Surface chemical composition and surface molecular mobility of diblock and random copolymers with hydrophobic and hydrophilic segments

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The A–B type diblock copolymer composed of polystyrene (PSt) and poly(methoxy poly(ethylene glycol) methacrylate) (PMPEGM) and their corresponding random copolymer were prepared. MPEGMs with different poly(ethylene glycol) (PEG) chain lengths were used to change the hydrophilicity and molecular mobility of hydrophilic segments. The surface chemical composition and surface molecular motion of these copolymers were investigated by X-ray photoelectron spectroscopy and dynamic contact angle measurement. The dependence of surface composition on casting solvents was prominent for the block copolymer system, whereas the random copolymer did not show this effect. Dynamic contact angle measurements revealed that the advancing contact angle decreased with successive immersion in water. Also, the motional scale of PMPEGM on the block copolymer surface increased with PEG side chain length. In contrast, the magnitude of advancing and receding contact angles for the random copolymer surface did not change with repeated immersion.

(Keywords: surface chemical composition; dynamic contact angle; surface dynamics; X-ray photoelectron spectroscopy; poly(methoxy poly(ethylene glycol) methacrylate))

INTRODUCTION

With an increase in the number of applications of polymeric materials as high functional polymers, surface properties are currently the subject of much attention. Polymer surface properties are closely related to the functionality of materials, e.g. adhesion, fracture, environmental compatibility, biocompatibility and electric properties. For multiphase polymers, the contribution of surface properties is complicated, since the components of multiphase polymers have different cohesive energies. The surface chemical composition of a multiphase polymer is organized in order to minimize interfacial free energy between the surface and its environment. Several reports have been done on the surface chemical composition of multiphase polymers[1–6]. However, few investigations have been made into the surface molecular mobility of multiphase polymers. The dynamic Wilhelmy plate technique which has been developed by Andrate *et al.* is a powerful tool for characterizing polymer surface dynamics[7,8]. They reported the contact angle hysteresis of some hydrogel systems, which was ascribed to the surface molecular mobility. However, most of the study was limited to the homopolymer system.

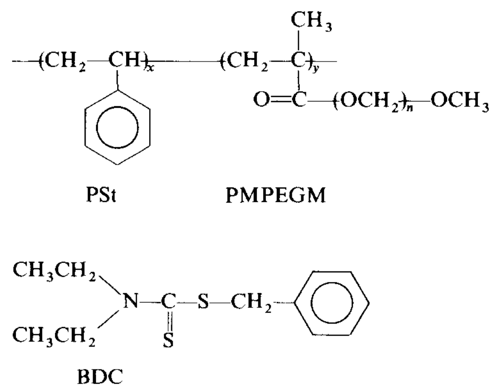
In this study, polystyrene(PSt)/poly(methoxy poly(ethylene glycol) methacrylate) (PMPEGM) diblock and random copolymers were prepared to investigate the effect of hydrophilicity on the surface chemical composition and surface molecular mobility. The hydrophilicity of MPEGM can be controlled by changing the molecular weight of PEG side chain.

EXPERIMENTAL

Materials

PSt/PMPEGM diblock copolymers were synthesized by living radical polymerization[9]. The chemical structures of the monomers and initiator (iniferter) are shown in *Scheme 1*, where n is the number of oxyethylene (OE) units.

Styrene monomer was used after distillation. MPEGM monomers were supplied by Shin Nakamura Kagaku Co. Ltd. The MPEGM has a long methoxy-end-capped polyethyleneglycol (PEG) with number of repeat units 2, 4, 9, 23. MPEGM was used without further purification. Styrene monomer was polymerized by benzyl-N,N-diethyldithiocarbamate (BDC) as an photo-iniferter. A telechelic polymer of St with viscosity-average molecular weight of 120 000 was obtained. This telechelic polymer was used as an iniferter and MPEGM was polymerized at one end of PSt to obtain St/MPEGM diblock copolymer.



