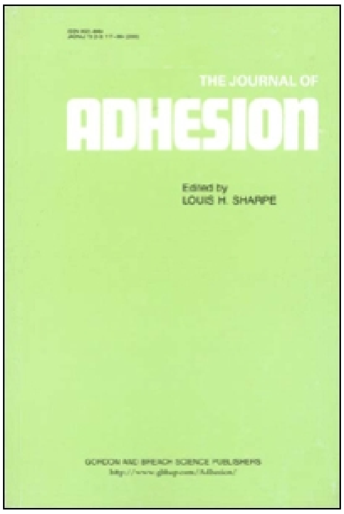

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Surface Molecular Mobility for Copolymers Having Both Hydrophobic and Hydrophilic Side Chains Via Dynamic Contact Angle Measurement*

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(In final form January 16, 1996)

The reorganization of a surface structure in response to a change in environmental media was investigated for copolymers having both hydrophobic polydimethylsiloxane (PDMS) and hydrophilic methoxypoly-ethyleneglycol (MPEG) side chains *via* dynamic contact angle (DCA). These copolymers showed a large contact angle hysteresis and a dependency of the advancing and receding contact angle on dipping velocity (DV). Composition dependency of DCA for these copolymers is also discussed. In addition to this, adhesion tension relaxation, $F(t)$, for MMA/MPEGMA/PDMSMA was determined. $F(t)$ in the advancing process increased with elapsed time and decreased in the receding process. These phenomena were explained by the adsorption and reorientation of hydrophilic segments to the water/copolymer interface in water. In XPS analysis, more oxygen atoms were detected on the surfaces of MMA/MPEGMA after immersion in water than before. For MMA/MPEGMA/PDMSMA, the atomic ratio of Si to C increased with an increase in PDMSMA content.

KEY WORDS: Surface reorganization; selective adsorption and orientation; effect of environment; contact angle hysteresis; adhesion of copolymers; X-ray photoelectron spectroscopy (XPS), adhesion tension relaxation; methoxypolyethylene glycol side chains; polydimenthysiloxane side chains.

INTRODUCTION

It is well known that a segment of a multicomponent system such as a copolymer selectively adsorbs and orients to the surface of the system so as to minimize interfacial free energy in response to an environmental medium. We[1–6] have already reported on this behavior *via* interfacial tension. Recently, the surface molecular mobility of a multicomponent polymeric system has been investigated *via* dynamic

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contact angle (DCA) measurements.[7] DCA is a useful tool to investigate these phenomena because a reorientation of surface segments directly reflects the contact angle hysteresis when a polymer is moved into a different medium.

In this study, we investigated this behavior on copolymers having both hydrophobic polydimethylsiloxane (PDMS) and hydrophilic methoxy-polyethyleneglycol (MPEG) side chain. Dynamic contact angle (DCA) for these copolymers were measured after dipping into and out of water. The following results were hypothesized: a low surface free energy PDMS segment would be predominant at the surface of these copolymers; in an aqueous environment, a PEG segment would reorient to the surface to lower interfacial free energy between the copolymer and water; and dipping in water would reduce the receding contact angle. In addition to measuring the DCA of these copolymer surfaces, an XPS spectrum was obtained.

EXPERIMENTAL

Materials

We synthesized two types of copolymers composed of methoxy polyethyleneglycol methacrylate (MPEGMA) and methylmethacrylate (MMA), (MMA/MPEGMA), and MMA, MPEGMA and polydimethylsiloxane-methacrylate (PDMSMA), (MMA/MPEGMA/ PDMSMA), having different compositions, in methylethylketone using *t*-butylperoxy(2-ethylhexanoate) as an initiator at 70°C. The molecular structures of these monomers are shown in Scheme 1.

$CH_2 = C(CH_3)COOCH_3$	MMA
$CH_2 = C(CH_3)COO(CH_2CH_2O)_nCH_3$	MPEGMA
$CH_2 = C(CH_3)COO(Si(CH_3)_2O)_nSi(CH_3)_3$	PDMSMA

SCHEME 1

All MMA/MPEGMA copolymers had the same composition (MMA/MPEGMA = 70/30 wt%) but the PEG chain length of MPEGMA differed. Therefore, the number of oxyethylene units of the PEG chain (*n*) was used for classification, using such nomenclature as MMA/MPEGMA(*n*). MMA/MPEGMA/PDMSMA terpolymers had the same MMA content (50 wt%) but different MPEGMA and PDMSMA content. In addition to this, only MPEGMA(23) was used for the polymerization of these copolymers, but the degree of polymerization of the PDMS chain in the PDMSMAs varied from 1000 to 5000. The molecular weight (Mw) was used for classification of PDMSMA using such nomenclature as PDMSMA(Mw), eq., PDMSMA(1000). The specimens for the DCA were prepared as follows: aluminum plates (20 mm wide, 50 mm length, 0.3 mm thickness) were dipped into a MEK solution (20 wt%) of the copolymers and then were dried in a vacuum oven at 90 °C for 20 hours.

