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Effect of end group of side chains on surface properties of diblock copolymers

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Summary

The A-B diblock copolymers with comb shape structure were prepared from styrene (St) and either methacrylate of poly(ethyleneglycol) monomethyl ether (MPEGM) or methacrylate of poly(ethyleneglycol) (HPEGM). The surface chemical analysis of the polymer at air-solid interface by means of X-ray photoelectron spectroscopy (XPS) revealed the enrichment of MPEGM for MPEGM/St and St for HPEGM/St diblock copolymers, which indicated that the end group of the side chain determined surface composition. Dynamic contact angle measurements revealed that the migration of hydrophilic poly(ethyleneglycol) at solid-water interface occurred upon immersing the film specimen in water.

Introduction

Block and graft copolymers usually consist of more than two components with different surface free energy. Therefore, microphase separated structure is generally formed due to the difference in cohesive energy of each component. It is well known that "bulk" polymer structures and "bulk" properties are time and temperature dependent [1]. It is also true for surface structure and surface properties. The surface structure in an aqueous environment is different from that in the air. Since the surface free energy of water is higher than air, the component with higher surface free energy is enriched at the water-solid interface, whereas the component with lower surface free energy is enriched at the air-solid interface. The size or hierarchy of structures ranging from blocks or domains to small side chain functional groups is responsible for polymer surface structure and dynamics [2].

The surface analysis techniques [2,3] such as X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) require ultra high vacuum environments. By these methods, we can obtain the surface structural information only under high vacuum. For applications where the polymer surface is exposed to water, the results of surface analysis under high vacuum would not correspond to the surface structure in an aqueous environment. The classical Wilhelmy plate procedure [4] enables the measurement of contact angle hysteresis at the interface of air-solid-probe liquid [3]. This contact angle hysteresis can be interpreted in terms of surface mobility, reorientability, and intrinsic wettability [1, 2].

In this study, diblock copolymers of styrene and methacrylate with hydrophilic side chains were prepared. The end groups of side chain were either methoxy or hydroxy group. The effect of end group on surface structure and dynamics of diblock copolymers were investigated by means of XPS and dynamic Wilhelmy plate technique.

EXPERIMENTAL

Material

The A-B type diblock-copolymers were prepared by a living radical polymerization [5, 6]. The A component is poly(styrene) (St), and the B components are poly[methacrylate of poly(ethyleneglycol) monomethyl ether] (MPEGM) or poly[methacrylate of poly(ethyleneglycol)] (HPEGM) with various numbers of oxyethylene (OE) units. Figure 1 shows chemical structures of the poly[methacrylate of poly(ethyleneglycol) monomethyl ether] (MPEGM)/poly(styrene) (PSt) and the poly[methacrylate of poly(ethyleneglycol)] (HPEGM)/PSt diblock copolymers. These diblock copolymers are designated as MPEGM/St and HPEGM/St, respectively. MPEGM and HPEGM have similar chemical structures, except for the end groups of the side chains; MPEGM and HPEGM have methoxy and hydroxy end groups, respectively. Weight percent of PSt in diblock copolymers is 50%. For all experiments, uniform thin films of these block copolymers were prepared from toluene solutions by solvent casting method.

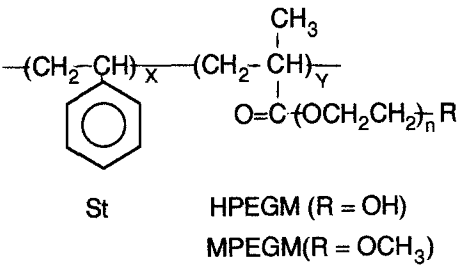


Figure 1. Chemical structure of diblock copolymers with different end group in side chain.

X-ray photoelectron spectroscopy

The surface chemical composition of the diblock copolymers was investigated by means of X-ray photoelectron spectroscopy (XPS). The XPS spectra were obtained with a Shimazu ESCA750 with a MgKα anode operating at 8kV and 30mA. The emission angle of the photoelectron which is defined as the angle between the electron path to the detector and the surface of the sample was 15 deg. Curve fitting of the C_{1s} spectra was accomplished using a nonlinear least square method [7]. A Gaussian-Lorentzian function was assumed for the curve-fitting.