Scheme 1

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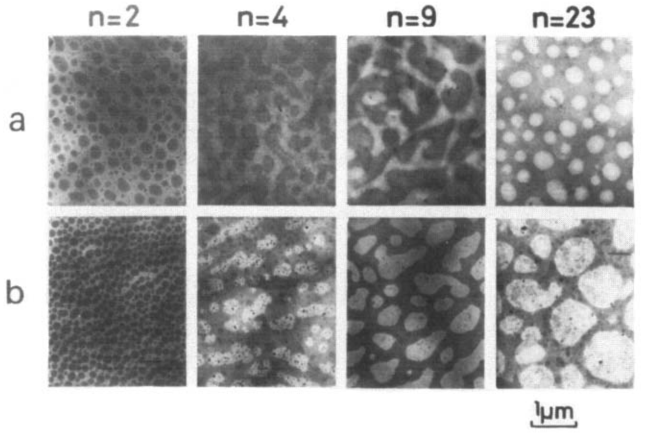

gure 1 Transmission electron micrographs of St/MPEGM block polymers (50 wt% St) prepared from (a) toluene and (b) :thylisobutylketone (MIBK); n = number of oxyethylene units

/MPEGM random copolymers were prepared by dical polymerization with azobisisobutylonitrile .IBN). All these diblock and random copolymers ntain 50 wt% styrene.

The synthesized copolymers were purified by reprecipitation. Film specimens were cast from their toluene methylisobutylketone (MIBK) solutions for surface .aracterization.

orphological observation

The morphology of copolymer thin films was observed transmission electron microscopy (TEM) (H-500 itachi Co. Ltd). The samples were prepared on carbon-coated copper grid from their solutions. MPEGM segments were stained with OsO_4 to enhance ntrast.

-ray photoelectron spectroscopy

The surface chemical composition of copolymer as investigated by X-ray photoelectron spectroscopy .p.s.) (ESCA750 Shimazu Co. Ltd) using Mg Kα as -ray source. The photoelectron emission angle was 15°. ie emission angle was defined as the angle between the rface parallel and the axis of the analyser lens system.

ynamic contact angle measurements

Dynamic contact angles were measured based on the ilhelmy plate technique[10]. Pre-purified water was rther purified by passing it through a Milli-Q system lillipore Co. Ltd). The dynamic contact angle equipment as designed to allow attachment of a tensile tester. A otor drives the crosshead to advance or withdraw the ater container at a controlled speed of 20 mm min^{-1}. ie surface tension was measured with a high sensitivity rain gauge. The diblock copolymers were coated on in Myler film (10 × 50 mm^2, 0.10 mm thick). A test ecimen was suspended by a fine thread. The basic uation for calculation of contact angle is:

$$F = mg + p\gamma_L \cos\theta - F_b \qquad (1)$$

here:

= total force;
= mass of the plate;
= acceleration due to gravity;
= perimeter of the plate;
γ_L = surface tension of water (72.6 mN m^{-1});
θ = contact angle;
F_b = buoyancy force.

The surface tension *versus* displacement curve was obtained at 293 K. The advancing contact angle was obtained from the surface tension at zero displacement during immersion of the specimen in the water. The receding contact angle was obtained from the surface tension at zero displacement during withdrawal of the specimen from the water.

RESULTS AND DISCUSSION

Morphological observation

Figure 1 shows the transmission electron micrographs of the block copolymers. The dark part corresponds to the PMPEGM domain stained with OsO_4. The size of the microphase separated structure tends to increase with PEG side chain length. However, the effect of solvents on the phase separated structure has not been clearly observed. The TEMs of the random copolymers did not show any evidence of microphase separation. Though the random copolymer is a kind of graft copolymer which may form the microphase separated structure, this polymer did not show any kind of microphase separated structure, due to the short PEG side chain length.

Surface chemical composition

Figure 2 shows the C_{1s} spectra of diblock copolymer (n = 23) at an emission angle of 15°. The peaks of neutral, ether and carbonyl carbons were observed at 285, 286.5 and 189.0 eV, respectively. The specimen cast from a toluene solution showed a higher fraction of neutral carbon on the surface. The specimen cast from a MIBK solution had a higher concentration of ether carbon. Since toluene is a good solvent for PSt, the PSt segment is enriched on the surface of the toluene cast film. These observations are similar to those made by O'Malley *et al.*[1] for the PEO/PSt block copolymer system.

