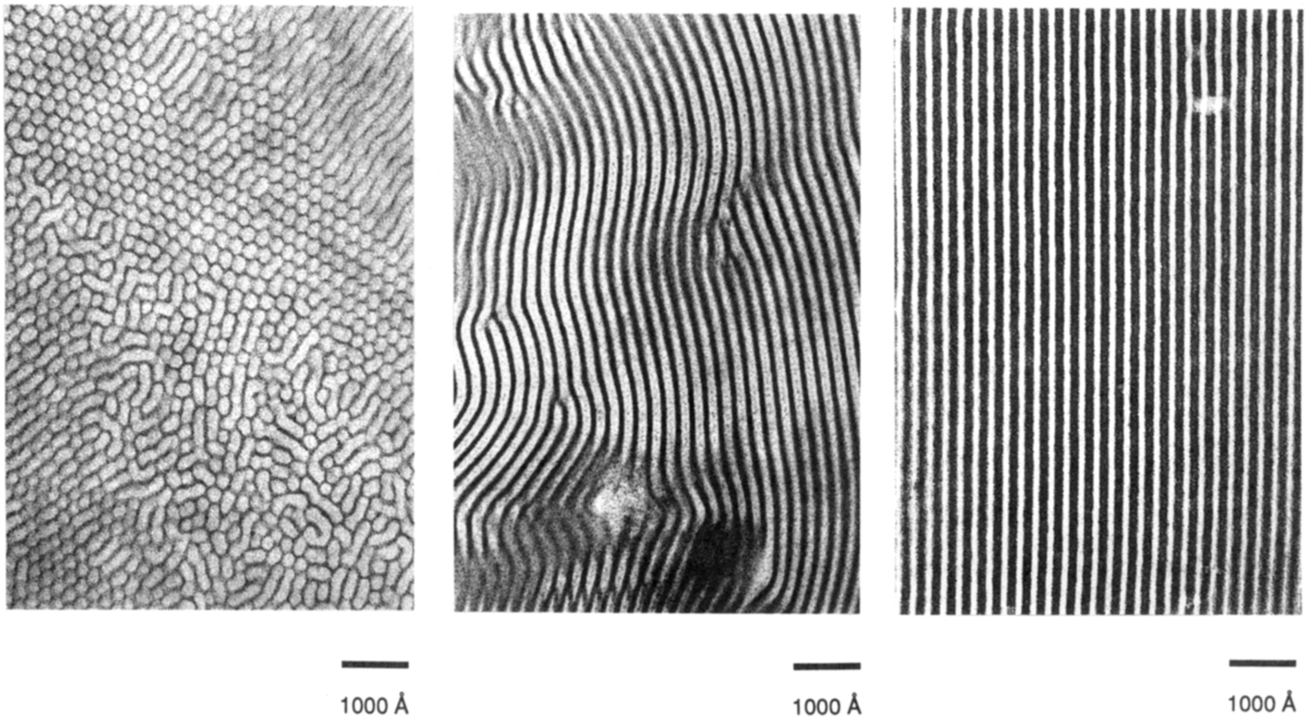


Figure 2. Electron micrographs of ultrathin sections of poly(styrene-*b*-DIMA) film cast from DMF solution (A), poly(4-octylstyrene-*b*-DIMA) film cast from DMF solution (B), and poly(isoprene-*b*-DIMA) film cast from THF/methanol (5/1, v/v) solution (C).

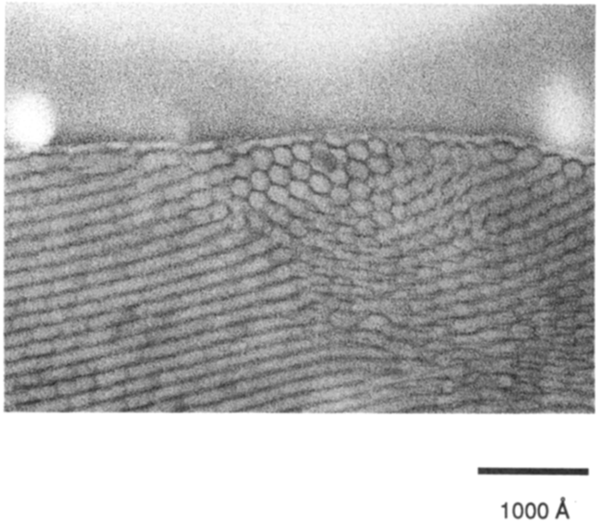


Figure 3. Electron micrograph of ultrathin cross section of poly(styrene-*b*-DIMA) film cast from DMF solution.