Dynamic contact angle measurements

The surface dynamic properties of block copolymer films were measured using the dynamic Wilhelmy plate technique [1, 4, 5, 8, 9]. The surface tension-immersion depth into water curves were obtained with dynamic contact angle measuring apparatus model DCA-20 (Orientec Co.). Water for the dynamic contact angle measurements was purified with a Milli-Q system (Millipore Co. Ltd.). Calculation of the surface tension and dynamic contact angles were done according to a procedure suggested by Andrade and coworkers [1].

Dielectric relaxation measurement

The dielectric relaxation measurements of HPEGM and MPEGM homopolymers were carried out by using an impedance analyzer (4192A, Yokogawa Hewlet Packard, Ltd.). Gold electrodes were vapor deposited on both flat surface of the specimens. The frequency dependence of dielectric loss tangent was measured during heating up the specimens to 400K at the heating rate of 1K min^{-1} in vacuo after the specimens were cooled to 170K by liquid N_2.

RESULTS AND DISCUSSION

XPS analysis

The surface composition of copolymers were analyzed with XPS. Figure 2 shows the C_{1s} spectra of MPEGM/St and HPEGM/St diblock copolymers with oxyethylene (OE) repeat unit of 4 and 4.7, respectively. The dominant peaks in both spectra are at 285.0 eV (C-C/C-H bonds) and at 286.5eV (C-O) bands. The peak at 285.0 eV is originated primarily from aromatic ring of poly(styrene) (PSt), whereas the peak at 286.5eV is assigned to ether carbon from poly(ethyleneglycol) in MPEGM and HPEGM. The shoulder around 289.0eV in MPEGM/St diblock copolymer is due to the ester carbonyl carbon of methacrylate moiety. Also, the satellite peak which arose from the shake-up of π electron of aromatic ring was observed for HPEGM/St diblock copolymer.

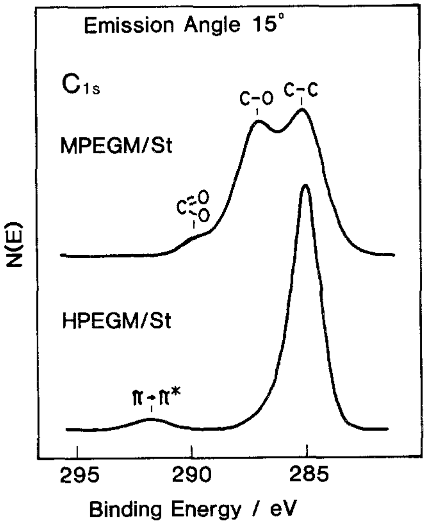


Figure 2. C_{1s} spectra of MPEGM (n=4)/St and HPEGM (n=4.7)/St diblock copolymers at the emission angle of 15 degree.

Large intensity of this satellite peak for HPEGM/St diblock copolymer indicates the enrichment of PSt at air-solid interface. On the other hand, ether carbon peak is not clearly observed for HPEGM/St diblock copolymer. Since in the case of MPEGM/St diblock copolymer, these peaks were observed in an opposite manner to these for HPEGM/St one, this indicated that the surface enrichment of PSt was not occurred on the surface of MPEGM/St diblock copolymer.

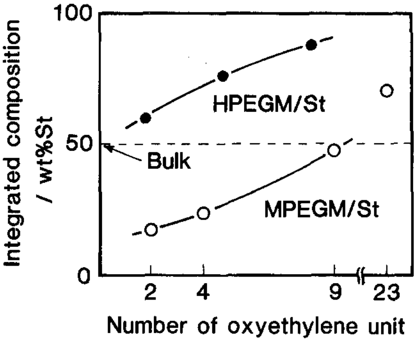


Figure 3. Variation of surface concentration of PSt with oxyethylene (OE) side chain length for HPEGM/St and MPEGM/St diblock copolymers.

The surface concentration of PSt can be evaluated from the area of each peak obtained from the curve fitting of original C_{1s} spectra. Figure 3 shows the surface concentration of PSt for MPEGM/St and HPEGM/St diblock copolymers with the number of oxyethylene (OE) units in the side chain. In the case of MPEGM/St diblock copolymer with the OE units less than 9, the surface concentration of PSt was smaller than those of bulk. The MPEGM/St diblock copolymer with the OE units of 23 showed enrichment of PSt on the surface. This is due to the increase in polar component of MPEGM block. On the other hand, PSt was dominant for the surface of HPEGM/St diblock copolymer. Since surface free energy of PEG is larger than that of PSt, the surface is enriched with PSt in order to minimize the interfacial free energy between air and solid surface. The large difference in the surface concentration of PSt between MPEGM/St and HPEGM/St diblock copolymers can be attributed to the difference in the end group structure. At the outer most surface, methoxy group can orient at the air-solid interface in order to minimize interfacial free energy. Whereas, the OH end group in HPEGM showed polar character similar to PEG side chains and PSt was enriched at air-solid interface.