The variation of the surface concentration of PSt with the number of oxyethylene units in MPEGM is shown

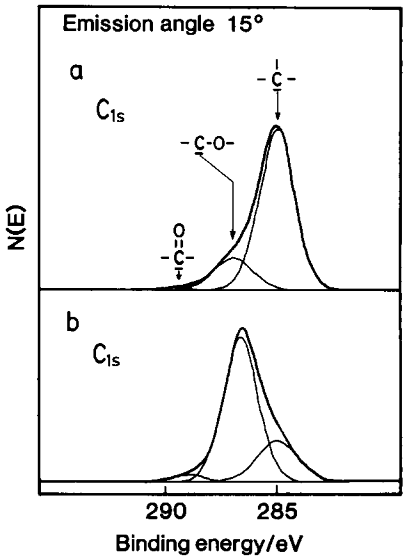

Figure 2 C_{1s} spectra for diblock copolymer (n = 23): (a) cast from toluene solution; (b) cast from MIBK solution

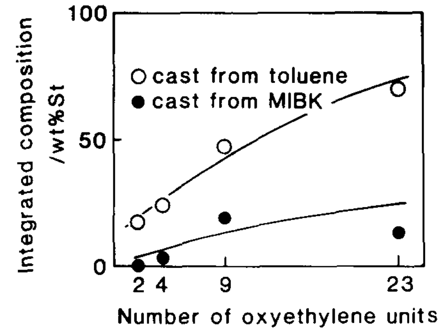

Figure 3 Variation of surface St concentration with number of oxyethylene units in diblock copolymers (50 wt% St)

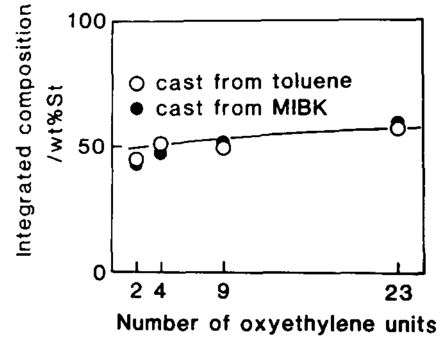

Figure 4 Variation of surface St concentration with number of oxyethylene units in random copolymers (50 wt% St)

in *Figure 3*. The surface concentration of PSt increased with PEG side chain length. Also, the PSt concentration on the surface cast from a toluene solution is higher than that cast from a MIBK solution. Though the surface free energy of the PSt segment is lower than that of MPEGM, the surface concentration of PSt was lower than that of PMPEGM for the copolymers with less than nine OE units. This enrichment of MPEGM on the surface is due to the hydrophobic end group effect[11]. To investigate this end group effect, the surface properties of polystyrene/-poly (hydroxy poly(ethylene glycol) methacrylate) diblock copolymer (having hydroxy end group) were investigated. This copolymer showed extensive enrichment of PSt on the surface. The details of the effect of –OH end groups will be published elsewhere[11]. Since the contribution of hydrophobic methoxy end groups to surface free energy increased with a decrease in PEG side chain length, the net surface free energy of MPEGM may decrease.

The relationships between the surface St concentration and the number of oxyethylene units in MPEGM for random copolymers are shown in *Figure 4*. The surface concentration of PSt corresponds to its bulk fraction, and both effects of a type of solvent and PEG side chain length have not been observed. This indicates that surface reorganization to minimize the interfacial free energy does not easily occur for the random copolymer system, since T_g of the random copolymer is higher than that for the block copolymer due to the restriction of molecular motion by phase mixing.

Dynamic contact angle

The difference in surface molecular mobility between the block copolymer and the random copolymer has been characterized by means of dynamic contact angle measurements. *Figure 5* shows contact angle hysteresis loops for the St/MPEGM ($n = 23$) block copolymer films prepared from toluene and MIBK solutions. The two loops showed different surface tension at the point of immersion. The higher surface tension corresponds to smaller contact angle, and this indicates that the surface is relatively hydrophilic. The lower surface tension (larger contact angle) indicates hydrophobic surface. Johnson and Dettre indicated that advancing contact angle is associated with the lower surface energy region[12]. Therefore, even though the microphase separated structure existed on the surface, hydrophobic components dominated the contribution to the advancing contact angle. The advancing contact angle for the toluene-cast sample is higher than that for the MIBK-cast sample. This indicates that the surface concentration of PSt might be higher in the toluene-cast sample. This result corresponds well with X.p.s. analysis. The receding contact angle was small due to large surface free energy of MPEGM. The driving force for this surface reorientation is the remarkable difference in surface free energy between the polymer surface and water.

