Hydrophobic and hydrophilic interpenetrating polymer networks (IPNs) composed of polystyrene and poly(2-hydroxyethyl methacrylate):
2. Gradient composition in the IPNs synthesized by photopolymerization

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Sequential interpenetrating polymer networks (SIPNs) composed of poly(2-hydroxyethyl methacrylate) (PHEMA) and polystyrene (PS) were synthesized by photopolymerization at room temperature. A common solvent, *N*,*N*-dimethylformamide, was used to impregnate the styrene monomer into the PHEMA network. The IPNs had a microphase-separated structure of the order of 100 nm. It was found that the gradient composition in the surface region (to a depth of 0.1 mm) was obtained by polymerization inhibition with oxygen which had diffused from the surfaces of the swollen PHEMA gel. X-ray photoelectron spectroscopy measurements revealed that the PS component was enriched in the surface of the IPN. Thermodynamic effects on the composition of the outermost surface layer are discussed.

(Keywords: interpenetrating networks; photopolymerization; gradient composition)

INTRODUCTION

Some of the multicomponent polymers, such as block and graft copolymers, are known to possess a microphase-separated morphology leading to unique properties at the surface as well as in bulk[1,2]. An interpenetrating polymer network (IPN) has a microphase-separated structure. An IPN is defined as a type of blend composed of two (or more) polymers in which at least one polymer has a crosslinked structure[3]. Physical interlocking among the component polymers makes the phase-separated structures frozen in. Although many studies have hitherto been performed on IPNs, most of them have been concerned with the bulk characteristics[3,4]. The structure and properties of an IPN surface remain obscure.

In our previous paper[5], sequencial IPNs (SIPNs) composed of hydrophobic polystyrene (PS) and hydrophilic poly(2-hydroxyethyl methacrylate) (PHEMA) were successfully synthesized by thermal polymerization using a common solvent, *N*,*N*-dimethylformamide (DMF), which dissolves the monomer and swells the polymer. The IPNs obtained exhibited a microphase-separated structure. However, the IPNs had a gradient composition, i.e. the polymer content decreased gradually towards the surface. Furthermore, measurements of the contact angle of water led to speculation that the IPNs had a PS-enriched surface layer. These discrepancies in the composition between the bulk and at the surface have not been previously reported for IPNs.

In this paper, a detailed study of the gradient composition of IPNs composed of PHEMA and PS has been carried out in order to clarify the formation mechanism of the gradient. The IPNs were synthesized by photopolymerization at room temperature, which enabled the effect of heat applied to the polymerization system, which leads to the evaporation of HEMA, to be ignored. The composition of the outermost layers of the IPNs obtained was analysed by X-ray photoelectron spectroscopy (X.p.s.). Thermodynamic effects on the surface composition are discussed.

EXPERIMENTAL

Materials

2-Hydroxyethyl methacrylate (HEMA) monomer was distilled under reduced pressure. Styrene monomer and divinylbenzene (DVB) were washed successively with 5% aqueous NaOH and deionized water, dried over anhydrous Na_2SO_4, and then distilled under reduced pressure. Diphenyl disulfide (DPDS) was recrystallized from methanol. DMF was dried over molecular sieves (4 Å) for 24 h and distilled under reduced pressure.

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Syntheses

Preparation of crosslinked PHEMA. PHEMA plates were prepared by bulk polymerization. Poly(tetrafluoroethylene) (PTFE) was employed as the mould, because highly hydrophilic PHEMA tends to adhere to hydrophilic moulds such as glass. A pair of PTFE sheets ($120 \times 120\,\text{mm}^2$) having a PTFE spacer (0.8 mm thick) were backed by two glass plates and clipped together. Crosslinker-free HEMA monomer containing 0.1 mol% DPDS, as a photoinitiator, was poured into the space between the PTFE sheets. (HEMA forms an infinite network even without any crosslinker because the alcoholic hydroxyl group of HEMA is easily subjected to chain transfer during polymerization[6–8].) The HEMA monomer was irradiated by a high pressure Hg lamp for 48 h to form a crosslinked PHEMA plate. The PHEMA plate prepared was extracted to remove impurities such as unreacted monomer in a Soxhlet extractor with DMF for 24 h. The PHEMA plate was stored in DMF being swollen until the preparation of the IPNs.