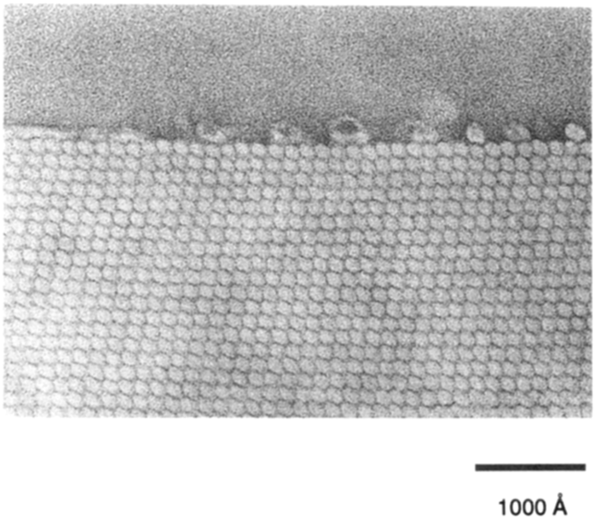


Figure 4. Electron micrograph of ultrathin cross section of wet sample of poly(styrene-*b*-DIMA). The sample was soaked in water for 1 h and then stained with aqueous OsO_4 solution.

film in water, the polystyrene layer covering the top surface of the as-cast film might be transformed to spheres wrapped with poly(DIMA) segments affording the hydrophilic surface. Thus, large-scale segmental rearrangement was visualized in response to the change in environment from dry to wet, which is the first evidence for surface reconstruction of a block copolymer recognized by direct TEM observation.

X-ray photoelectron spectroscopy (XPS) was used to quantify the surface composition. Especially, angular-dependent XPS demonstrates that the surface has a gradient of composition. The higher angles penetrate deeper into the surface; *e.g.*, 80° TOA is present in the outer ~100 Å of the sample surface. The sample depth decreases from about 100 to 15 Å as the TOA decreases from 80 to 10°. The XPS survey spectra of the as-cast films of the three block copolymers at 10° TOA and of poly(DIMA) homopolymer at 45° TOA are shown in Figure 5. Only the C_{1s} and O_{1s} peaks were observed for all samples, suggesting that the samples were free from surface contamination. The surface compositions of the block copolymers determined based on the O/C atomic ratios from survey scans are summarized in Table 2. In all cases, surface concentrations of hydrophobic segments at a sampling depth up to 100 Å are higher than those in the bulk and increase gradually as the XPS sampling depth decreases. The detected surface enrichment of the hydrophobic segments may be attributed to the lower surface energy of the hydrophobic segment. Among the three block copolymers, surface enrichment of the hydrophobic segment was most significant for poly(isoprene-*b*-DIMA) relative to the other two block copolymers. Although the surface structure of the as-cast film is a nonequilibrium state, the polyisoprene segment with its low T_g and low surface energy may cause a clear segregation by vigorous chain motion, resulting in enrichment of polyisoprene segments in the top surface.