Dynamic Contact Angle Measurement

For dynamic contact angle (DCA) measurement, we employed an instrument made by Orientec Corporation (DCA 20), applying the Wilhelmy plate technique used for measuring the surface tension of a liquid.

In Figure 1, the principle of the Wilhemy method[8] is shown. A sample plate, , hanging onto a load cell, is dipped into and out of a standard liquid giving the contact angle. Condition A shows the plate hanging onto the load cell. The force (F) applied to the load cell can be described as follows:

$$F = mg, \tag{1}$$

where m is the mass of the plate and g is the acceleration of gravity. Condition B shows the bottom of the plate just coming into contact with the liquid surface. Here F can be described as follows:

$$F = mg + P\gamma_L \cos\theta, \tag{2}$$

where P is the perimeter of the plate, γ_L is the surface tension of the liquid, and θ is the contact angle. Condition C shows the plate dipping into the liquid. F can be described as follows:

$$F = mg + P\gamma_L \cos\theta - F_b \tag{3}$$

where F_b is the buoyancy.

If zero adjusting of the recorder is performed in condition A, the mass of the plate can be neglected in Eq. (2). Then F can be described as follows:

$$F = P\gamma_L \cos\theta. \tag{4}$$

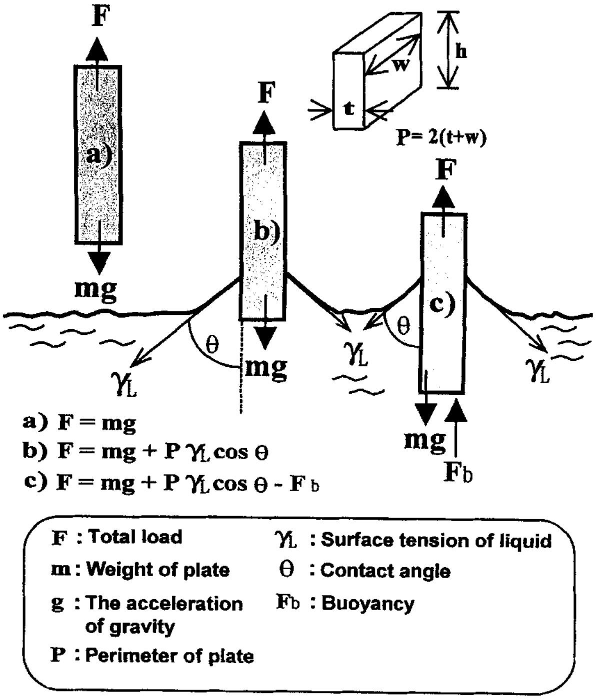

FIGURE 1 Scheme of principle of dynamic contact angle measurements by Wilhelmy method.

Young's equation is also held as follows:

$$\gamma_L \cos\theta = \gamma_S - \gamma_{SL} = \frac{F}{P}, \tag{5}$$

where γ_{SL} is the interfacial tension between the sample plate and the liquid.

If γ_L is known, we can calculate the contact angle (θ) by measuring F and P. The term, $\gamma_L\cos\theta$, is called the adhesion tension. The contact angles in the dipping in and out processes are called the advancing contact angle (θ_A) and receding contact angle (θ_R), respectively. This is performed as follows: first, the sample plate is mounted so that the bottom is 5 mm over the liquid surface; then it is lowered 20 mm at a certain constant velocity and immediately returned to its original starting point, i.e, 5 mm above the surface of the liquid.

Adhesion Tension Relaxation Measurement

In the DCA experiment, we found that DCAs for some copolymers varied depending on the dipping velocity. From this fact, it was hypothesized that γ_{SL} in the advancing process and γ_S in the receding process in Eq. (5) exhibited a relaxation during these processes. Therefore, we measured adhesion tension relaxation using the same sample plate and instrument as for the DCA. The measurement was performed as follows: first, the sample plate was mounted so that the bottom was just in contact with the liquid surface; then it was lowered 10 mm at a velocity of 100 mm/min and stopped. At this position, the force ($F_A(t)$) applied to the sample plate in the advancing process was measured as a function of elapsed time(t) for 30 min. After that, the plate was lowered a further 10 mm and after an elapse of 30 min, it was returned to the previous position and $F_R(t)$ in the receding process was similarly measured for 30 min. Here $F_A(t)$ and $F_R(t)$ could be described, respectively, as follows:

$$F_A(t) + F_b = P\gamma_L\cos\theta_A(t) = P(\gamma_{S,A}(t) - \gamma_{SL,A}(t)) \tag{6}$$

$$F_R(t) + F_b = P\gamma_L\cos\theta_R(t) = P(\gamma_{S,R}(t) - \gamma_{SL,R}(t)) \tag{7}$$

where the buoyancy, F_b, is constant value that does not depend on time.