Preparation of PHEMA←PS IPNs. The designation 'PHEMA←PS IPN' indicates an IPN prepared by a SIPN method, i.e. styrene monomer swollen into the PHEMA plate, and polymerized *in situ*. However, styrene monomer could not swell a crosslinked PHEMA, because styrene is a hydrophobic monomer and PHEMA is a hydrophilic polymer. As described in our previous paper[5], DMF was employed as a common solvent to impregnate the styrene monomer into the PHEMA plate.

Styrene monomer containing 0.1 mol% DPDS and 0 or 1.0 mol% DVB, as crosslinker, were mixed with DMF. The styrene monomer concentration was 30, 40, 50 or 60 vol%. The PHEMA plate swollen with DMF was soaked in this solution and left to swell at 25°C for 24 h. Then the swollen PHEMA was put between a pair of PTFE sheets backed by soft glass plates, and irradiated by a high pressure Hg lamp to form PHEMA←PS IPN. The irradiation was carried out in air for most of the IPNs. A water filter was placed between the high pressure Hg lamp and the swollen PHEMA gel to absorb the i.r. rays which raise the temperature of the polymerization system. This filter was made up of two Pyrex glass plates (3 cm apart). Cold water circulating between the glass plates absorbed the i.r. rays. The IPNs prepared were extracted in a Soxhlet extractor with DMF for 24 h, followed by extraction with acetone, and were dried at 70°C for 24 h in vacuo.

Measurements

Monomer unit composition of bulk IPNs. Monomer unit compositions of the IPNs were determined by Fourier transform i.r. (*FT*i.r.) spectroscopy. The specimens were prepared by a KBr method. About 2 mg of a bulk IPN and 200 mg of KBr powder were used for the preparation of a KBr tablet (13 mm diameter). The measurements were carried out on a *FT*i.r. spectrometer (Jasco, FT/IR-8000). The ratio of the optical density characteristic of PHEMA ($1728\,\text{cm}^{-1}$) and PS ($698\,\text{cm}^{-1}$) was converted into the mole fraction of the monomer unit of the two polymers in the IPN using the individual molar absorption coefficients at the two absorptions. The characteristic molar absorption coefficients of PHEMA at $1728\,\text{cm}^{-1}$ and of PS at $698\,\text{cm}^{-1}$ were 8.0 and $9.3\,\text{m}^2\,\text{mol}^{-1}$, respectively, as evaluated for the corresponding homopolymers.

Transmission electron microscopy (TEM). The IPNs were cut into thin sections by an ultramicrotome (Jeol, JUM-7) with an artificial sapphire knife (Sunkay Laboratories Inc., Crystome ASM-45) attached to it. The specimens (0.1 μm thick) were treated with osmium tetraoxide vapour in order to stain the hydrophilic microdomains of PHEMA selectively. The phase structure was observed by a transmission electron microscope (Jeol, JEM-200CX) at an accelerating voltage of 80 kV.

Scanning electron microscopy (SEM). The IPN plate was cooled in liquified nitrogen and was fractured into two pieces. The fracture surface was coated with Au (5 nm) using an ion sputtering apparatus (Jeol, JFC-1500) and observed by a scanning electron microscope (Jeol, JSM-820).

Depth profile of an IPN. Monomer unit composition as a function of the depth from the surface was estimated by micro KBr/*FT*i.r. measurement. Approximately 5 μg of the sample was scraped from the surface of the IPN plate by a knife, and the sample was formed into a micro KBr tablet with ~1 mg KBr powder. After the *FT*i.r. spectrum of the micro KBr tablet was recorded, an arbitrary thickness (10–100 μm) of the IPN surface layer was removed by a knife. Then the sample for *FT*i.r. measurement at a certain depth from the original surface was scraped off from the new surface. The depth from the original surface was determined by measuring the thickness of the remaining IPN plate with a micrometer. A sample plate had been previously divided into two pieces. The scraping and measurement were performed on the irradiated surface for one piece, and on the back surface for another piece. The scraping and measurement were repeated until the middle layer of the IPN was exposed in each piece.