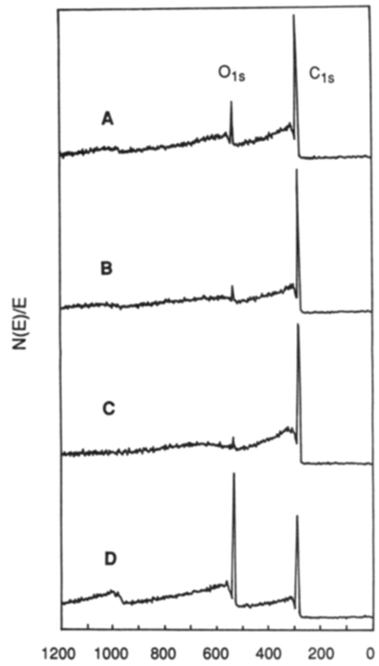


Figure 5. XPS survey spectra of as-cast films of poly(styrene-*b*-DIMA) (A), poly(4-octylstyrene-*b*-DIMA) (B), and poly(isoprene-*b*-DIMA) (C) at 10° TOA and poly(DIMA) homopolymer (D) at 45° TOA.

The surface rearrangement of the polymer films was also investigated by XPS. Recently, using the freeze–dry technique, Lewis and Ratner showed that poly(styrene-*b*-HEMA) exhibited an enrichment in the poly(HEMA) segment at the surface when hydrated and a reversal toward polystyrene-enriched surface when vacuum-dried.[24] Furthermore, they described that rearrangement of the hydrated surface structure back to a dehydrated structure under vacuum conditions at room temperature proceeded rather slowly. In expectation of such slow rearrangement of the hydrated surface, the composition of the wet surface was directly measured for poly(styrene-*b*-DIMA) film here under vacuum conditions at room temperature without using the freeze–dry technique. The rearrangement was studied by a combination of XPS data of the dry and wet samples with variable TOA. Figure 6 shows the high-resolution C_{1s} spectra at 80 and 10° TOA of poly(styrene-*b*-DIMA) film after various treatments. The spectra were resolved into peaks at 285.0, 286.6, 288.9, and 291.5 eV due to the *C*–C, *C*–O, O–*C*═O, and π–π^* shake-up satellite components. Table 3 shows the elemental composition and monomer unit percent data obtained from the survey scan for the poly(styrene-*b*-DIMA) film treated under the same conditions as those for the high-resolution scan. In the case of the as-cast film, the outermost surface at 10° TOA shows appreciable intensity of the π–π^* shake-up satellite peak and relatively weak intensities of the O–*C*═O and *C*–O peaks as compared with those at 80° TOA (Figure

Table 2. Surface Composition of the As-Cast Films by XPS Measurements

sample	takeoff angle, deg	atomic percent, %		monomer unit percent, %[a]	
		carbon	oxygen	hydrophobic monomer	DIMA
poly(styrene-*b*-DIMA)[b]	80	84.7	15.3	65.5	34.5
	45	87.7	12.3	72.9	27.1
	20	89.4	10.6	77.0	23.0
	10	92.3	7.7	83.5	16.5
	bulk	83.5	16.5	62.3	37.7
poly(4-octylstyrene-*b*-DIMA)[c]	80	90.1	9.9	65.4	34.6
	45	91.8	8.2	70.1	29.9
	20	94.4	5.6	79.1	20.9
	10	94.4	5.6	79.1	20.9
	bulk	84.5	15.5	48.2	51.8
poly(isoprene-*b*-DIMA)[d]	80	88.9	11.1	83.3	16.7
	45	93.4	6.6	90.9	9.1
	20	97.3	2.7	96.4	3.6
	10	98.6	1.4	98.1	1.9
	bulk	81.5	18.5	67.9	32.9

[a] Monomer unit percent was determined from the composition of carbon and oxygen. [b–d] The films were cast from a solution of (*b*) DMF, (*c*) benzene/methanol (4/1, v/v), or (*d*) THF/methanol (5/1, v/v) by spin-coating.