As the surface tension of the sample plate did not depend on the elapsed time in the advancing process, $\gamma_{S,A}(t)$ became a constant value. Then Eq. (6) was rewritten as:

$$F_A(t) + F_b = P\gamma_L\cos\theta_A(t) = P(\gamma_S - \gamma_{SL,A}(t)) \tag{8}$$

Therefore, the variation of $F_A(t)$ with elapsed time was due only to that of $\gamma_{SL,A}(t)$ which depended on the rate of reorientation of the PEG segment to the copolymer/water interface. On the other hand in the receding process, as the surface of the plate was hydrated in water, the interfacial tension of the sample plate to water did not depend on the elapsed time. Therfore, $\gamma_{SL,R}(t)$ was rewritten to $\gamma_{SL,aq.}$, where $\gamma_{SL,aq.}$ is that interfacial tension of the hydrated copolymer/water interface.

Eq. (7) was rewritten as:

$$F_R(t) + F_b = P\gamma_L \cos\theta_R(t) = P(\gamma_{S,R}(t) - \gamma_{SL,aq.}) \tag{9}$$

Therefore, the variation of $F_R(t)$ was due only to that of $\gamma_{S,R}(t)$ which depended on the rate of reorientation of the PDMS segment in the part of the plate which was retracted from the water into the air.

XPS Spectrum Measurement

XPS spectra were measured by a Shimazu Manufacturing Ltd. ESCA 850 X-ray photoelectron spectrometer using a Mg $K\alpha$ X-ray source. The X-ray gun was operated as 8 kV and 30 mA, and the analyzer chamber pressure was $1 \times 10^{-6} - 10^{-7}$ Pa. Depth profiles were determined using the variable photoelectron take-off angle method. For this experiment, five types of sample holders, whose take off angles (ϕ) were 90, 60, 45, 30 and 15 degrees, respectively, were used. The sampling depth for each take off angle $d(\phi)$ is described as follows:

$$d(\phi) = d\sin\phi \tag{10}$$

where d is the sampling depth for the take off angle $\phi = 90$ degrees.

RESULTS

Dynamic Contact Angle

Figure 2 shows dynamic contact angles as a function of the number (n) of oxyethylene (OE) units of the PEG side chain for MMA/MPEGMA(n). Advancing contact angles (θ_A) decreased with an increase in n, because of an increase in the hydrophilicity of the copolymers. Receding contact angles (θ_R) initially decreased with an increase in n to a minimum value of $n = 9$, and then increased after that. Large hysteresis in DCA ($\Delta\theta = \theta_A - \theta_R$) was shown. This was due to the adsorption and reorientation of hydrophilic PEG side chains to the copolymer/water interface in water, resulting in a reduction of adhesion tension.

Figure 3 shown DCA as a function of the dipping velocity (DV) for MMA/MPEGMA(23). In a slower DV region (> 10 mm/min), θ_A did not depend on DV, but increased with an increase in it in a region faster than 5 mm/min. θ_R did not depend on DV and maintained a constant value.

Figure 4 shows DCA as a function of PDMSMA content for MMA/MPEGMA/PDMSMA, having a fixed molecular weight (1000) of MPEGMA (23) and a different PDMSMA ranging from 1000 to 5000. θ_A showed an approximately constant value, independent of PDMSMA content in a region of larger than 5 wt% content. θ_R exhibited different behavior depending on the molecular weight of PDMSMA. For shorter PDMS chain length (Mw = 1000), θ_R initially showed a low value of 40 degrees and increased with an increase in PDMS content in a region where the content was more than 30 wt% while, for longer chain length (Mw = 3000), θ_R increased from its initial value and reached a maximum value at 30 wt%.