Figure 6 shows a schematic representation of the surface reorganization of the block copolymer during the advancing and receding processes of dynamic contact angle measurements. *Figures 6a* and *b* correspond to the block copolymer with short and long PEG side chains, respectively. During the advancing process, the methoxy groups tend to embed into the polymer matrix and OE groups tend to hydrate in order to minimize interfacial free energy between solid surface and water. For the block copolymer with long PEG side chains, relatively large-scale reorientation is necessary. During the receding process, the methoxy groups orient to the air–solid interface in order to minimize air–solid interfacial free energy. The block copolymer with short OE chains shows fast reorientation of methoxy end group. The block copolymer with long PEG side chains cannot exhibit fast reorientation due to the high degree of hydration of OE chains. Thus the block copolymer with long OE chains has hydrophilic moiety on the surface

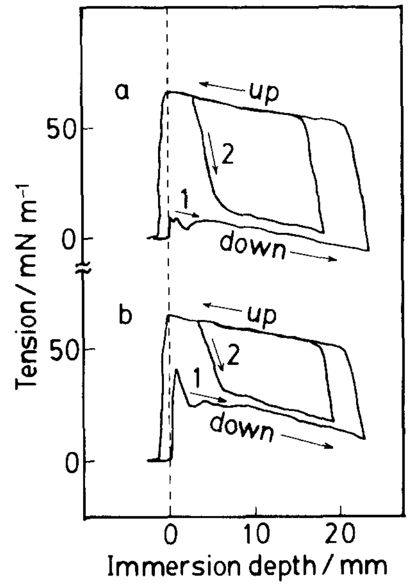

Figure 5 Dynamic contact angle hysteresis loops for diblock copolymers (50 wt% St, $n = 23$): (a) cast from toluene solution; (b) cast from MIBK solution

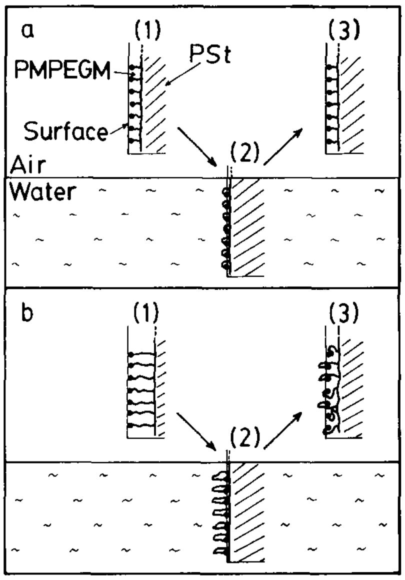

Figure 6 Schematic representation of the surface molecular motion'on immersion into and withdrawal from the water phase. (a) Quick reorientation (short side chain); 1, before immersion; 2, changes to hydrophilic surface; 3, returns to hydrophobic surface after withdrawal. (b) Slow reorientation (long side chain): 1, before immersion; 2, changes to hydrophilic surface; 3, even though withdrawn to air, a hydrophilic contribution still exists on the surface

after the first cycle. On the second immersion, the second loop followed the first cycle. If the surface rearrangement of molecular chains occurred slowly, the second loop would not follow the first cycle; hydrophilic PMPEGM segments are still hydrated at the second immersion, so the surface might show higher surface tension than that on the first immersion. For the block copolymer with a higher fraction of MPEGM, the copolymer surface exhibited a decrease in advancing contact angle for the second cycle. This indicates that reorientation of the greatly hydrated hydrophilic molecule at the surface did not occur rapidly during the withdrawal process. Therefore, the time required for reorientation might depend on the state of hydration.

The variation of dynamic contact angle with the number of OE units in MPEGM is shown in *Figure 7*. The advancing and receding contact angles were calculated for the first cycle experiments and they decreased with an increase in the number of OE units in MPEGM. The X.p.s. results indicate an increase in the surface concentration of St with an increase in PEG side chain length. The decrease in advancing contact angle observed is opposite to the trend of the X.p.s. results. This may indicate that, even though the components with lower surface free energy exist on the surface, there was a significant contribution of hydrophilic components due to the small fraction of hydrophobic groups in MPEGM. The large receding contact angle for the sample with $n=2$ may be due to the hydrophobic effect of methoxy end groups. The small magnitude of receding contact angles for block copolymers may be due to the reorientation of PEG side chains in order to minimize interfacial free energy between the surface and water.

The magnitudes of advancing contact angles were strongly dependent on the type of solvent, toluene or MIBK. The advancing contact angle for the specimen cast from a toluene solution was higher than that for the specimen cast from a MIBK solution due to the enrichment of St on the surface. The magnitudes of receding contact angles were weakly dependent on the type of solvent. Since molecular chains on the surface easily reorient during an immersion process, the surface of diblock copolymer became hydrophilic in water. This surface rearrangement is due to high molecular mobility of MPEGM segments.