The contact angle of water on the IPN surface was measured by a sessile drop contact angle meter (Kyowa Interface Science, CA-D).

The monomer unit composition at the outermost layer of the IPN was calculated from the ratio of O_{1s} and C_{1s} determined using an X-ray photoelectron spectroscope (Surface Science instrument, S-probe). Angle-resolve studies were performed to probe the depth profile in the outermost layer of the IPN. Take-off angles of 90 and 15° were used for sampling depths of ~10 and ~1 nm, respectively. The X.p.s. measurements were carried out at five different places on the IPN surface.

Designation of the IPNs

The component polymers of an IPN are designated HX*n* ($n=0$) and SX*n* ($n=0, 1$), where H and S represent PHEMA and PS, respectively, and X*n* represents the mole per cent of crosslinker. The number at the end of the sample name describes the concentration of styrene monomer in DMF used for swelling the PHEMA. For example, the IPN 'HX0←SX0-30' consists of crosslinker-free PHEMA and PS containing 1.0 mol% DVB, and was prepared from PHEMA soaked in DMF solution containing 30 vol% styrene monomer.

RESULTS AND DISCUSSION

Bulk characteristics of the photopolymerized IPNs

Before discussing the surface peculiarities of the IPNs, the bulk characteristics of photopolymerized IPNs will

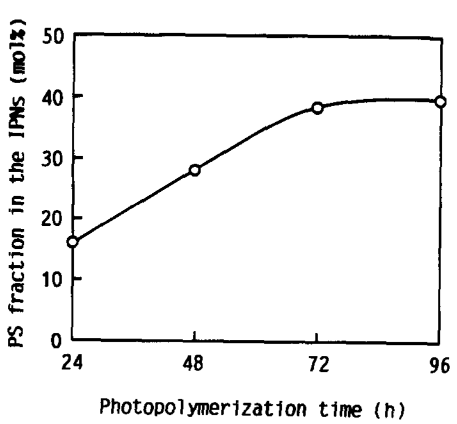

Figure 1 Change in the PS fraction in HX0←SX1-50 IPNs *versus* photopolymerization time

be compared with those of thermally polymerized ones. The photopolymerization method is a very common technique for synthesizing polymers and is widely used for preparing IPNs. It should be noted, however, that the heterogeneous reaction could occur in the case of photopolymerization due to the distribution of the incident light intensity through the irradiated system. Since the present study aims to analyse the depth profile of the IPN prepared, it is preferable that polymerization proceeds as homogeneously as possible in the irradiated gel. This requirement was able to be achieved by laying soft glass plates between the light source and the gel, and by limiting the concentration of the initiator. The soft glass plates cut off the light with a wavelength of <300 nm, and beyond which the optical density of the swollen gel plate becomes less than unity for the DPDS concentration used in the present study.

On the other hand, the rate of polymerization decreased under the experimental conditions for the homogeneous reaction. The change in the mole fraction of the PS monomer unit in the IPNs is shown in *Figure 1*. These IPNs were prepared from PHEMA gel swollen with DMF solution containing 50 vol% styrene monomer of which 1 mol% was replaced by DVB. The PS content in the IPNs increased continuously with irradiation time up to 72 h. When the PHEMA gel swollen with styrene monomer and DMF is irradiated for more than 72 h, the PS content in the IPN is not dependent on time and is ~40 mol%. It should be emphasized here that the PS content shown in *Figure 1* does not correspond to the conversion of styrene into PS. As reported by Jin *et al.*[9] and Lipatov *et al.*[10], radical polymerization during IPN formation does not suffer vitrification and the final conversion tends to reach 100% when the reaction medium is an elastic network. The saturation of the PS content shown in *Figure 1* is interpreted as being the result of the exclusion of styrene from the swollen gel during IPN formation and/or that of untrapped PS by Soxhlet extraction.