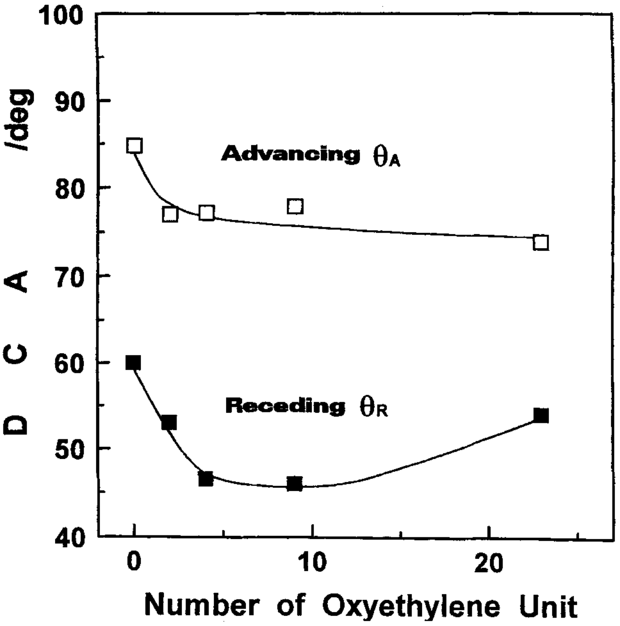

FIGURE 2 Dynamic contact angles as a function of the number of OE units in side chain for MMA/MPEGMA (23)(70/30wt%) copolymers.

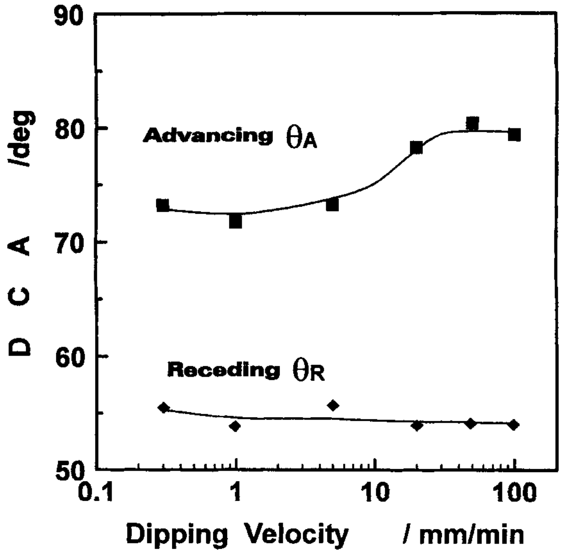

FIGURE 3 Dynamic contact angles of MMA/MPEGMA(23)(70/30 wt%) copolymer plotted against dipping velocity.

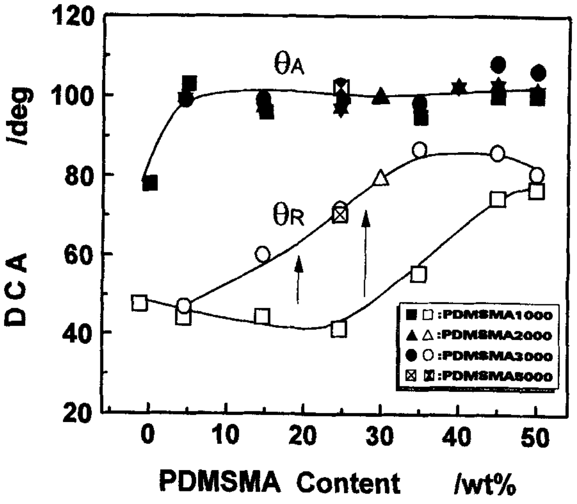

FIGURE 4 Dynamic contact angles for MMA(50 wt%)/MPEGMA/PDMSMA (variable) copolymers with different molecular weight as a function of PDMSMA content.

Figure 5 shows the relationship between DCA and PDMSMA content for two dipping velocities (DV) for MMA/MPEGMA/PDMSMA (1000), respectively. θ_A was not dependent on DV, but θ_R exhibited a different behavior. In the case of faster dipping (DV = 100 mm/min), θ_R increased with an increase in PDMSMA content from the low content, because it did not have enough time to reorganize the chemical composition of the polymer surface in the aqueous environment. In contrast, during slower dipping (20 mm/min), θ_R maintained a low value up to a PDMSMA content of 30 wt%, since the hydrophilic polyether segment was able to adsorb and reorient to the water/polymer interface.

Figure 6 shows the relationship between DCA and PDMSMA content for two dipping velocities (DV) for MMA/MPEGMA/PDMSMA (3000), respectively. θ_A also was not dependent on DV and, in contrast to the last figure, θ_R exhibited the same behavior to both DVs. θ_R for both DVs increased with an increase in PDMSMA content from the low one and produced a single curve.