Dynamic contact angle

The surface molecular mobility of these block copolymers were investigated by means of dynamic contact angle measurements on the basis of Wilhelmy plate technique (using water as a probe liquid). Figure 4 shows the dynamic contact angle curves for MPEGM/St and HPEGM/St diblock copolymers with the OE units of 4 and 4.7, respectively. The advancing angle for HPEGM/St diblock copolymer was larger than that for

MPEGM/St diblock copolymer. This is ascribed to the large concentration of PSt on the air facing surface of HPEGM/St diblock copolymer. The receding contact angles for the diblock copolymers were small in magnitude, that indicated the remarkable contribution of PEG component to receding angle. The surface tension at the second immersion cycle for MPEGM/St diblock copolymer did not coincide with that at the first immersion cycle. Since the surface of MPEGM/St diblock copolymer at the air-solid interface is enriched with MPEGM, the surface of MPEGM/St diblock copolymer is easily hydrated and the MPEGM segment swells in water. Thus in the case of MPEGM/St diblock copolymer, once the surface is hydrated, it is difficult to dehydrate the surface. In the case of HPEGM/St diblock copolymer, the surface tension at second immersion cycle coincided with that at the first immersion cycle. This indicates that the surface reorganization of this polymer is reversible with the environmental change. Therefore it seems reasonable to consider that the overlayer of PSt at the air-solid interface of HPEGM/St diblock copolymer inhibits large scale surface reorganization due to the relatively high glass transition temperature of PSt. The dielectric relaxation measurements of HPEGM and MPEGM homopolymer were carried out in order to characterize molecular mobility of the side chains. The activation energy of the side chain relaxation for

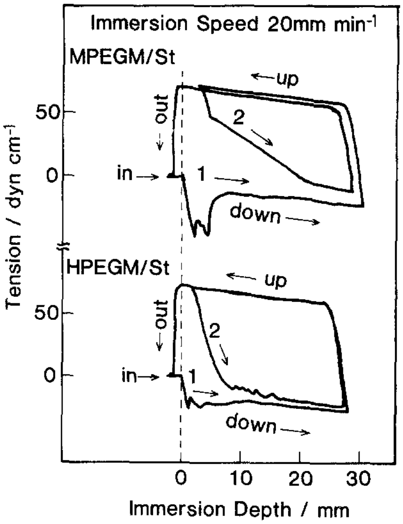


Figure 4. Dynamic contact angle loops for MPEGM (n=4)/St and HPEGM(n=4.7)/St diblock copolymers.

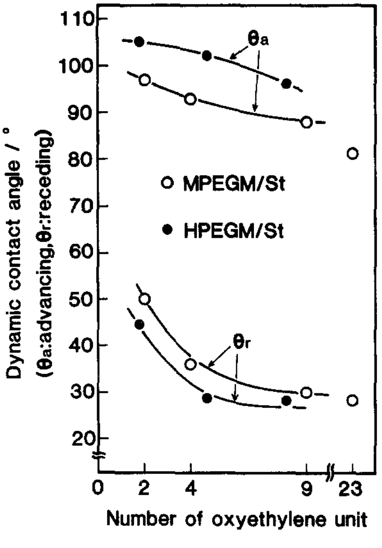


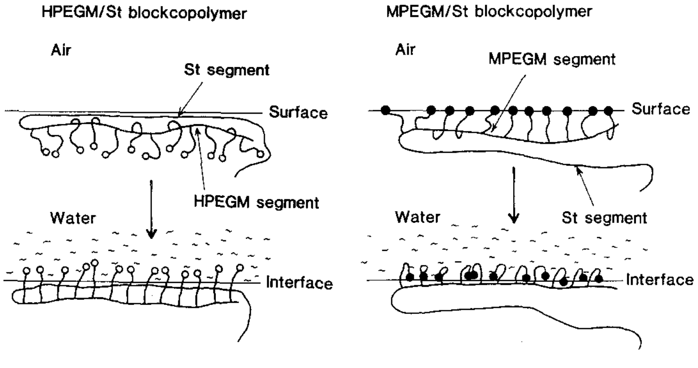
Figure 5. Variation of advancing and receding angles for MPEGM/St and HPEGM/St (b) diblock copolymer with oxyethylene (OE) side chain length.