The dependence of the mole fraction of the PS monomer in the PHEMA←PS IPNs prepared by photopolymerization on the styrene concentration in the swelling agent is shown in *Figure 2*. PS in the IPNs was polymerized by irradiation for 96 h. The dependence for thermally polymerized PHEMA←PS IPNs has been reported previously and is reproduced in *Figure 2* for comparison. The effects of both styrene monomer concentration in the swelling agent and crosslinker on the PS contents in the IPNs are similar for both the photopolymerized and thermally polymerized IPNs. These effects were explained in our previous paper[5]. Regarding the above-mentioned features, the formation of an IPN proceeds in a similar manner in both photopolymerization and thermal polymerization.

A clear difference between the two polymerization systems exists in that the PS contents in the IPNs prepared by photopolymerization are higher than those prepared by thermal polymerization. This observation can be explained as follows. In the thermal polymerization system, due to the applied heat, the styrene monomer would be removed from the swollen PHEMA gel by evaporation. Additionally, the applied heat could also evaporate the common solvent (DMF), followed by shrinkage of the PHEMA gel resulting in the exclusion of styrene monomer from the gel. On the contrary, in the photopolymerization system, the styrene monomer impregnated in the swollen PHEMA gel scarcely evaporated because the polymerization system was maintained at room temperature. The shrinkage of the gel due to evaporation of DMF was also prevented.

The morphology of HX0←SX1-30 IPN photopolymerized for 96 h observed by TEM is shown in *Figure 3*. The dark area in the micrograph is the PHEMA domain. The IPN has a distinct microphase-separated

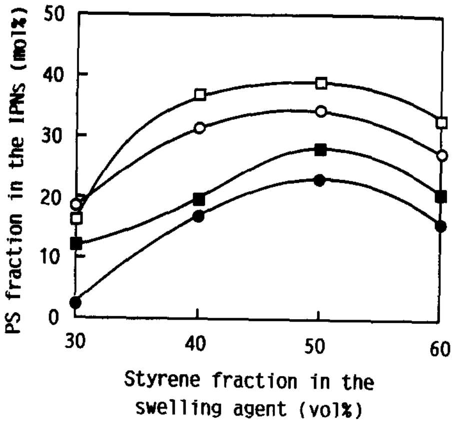

Figure 2 PS fraction in HX0←SX*n* IPNs prepared by photopolymerization for 96 h (○, □) and by thermal polymerization (●, ■). HX0←SX0 (○, ●); HX0←SX1 (□, ■)

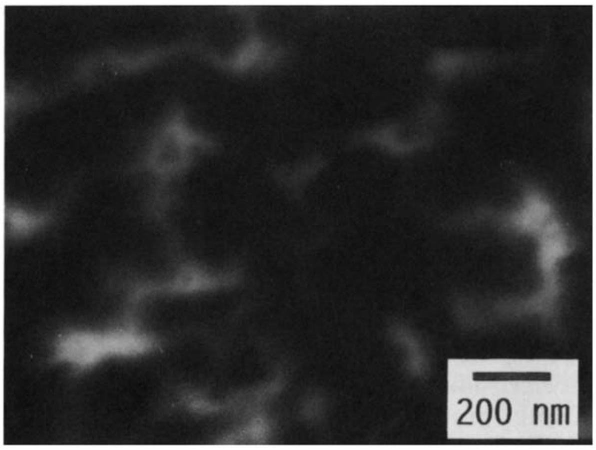

Figure 3 TEM micrograph of an ultrathin section of HX0←SX1-30 IPN photopolymerized for 96 h

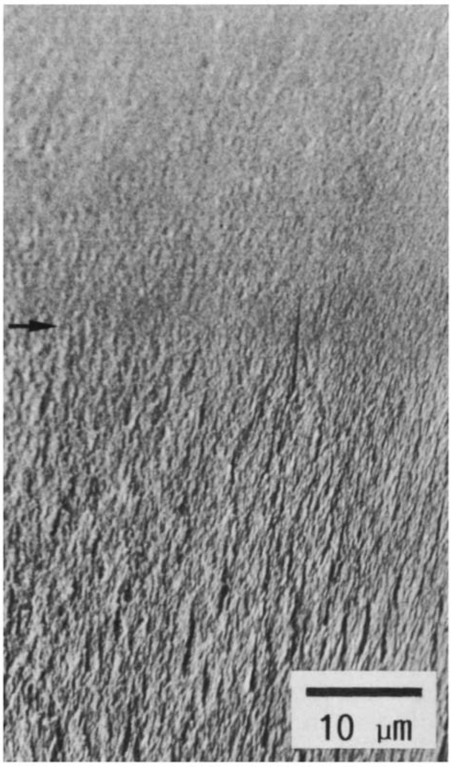

Figure 4 SEM micrograph of the fracture surface of HX0←SX0-50 IPN photopolymerized for 96 h. The irradiated side is located towards the top. The arrow indicates the depth (~100 μm) from the irradiated surface