Adhesion Tension Relaxation

Figure 7 shows the adhesion tension relaxation ($F(t)$), for MMA/MPEGMA(23)/PDMSMA (1000), respectively, with three kinds of compositions (MMA/MPEGMA/PDMSMA; 50/49/1, 50/25/25 and 50/0/50 respectively). $F_A(t)$ increased wtih elapsed time. This was due to the reorientation of the PEG segment to the copolymer/water interface, resulting in a reduction of $\gamma_{SL,A}(t)$ in Eqs. (6) and (8). A larger relazation of $F_A(t)$ was observed for a copolymer with more MPEGMA content than less. It was clear that it took a significantly long time for the PEG segment to reorient to the water/copolymer interface. The surface without

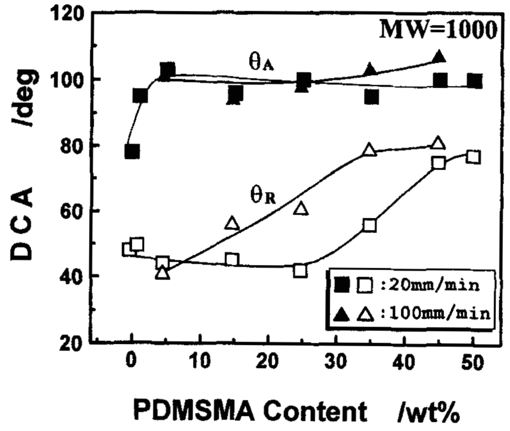

FIGURE 5 Dynamic contact angles for MMA/MPEGMA(23)/PDMSMA(1000) copolymers as a function of PDMSMA content. Molecular Weight: *Ca.* 1040.

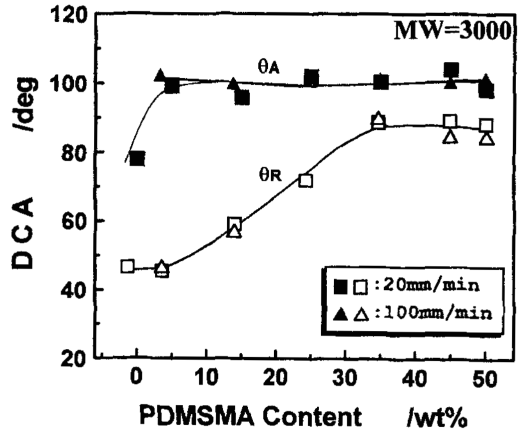

FIGURE 6 Dynamic contact angles for MMA/MPEGMA(23)/PDMSMA(1000) copolymers as a function of PDMSMA content. Molecular Weight: *Ca.* 3700.

MPEGMA exhibited only a little relaxation of $F_A(t)$, showing that a little reorganization of surface structure occurred.

On the other hand, $F_R(t)$ decreased with elapsed time. This was due to the reorientation of the PDMS segment and methoxy terminal group MPEGMA to the surface that was retracted from the water to the air, resulting in a reduction of $\gamma_{S,R}(t)$ in Eqs. (7) and (9). The largest relaxation of $F_R(t)$ was observed for the copolymer with the same content of both MPEGMA and PDMSMA (25/25).

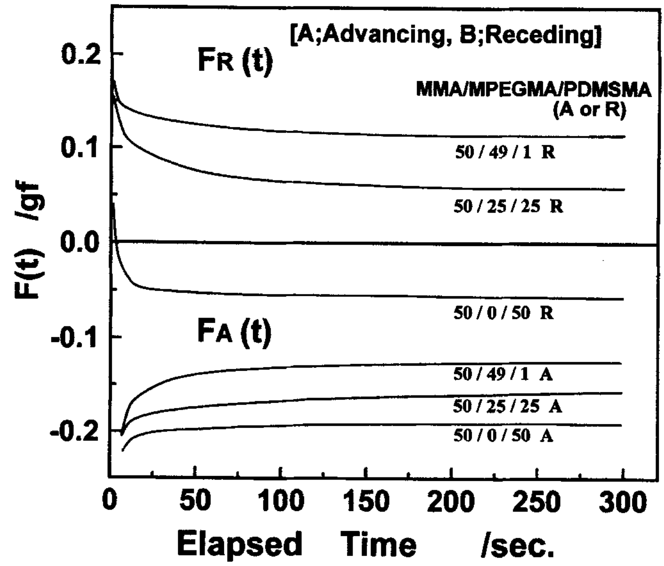

FIGURE 7 Relaxation of adhesion tension in advancing and receding process for MMA/MPEGMA (23)/PDMSMA(1000) copolymers.