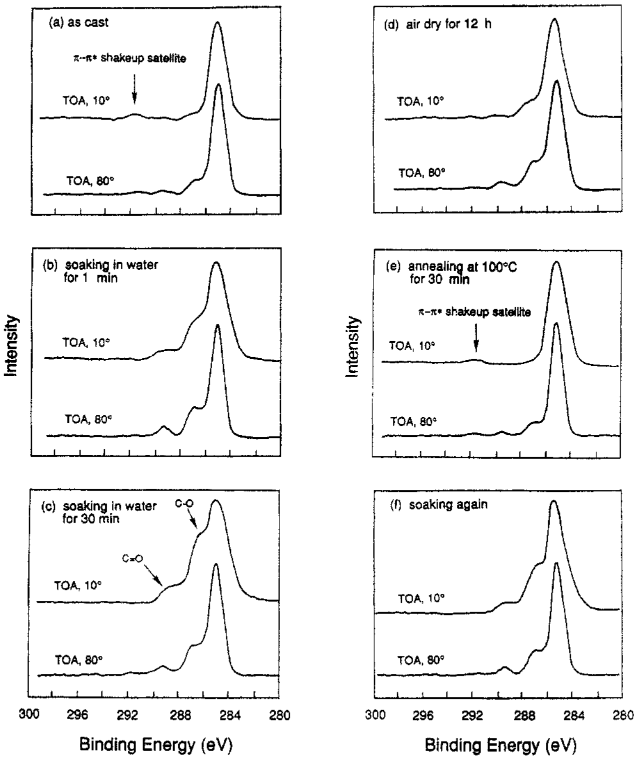


Figure 6. XPS C_{1s} spectra of poly(styrene-*b*-DIMA) film at TOA of 10 and 80° under various conditions: The sample was prepared from benzene/methanol (4/1, v/v) solution by spin-coating (a). The sample was soaked in water for 1 (b) and 30 min (c). The air-dry treatment was carried out at room temperature for 12 h (d) after soaking in water for 30 min. The annealing treatment was performed at 100 °C for 30 min after soaking in water for 30 min (e). The sample was immersed again in water for 30 min after soaking in water for 30 min and annealing at 100 °C for 30 min (f).

6a). As shown in Table 3, the outermost surface at 10° TOA consists of 76% polystyrene, while the bulk value is 62%. These results indicated that the outermost surface region of poly(styrene-*b*-DIMA) was enriched with polystyrene segment, which is consistent with the result of TEM observation. When the sample was soaked in water for 1 and 30 min (Figure 6b,c), the relative intensities of the O–*C*=O and *C*–O peaks increased, whereas the π–π^* shake-up satellite peak disappeared. Such spectral change is more significant in the shallow surface region (10° TOA) than in the inner region (80° TOA). The poly(DIMA) composition at 10° TOA was increased from 24% for the as-cast film to 62 and 67% for the sample soaked in water for 1 and 30 min, respectively (Table 3). Thus, it is substantiated that the polystyrene-enriched surface was transformed to the poly(DIMA)-enriched surface in response to the change in environment from dry to wet, and such rearrangement seemed to be almost finished in a few minutes. Next, reconstruction of the hydrated surface structure of poly(styrene-*b*-DIMA) back to a dehydrated one was traced under air-drying (Table 3). The poly(DIMA) content in the surface was moderately reduced by air-drying for 30 min. However, the reversal back to a hydrophobic surface of the original as-cast film was not completely attained even after air-drying for 12 h. Such slow and imperfect reconstruction may be due to the absorbed water in the hygroscopic poly(DIMA) segment, which was not completely removed by air-drying. Hence, annealing the sample film in air was examined to achieve reconstruction back to the hydrophobic surface. After heating the hydrated sample at 100 °C for 30 min, the π–π^* shake-up satellite peak again appeared (Figure 6e) and the polystyrene content in the outermost surface at 10° TOA exceeded that of the as-cast film (Table 3), indicating that the hydrated surface was rearranged back to a dehydrated surface. Soaking the sample again caused an increase of oxygen content in the surface at 10° TOA and a change in the high-resolution C_{1s} spectra, indicating that the surface was enriched in poly(DIMA) segments again (Figure 6f and Table 3). Thus, all of the XPS data obtained here confirmed occurrence of the surface rearrangement of the poly(styrene-*b*-DIMA) film in response to different treatments, such as soaking in water, air-drying, and annealing.