structure, with dimensions on the order of 100 nm. The domain size is one order larger than that of the thermally polymerized HX0←SX1-30 IPN reported in our previous paper[5]. In general, the morphology of a SIPN is determined mainly by the crosslinking density of polymer I[3], but it is known to be influenced by the viscosity of the reaction system[11–13]. In the photopolymerization system, since the common solvent (DMF) did not evaporate, the viscosity of the system was low and a relatively large domain size was considered to be obtained.

Depth profile of an IPN

Observation of the fracture surface gives significant information on the composition or the structure of the IPN. *Figure 4* is a SEM micrograph of the fracture surface of the HX0←SX0-50 IPN photopolymerized for 96 h. The irradiated side of the IPN is located towards the top of the micrograph. The arrow indicates the depth (~100 μm) from the irradiated surface. As shown in *Figure 4*, the fracture surface of the outside region is relatively flat, whereas that of the inner region is rough. There is a boundary between the flat and rough regions, which corresponds to the outer and inner regions, respectively. The fracture surface of the outer region near the back side was also flat (not shown). Since the fracture surfaces of the homopolymer plates of PS and PHEMA were flat, as reported in our previous paper[5], this implies that there are some differences in composition between the outer and inner regions.

Depth profiles of the composition are shown throughout the thickness of the plates in *Figure 5* for HX0←SX1-50 IPNs photopolymerized for 48 and 96 h. The irradiated surface is set as the depth being 0 mm in the figure. The IPN was fully cured by photopolymerization for 96 h in air (see *Figure 1*). The depth profile of the thermally fully cured IPN reported in our previous paper[5] is also given in *Figure 5*. The depth profile was estimated by *FT*i.r. measurement for the IPNs scraped by the knife. It is obvious that the PS content increases continuously from the surface to a depth of ~0.1 mm in all the IPNs regardless of the polymerization method used. Therefore, a factor other than evaporation of styrene monomer from the gel should govern the formation of the gradient composition. The effect of evaporation of styrene monomer is reflected only by a decrease in composition for the thermally polymerized IPN as mentioned earlier.

With respect to the photopolymerized IPNs, attention should be paid to the following facts: the gradient composition is found in both the irradiated and the back surfaces; the intensity of the incident light is not strongly dependent on the depth through the gel; and the composition in the inner region at a depth of >0.1 mm from the surface is almost constant. With irradiation time, the composition increases in the gradient region as well as in the inner region.

A possible explanation for the formation of the gradient composition is that the polymerization of styrene is inhibited by oxygen diffused from the surfaces of the gel. In order to confirm this hypothesis, IPNs were photopolymerized in an inert atmosphere. *Figure 6* shows the monomer unit compositions of HX0←SX1-50 IPN polymerized in N_2 for 48 h. No decrease in PS content is found near the surfaces. On the contrary, the PS component is enriched in the outer layers as discussed in the following section. In addition, the bulk content of PS in the IPN is higher in N_2 atmosphere than that for the IPN polymerized in air for the same time periods used in *Figure 5* (48 h). These results lead to the conclusion that the gradient composition in the surface region was obtained by the inhibition of polymerization by oxygen diffused from the surfaces of the swollen PHEMA gel.