X ray Photoelectron Spectroscopy

Figure 8 shows the depth-profiles of atomic ratio of PEG ether carbon to oxidized carbon for MMA/MPEGMA(23) *via* XPS before and after immersion in water. For the surfaces after immersion in water, more oxygen atoms were detected than before immersion. From these facts, it was clear that the hydrophilic PEG chains adsorbed and reoriented to the copolymer/water interface to reduce interfacial free energy. We have already discussed these data in detail elsewhere.[11]

Figure 9 shows the atomic ratio of Si_{2p} to C_{1s} as a function of PDMSMA content for MMA/MPEGMA/PDMSMA *via* XPS, determined with two types of sample holder (90 and 15 degrees). The atomic ratio of Si to C increased with an increase in PDMSMA content. The copolymer surfaces with a longer PDMS chain had more Si atoms than shorter ones. More Si atoms were detected in the 15-degree sample holder than the 90-degree one. It was clear that in the surface with a low content of PDMSMA, the PDMS and PEG segments coexisted, and in a higher content and longer PDMS side chain, the PDMS segment predominated.

DISCUSSION

Contact Angle Hysteresis

The copolymers used in this work exhibit a relatively large contact angle hysteresis as shown in Figures 2–6. The factors responsible for contact angle hysteresis of a polymer include: (1) surface contamination; (2) surface roughness; (3) heterogeneity

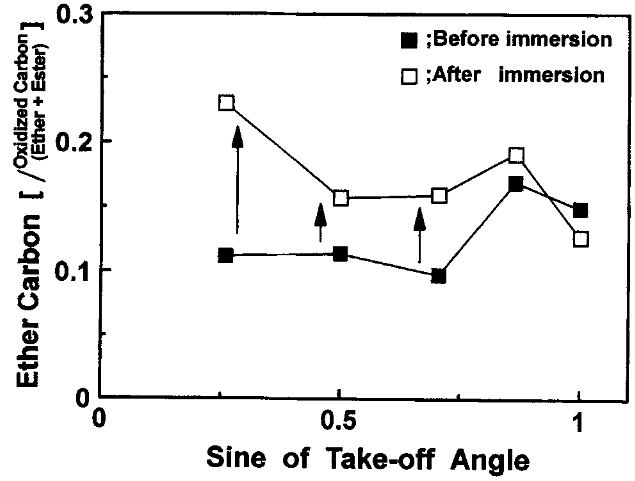

FIGURE 8 Depth-profile of atomic ratio of PEG ether carbon (MPEGMA) to oxidized carbon for MMA/MPEGMA(23)(70/30 wt%) copolymer before and after immersion in water, *via* XPS.

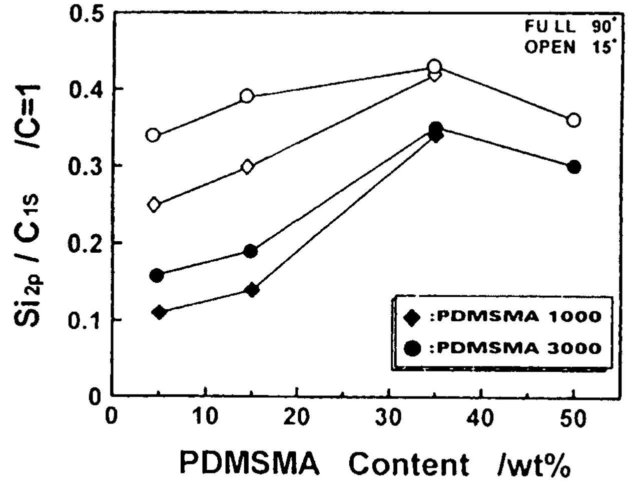

FIGURE 9 Atomic ratios of Si_{2p} to C_{1s} obtained with two photoclectron take-off angles (15° and 90°) for MMA/MPEGMA(23)/PDMSMA copolymers plotted against PDMSMA content.

of the surface structure; (4) reorientation or mobility of one or more surface segments; (5) swelling; (6) deformation, and so on. The most important factor in this study is the reorientation or mobility of a segment of the polymer surface. As shown *via* XPS measurement (Fig. 8), the surface phases of MMA/MPEGMA copolymers cast from MEK are composed of a methoxy terminal group and MMA and PEG segments. In particular, the methoxy group and MMA segment, having relatively low surface free energy, can adsorb and orient to the outermost surface layer of the copolymers. We[9] have already reported that the terminal methoxy group of PEG has a very low surface tension. Therefore, they present a hydrophobic surface and high (water) contact angle (advancing). However, when these copolymers are dipped into water, the hydrophilic PEG segments adsorb and reorient into the copolymer/water interface so as to minimize interfacial tension (γ_{SL} in Eq. (5)). Because the hydrated part of the sample plate exposed from the water into the air in the receding process has a high surface tension (γ_S) and the part in water maintains a low γ_{SL}, they exhibit low receding contact angles resulting in a high contact angle hysteresis.