Figure 8 indicates the variation of advancing and receding contact angles for random copolymers with

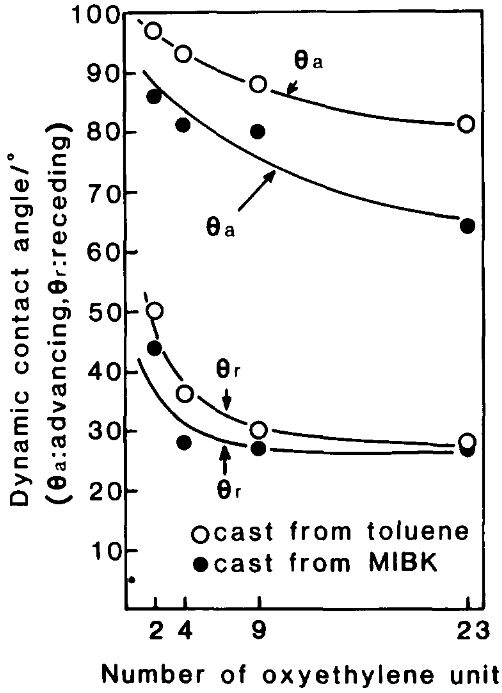

Figure 7 Variation of advancing and receding contact angles at first cycle for diblock copolymers (50 wt% St) with number of oxyethylene units in MPEGM

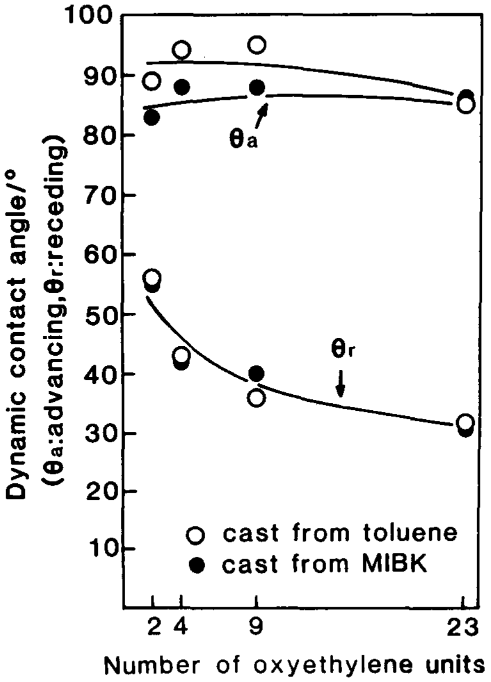

Figure 8 Variation of advancing and receding contact angles at first cycle for random copolymers (50 wt% St) with number of oxyethylene units in MPEGM

the number of OE units in MPEGM. The advancing contact angle showed almost no dependence on the type of solvent or on the length of OE units. However, the receding contact angle did depend on the length of OE units. Since the fraction of methoxy end groups in MPEGM increased with a decrease in PEG side chain length, this might reflect the hydrophobicity of the PMPEGM phase. This behaviour also corresponds to the X.p.s. results, i.e. no dependence on PEG side chain length of surface St concentration. Since MPEGM with longer side chains has a larger contribution of hydrophilicity than that with shorter side chains, the receding contact angle of random copolymer with longer PEG side chains became smaller (more hydrophilic). The receding contact angles for random copolymers were larger than those for block copolymers. This may be due to the phase mixing between hydrophobic St and hydrophilic MPEGM, since random copolymers did not show phase separated structure.

CONCLUSION

The surface molecular motion and surface chemical composition of block copolymers and random copolymers prepared from styrene (St) and methoxy poly(ethylene glycol) methacrylate (MPEGM) with various poly(ethylene glycol) side chain lengths were investigated on the basis of X-ray photoelectron spectroscopy and dynamic contact angle measurement. The enrichment of PSt components on the block copolymer surface became prominent with an increase in PEG chain length. The block copolymer film cast from a good solvent of PSt showed enrichment of PSt on the surface. However, the remarkable effects of PEG side chain length and solvent on the surface concentration of PSt or PMPEGM components have not been observed for random copolymers. The block copolymer with long PEG side chains showed large scale molecular rearrangement at the surface due to phase separation. The random copolymers did not show a dependence on the immersion cycle due to the small scale of molecular rearrangement at the surface. This result clearly indicates the effect of copolymer structure on the surface molecular motion and the surface composition at the copolymer surface.

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