HPEGM was larger than that for MPEGM. The difference in magnitude of activation energy may be attributed to the formation of hydrogen bonding network in the HPEGM homopolymer. These results also suggest that the large scale surface structural reorganization may easily occur for MPEGM/St diblock copolymer.

Figure 5 shows the variation of advancing and receding contact angles with the number of OE units for HPEGM/Stand MPEGM/St diblock copolymers. The magnitudes of advancing and receding contact angles decreased with an increase in OE chain length. The advancing angle for HPEGM/St diblock copolymer are higher than that for MPEGM/St one, whereas the case of the receding angle was reverse. The large magnitude of the advancing angle of HPEGM/St diblock copolymer reflects the enrichment of PSt at the air-solid interface which is in good agreement with the XPS results. The small receding angles observed for HPEGM/St and MPEGM/St diblock copolymers indicate that contribution of PEG chain on receding angle is very large. Since the receding contact angle was measured after hydration, the components with large surface free energy may easily orient or rearrange their segments at the the water-solid interface, if the segments of the components have sufficient thermal mobility.

The complexity of contact angle hysteresis was suggested by Johnson and Dettre [10]. Surface heterogeneity, surface roughness or surface deformation may contribute to the contact angle hysteresis. Also, swelling and surface reorganization may influence the dynamic contact angle. Johnson and Dettre revealed that the lower surface free energy component dominated for advancing contact angle, whereas higher surface free energy component dominated for receding contact angle. Since the polymer system studied here has microphase separated structure, theresult of Figure 5 suggests that either the existence of microphase separated structure or surface reorganization at the air-solid interface contributes to the contact angle hysteresis .

The contribution of molecular reorganization to the contact angle hysteresis is closely related to the bulk molecular mobility. The glass transition temperature (Tg) of the PSt phase is much higher than room temperature (293K). On the other hand, Tg of the PEG phase is lower than room temperature and decreased in the hydrated state due to the plasticization effect of water. XPS data of HPEGM/St diblock copolymer suggested the enrichment of PSt at air-solid interface. Thus, in the case of HPEGM/St diblock copolymer, only local reorganization of the component segments might be possible to minimize the interfacial free energy between solid and water as shown in Figure 6 (a). Since dehydration during withdrawal of the specimen from water easily occurs, dependence of advancing contact angle on immersion cycle for HPEGM/St diblock copolymer is small as shown in Figure 4. On the other hand, MPEGM/St diblock copolymer showed large increase



(a) (b)

Figure 6. Schematic representation of the surface structure of HPEGM/St (a) and MPEGM/St (b) diblock copolymers in air and in the hydrated-state.

in tension at the air-solid-water interface on the second immersion cycle (Figure 6(b)). XPS data for MPEGM/St diblock copolymer suggested the orientation of methoxy end group at air-solid interface. These results indicate that the reorientation of methoxy end group is necessary to obtain the environmentally stable specimen surface with respect to the interfacial free energy. From the results obtained above, it may be concluded that either short time scale molecular reorganization occurs as the surface environment changes or that the surface heterogeneity exists at the surface. Further analytical technique would be necessary to reveal the origin of contact angle hysteresis.

Conclusion

Surface characterization of diblock copolymers composed of hydrophobic PSt and poly(methacrylate) with hydrophilic PEG side chains revealed that the end group of hydrophilic chain has large influence on surface chemical composition depending on its environments. The diblock copolymer of which side chain is endcapped with methoxy group showed enrichment of the MPEGM group at the air-solid interface due to the hydrophobic character of methoxy end group. On the other hand, diblock copolymer of which side chain is endcapped with -OH group showed an enrichment of PSt at the air-solid interface. The dynamic contact angle measurements revealed that the surface composition depended upon the environmental change; in the hydrated-state, the surface was enriched with hydrophilic PEG side chains, whereas in the air, the surface was enriched with hydrophobic moiety. The driving force of surface structural reorganization is the difference in surface free energy between solid surface and environment.

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