Teraya *et al.*[10] have reported on the DCA for random and block copolymers of MPEGMA and styrene(St). For block copolymers, both θ_A and θ_R decrease with an increase in PEG chain length (*n*) and exhibit a large contact angle hysteresis, but θ_A for random copolymers shows no dependence on *n*. The behavior of θ_A for random copolymers is different from our results on random copolymers of MMA and MPEGMA. For MPEGMA/St, it is difficult to reorganize the surface structure because a bulky and hydrophobic phenyl group of St interrupts the motion of the PEG segment. It is suggested that the MMA segment, having a hydrophilic ester group, is not an obstacle to reorientation of the PEG segment. Other results of DCA for MMA/MPEGMA copolymers have been reported in detail elsewhere.[11]

MMA/MPEGMA/PDMSMA copolymers, incorporating a relatively low content of PDMSMA exhibit a large contact angle hysteresis as shown in Figures 4, 5 and 6. It is shown *via* XPS analysis that the PDMS segment, which has an extremely low surface free energy, concentrated on the cast surface, and resulted in a large advancing contact angle. The PEG segment of MPEGMA, however, reorients to the copolymer/water interface when the copolymer is dipped into water so as to reduce interfacial free energy, resulting in a low receding contact angle. This is why they can exhibit a large contact angle hysteresis in a low content region.

Composition Dependence of DCA

The advancing contact angles (θ_A) for MMA/MPEGMA/PDMSMA copolymers show an approximately constant value with respect to their composition as shown in Figure 4. As the PDMS segment easily adsorbs and orients to the surface due to its extremely low surface free energy, the surfaces of these copolymers exhibit a high contact angle, even if they have a low PDMSMA content. In contrast, the receding contact angles exhibit a remarkable composition dependency. An interesting behavior on the dependency in θ_R is observed, varying according to the molecular weight (Mw) of PDMSMA. For the surface of the copolymers wtih PDMSMA(1000), θ_R initially shows low values of 40 degrees and increases with an increase in PDMSMA content in a region where the content is more than 30 wt%, while for those with PDMSMA(3000), they increase from its initial value and reach a maximum at 30 wt%. Although the data is only one point for each Mw of 2000 and 5000, it falls on the curve for Mw with 3000. We have calculated the side chain lengths for each monomer, and obtained 105, 67 and 202 Angstrom for MPEGMA(23), PDMSMA(1000) and PDMSMA(3000), respectively. Based on this fact, it is clear that if the PDMS segment is longer than the PEG side chain, the reorientation of the PEG segment is interrupted by it, and if it is shorter than PEG, PEG is smoothly able to adsorb and reorient.

Efiect of Dipping Velocity

For MMA/MPEGMA(23) copolymers, θ_As show high values in faster DV (>10 mm/min), while they show low values in slower DV, as shown in Figure 3. In the advancing process, γ_{SL} varies with the reorientation of the PEG segment, but γ_S does not vary but maintains a constant value in Eq. (5). In a faster DV, the meniscus line of the water to the sample plate progresses so fast that there is not enough time for the PEG segment to the reorient to water/copolymer interface. As adhesion tension is determined by a low γ_S and high γ_{SL}, θ_A displays high values. On the other hand, in a slower DV, since the PEG segement is able to reorient, following the progress in the meniscus line, adhesion tension is determined by a low γ_S and a reduced γ_{SL}, resulting in a low θ_A.

For MMA/MPEGMA(23)/PDMSMA(1000, or 3000) copolymers, θ_A does not exhibit any DV dependency, since the PDMS segment concentrates onto the surface of these copolymers, and the reorientation the PEG segment can not easily occur during the advancing process as shown in Figures 4, 5 and 6. As shown in Figure 7, it takes 3–4 minutes for the $F_A(t)$ of these copolymers to relax to equilibrium value. Therefore, there is not enough time for the PEG segment to reorient in the advancing process. on the other hand, θ_R of the copolymer with PDMSMA(1000) exhibits different behavior depending on the DV as shown in Figures 5. For a slower DV(20 mm/min), θ_R maintains low values (50–40 degrees) up to a content of 25 wt%, at which point the copolymer has the same content of both MPEGMA and PDMSMA, followed by an increase. However, for a faster DV(100 mm/min), θ_R increases from a low content. In the low PDMSMA content region (*i.e.*, less than 25 wt%) and in a slower DV, there is only a little time for the PEG segment to migrate to the interface to overcome the interruption of the PDMS layer. Therefore, γ_{SL} can be significantly reduced but not equilibrate. In a faster DV, however, γ_{SL} can not be so reduced that θ_R shows a relatively high value, because there is little time for the segement to migrate and reorient to the interface, and overcome the interruption of the PDMS layer.