Changes of surface composition and structure are reflected in the contact angle of a water droplet on the surface. Some of the conclusions in the literature on restructuring of polymer surfaces are based on contact angle data.[7–11] Thus, surface rearrangements of the three block copolymers were also studied by contact angle measurement. After the film samples were treated under various conditions (as-cast, soaking in water, air-drying, and annealing at 100 °C), the contact angle of a water droplet, θ, on the film was measured at room temperature. The values of $\cos\theta$ versus treating period under the various conditions are shown in Figure 7. The as-cast film of poly(styrene-*b*-DIMA) showed a very high contact angle (θ = 85°), comparable to that of polystyrene, indicating that the outermost surface was almost covered with polystyrene segments. This is consistent with the results of the TEM observation and XPS measurement in this study. After the polymer film was soaked in water, the contact angle

Table 3. Surface Composition of Poly(styrene-*b*-DIMA) under Various Conditions by XPS Measurement

conditions	takeoff angle, deg	atomic percent, % carbon	atomic percent, % oxygen	monomer unit percent, %[a] styrene	monomer unit percent, %[a] DIMA
as cast[b]	80	87.9	12.1	73.5	26.5
	10	88.9	11.1	75.9	24.1
soaking in water for 1 min	80	78.6	21.4	49.0	51.0
	10	74.9	25.1	38.1	61.9
soaking in water for 30 min	80	76.7	23.2	43.5	56.5
	10	73.2	26.8	32.9	67.1
air-dry for 30 min after soaking[c]	80	80.5	19.5	54.8	45.2
	10	79.8	20.2	52.5	47.5
air-dry for 12 h after soaking[c]	80	80.7	19.3	54.9	45.1
	10	82.0	18.0	58.5	41.5
annealing after soaking[d]	80	89.0	11.0	76.1	23.9
	10	93.8	6.2	87.0	13.0
soaking again after annealing[e]	80	81.3	18.7	56.6	43.4
	10	75.0	25.0	38.3	61.7
bulk		83.5	16.5	62.3	37.7

[a] Monomer unit percent was determined from the composition of carbon and oxygen. [b] The sample was cast from a solution of benzene/methanol (4/1, v/v) by spin-coating. [c] The air-dry treatment was carried out at room temperature after soaking in water for 30 min. [d] The annealing treatment was performed at 100 °C for 30 min after soaking in water for 30 min. [e] The sample was immersed again in water for 30 min after soaking in water for 30 min and annealing at 100 °C for 30 min.

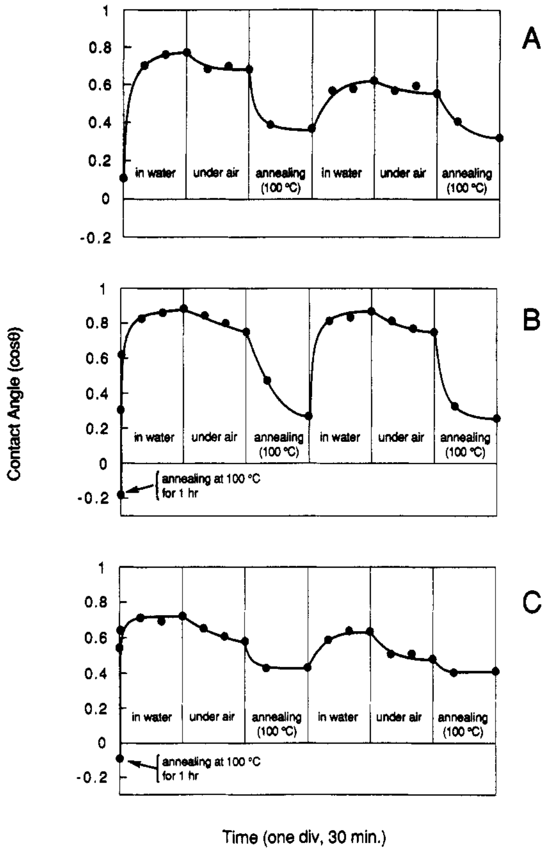


Figure 7. Contact angle of a water droplet on poly(styrene-*b*-DIMA) (A), poly(4-octylstyrene-*b*-DIMA) (B), and poly(isoprene-*b*-DIMA) (C) films under various conditions.

decreased dramatically within 10 min, suggesting that the polystyrene layer covering the as-cast surface was substituted with the poly(DIMA) domain during contact with water. However, the resulting hydrophilic surface did not revert to the hydrophobic surface by air-drying. The value of cos θ did not decrease back to the original one of the as-cast sample even after annealing at 100 °C in air for 10–30 min. This surface behavior of the poly(styrene-*b*-DIMA) film observed by contact angle measurement after soaking in water and air-drying is consistent with the result of the XPS measurement. Although the XPS data suggested surface rearrangement back to the original one through annealing treatment as described in the preceding paragraph, such clear reversal was not confirmed by the contact angle measurement. The difference between the results of XPS and contact angle measurements after annealing may be caused from the difference of measurable sampling depth and the inherent nature of these two analytical methods. It is considered that the sampling depth of XPS measurement at shallow TOA is approximately 15 Å, whereas that of contact angle measurement is only the outermost layer (~3 Å). Furthermore, contact angle studies are occasionally subject to artifacts due to lateral heterogeneity, roughness, and liquid absorption. Especially, absorption of water in the poly(DIMA) domain may relevantly affect the contact angle. In spite of the short contacting time of water on the sample surface for the measurement, the surface structure might be appreciably changed by absorption of water. In contrast, the reversal of the wet surface of poly(styrene-*b*-HEMA) film back to hydrophobic one was clearly observed by contact angle measurement and XPS measurement through annealing in air.[25] The reason for the incomplete reversal of poly(styrene-*b*-DIMA) to the original polystyrene-enriched surface may be attributable to a strong interaction of the poly(DIMA) segment with water compared with that of poly(HEMA) and water.

When a water droplet was placed on the as-cast films of poly(4-octylstyrene-*b*-DIMA) and poly(isoprene-*b*-DIMA), the contact angle rapidly lowered within a few seconds. It is, therefore, difficult to determine accurate contact angles for the as-cast films, which corresponds to the rapid rearrangement at the water–polymer interface. The reason for such rapid reconstruction may be the low glass transition temperature of each block component: poly(4-octylstyrene), −42 °C; polyisoprene, −69 °C. Furthermore, the apparent glass transition temperature of poly(DIMA) (T_g = 69 °C) plasticized with water should be lowered markedly. After the as-cast films were annealed at 100 °C for 1 h, the hydrophobic surfaces of the poly(4-octylstyrene-*b*-DIMA) and poly(isoprene-*b*-DIMA) films became somewhat stable. Thus, the contact angles of the dry surfaces can be measured. The very quick rearrangement of the dehydrated surface structure to the hydrated one occurred at the polymer–water interface (Figure 7B,C). The reversal of the hydrated poly(4-octylstyrene-*b*-DIMA) film to the dehydrated one was similar to the case of the poly(styrene-*b*-DIMA) film as shown in Figure 7B. However, the surface restructuring of the poly(isoprene-*b*-DIMA) film was ambiguous (Figure 7C). It is difficult, at this stage, to explain clearly the difference between the surface behaviors of the three block copolymers followed by the contact angle measurement.

In this study, the results from the TEM observation, XPS measurements, and contact angle measurements consistently indicate that the as-cast film of poly(styrene-*b*-DIMA) exhibits the enrichment of polystyrene segments in the top surface region and that the polystyrene layer at the surface is substituted with the hydrated poly(DIMA) segment by soaking the film in water. Especially by TEM observation, such surface rearrangement was explicitly confirmed to proceed through segmental replacement as a whole, rather than rotational migration of moieties on the polymer chain. The reversal of the hydrated surface back to the hydrophobic one through annealing treatment was detected by XPS, although the contact angle measurement did not give the consistent result satisfactorily. In the cases of poly(4-octylstyrene-*b*-DIMA) and poly(isoprene-*b*-DIMA) films, the observed surface structure was somewhat complex and seemed to involve dynamic changes in the measurement process.

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