Conversely, for the copolymer with PDMSMA(3000), θ_A also does not exhibit DV dependency, as shown in Figure 6, and θ_R for both DVs shows the same behavior, which appears to be a faster case in the previous figure. It can be seen *via* XPS that these copolymer surfaces incorporate more PDMS segments than with PDMSMA(1000) in a low content region, as shown in Figure 9. As a result, they have a thicker PDMS surface layer than those with PDMSMA(1000). In this case, it is difficult for the PEG segment to migrate to the interface to overcome the obstacle of the PDMS layer even with a relatively low PDMSMA content. Thus, it takes so long a time for reorganization of the surface structure to occur that the difference in DV dependency is not observed.

Adhesion Tension Relaxation

As shown in Figure 7, $F_A(t)$ increases with elapsed time. This is due to the relaxation of $\gamma_{SL,A}(t)$ in Eq. (8). Takahara *et al.*[12] have also reported that adhesion tension increases with elapsed time for some segmented poly(etherurethaneureas). We can obtain some information on the mobility of a surface molecule from these data. It takes about 5 minutes for $F_A(t)$ to equilibrate to the two copolymers of MMA/PEMSMA(50/50) and MMA/MPEGMA/PDMSMA (50/49/1) which has a little PDMSMA. However, for a copolymer, incorporating the same content of MPEGMA and PDMSMA, $F_A(t)$ does not equilibrate within the time measured (30 minutes), even though that is not so clear in the figure. The cast surface of this copolymer is composed of PDMS, PEG, and a methoxy group, and has a complex structure, as shown *via* XPS investigation. When this copolymer is dipped into water and the reorganization of the structure occurs, the migration movement of the PEG segment to the interface is disturbed by the PDMS surface layers. As a result, it takes such a long time to swap PDMS for PEG that $F_A(t)$ is not able to equilibrate in a short time.

Conversely, $F_R(t)$ decreases with elapsed time. This is due to the relaxation of $\gamma_{S,R}(t)$ in Eq. (9). The decrease in $\delta_{S,R}(t)$ is responsible for the competitive reorientation of the PDMS segment and methoxy group to the surface exposed from the water into the air, as described above. In this case, the reorganization of the surface structure starts from the hydrated surface where the PEG segement was predominant. All $F_R(t)$s equilibrate within 5 minutes. $F_R(t)$ for MMA/MPEGMA/PDMSMA (50/25/25) exhibits the largest relaxation but in contrast to $F_A(t)$ takes 5 minutes to equilibrate. In the receding process, the reorganization can easily take place because the surface molecules have become very mobile by hydration.

CONCLUSION

The reorganization of a surface structure in response to a change in environmetnal media was investigated for MMA/MPEGMA and MMA/MPEGMA/PDMSMA copolymers *via* dynamic contact angle (DCA). All of these copolymers showed a large contact angle hysteresis due to adsorption and reorientation of the hydrophilic PEG segment to the water/copolymer interface. Dependency of the advancing and receding contact angle on dipping velocity (DV) was observed for MMA/MPEGMA and MMA/MPEGMA/PDMSMA copolymers, respectively. θ_As for MMA/MPEGMA/PDMSMA did not depend on the composition of the copolymer. In contrast to this, θ_Rs depended strongly on the composition and exhibited a different dependency, depending on the molecular weight of PDMSMA. Adhesion tension relaxation, $F(t)$, for MMA/MPEGMA/PDMSMA also was determined. $F_A(t)$ increased with elapsed time due to reorientation of the PEG segment to the water/copolymer interface, and $F_R(t)$ decreased due to the reorientation of the PDMS segment to the surface which was retracted from the water into the air. In XPS analysis, more oxygen atoms were detected on the surfaces of MMA/MPEGMA(23) after immersion in water than before. From this fact, it was clear that the hydrophilic PEG chains adsorbed and reoriented to the copolymer/water interface to reduce interfacial free energy. For MMA/MPEGMA/PDMSMA, the atomic ratio of Si to C increased with an increase in PDMSMA content. More Si atoms were detected with a 15-degree sample holder than a 90-degree one. It was clear that in the surface with a low content of PDMSMA, the PDMS and PEG segments coexisted, and in the case with a high content and longer PDMS side chain, the PDMS segment predominated.

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