Recently, the so-called gradient polymer, with a composition and/or structure which varies gradually with position in the multicomponent polymer system, has been attracting attention[14–17]. Though numerous methods

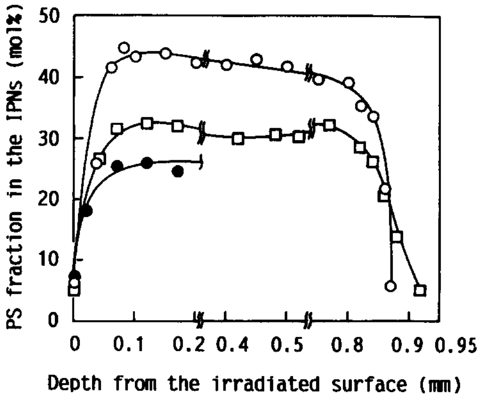

Figure 5 Depth profile of the composition of HX0←SX1-50 IPNs. The IPNs were photopolymerized in air for 48 h (□) and 96 h (○) or were fully cured by thermal polymerization for 31 h at a maximum temperature of 130°C (●). The irradiated surface is set with the depth equal to zero. PS fraction is represented throughout the thickness for the photopolymerized IPNs

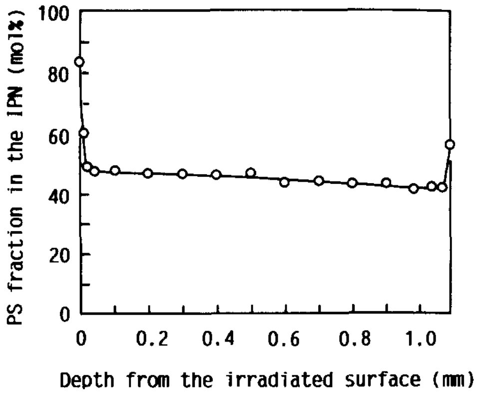

Figure 6 Depth profile of the composition of HX0←SX1-50 IPN photopolymerized in N_2 atmosphere for 48 h. The irradiated surface is set with the depth equal to zero

Table 1 PS fraction in the outermost layers of the IPNs[a] measured by X.p.s.

Polymerization atmosphere	Side[b]	Take-off angle (deg)	Sampling depth (nm)	PS fraction (mol%)
Air	Front	90	~10	23.3
	Back	90	~10	14.4
	Front	15	~1	37.7
	Back	15	~1	32.1
N_2	Front	90	~10	86.2
	Back	90	~10	69.8

[a] HX0←SX1-50 photopolymerized for 48 h

[b] 'Front' is the irradiated side and 'back' is the reverse side of the irradiated surface

have been applied to produce a gradient polymer, none of them is based on the inhibition of polymerization suggested in the present system studied. Since monomers undergoing radical polymerization are easily inhibited by many compounds, the inhibition of polymerization could be a novel method for preparing gradient polymers. The gradient structure would be controllable by choosing an appropriate species and concentration for the inhibitor as is easily done in the present system (by varying the oxygen pressure).

Depth profile in the outermost layers of an IPN

It seems strange that the PS content of HX0←SX1 IPN photopolymerized in N_2 was very high in the surface, region (to a depth of 0.02 mm) as shown in *Figure 6*. Such an enrichment of the PS component in a very thin surface layer cannot be attributed to the kinetic factors of polymerization. Moreoever, the PS content at the outermost layer was suggested to be rather high by the contact angle measurements even for the IPNs polymerized in air. The contact angles of water on the PS and PHEMA homopolymer surfaces were 90 and 45°, respectively, using the present experimental conditions, while those on the irradiated surfaces of HX0←SX1 IPNs photopolymerized in air were ~82° in spite of the fact that the PS contents at the surface region were quite low (see *Figure 5*). These results imply that a very thin PS-enriched layer is present as the outermost layer of the IPN.

In order to clarify the surface composition of the IPNs, X.p.s. analysis was performed for HX0←SX1-50 IPNs photopolymerized for 48 h. Sampling depths of ~10 and ~1 nm were accomplished using take-off angles of 90 and 15°, respectively. The surface composition of the IPNs was calculated from the atomic C and O compositions, by assuming that the O atom originates only from the PHEMA molecules. The results are summarized in *Table 1*. As regards the IPN polymerized in N_2 atmosphere, the PS contents in the irradiated and back surface regions to a depth of 10 nm are 86.2 and 69.8 mol%, respectively. These values are in good agreement with those obtained by *FT*i.r. measurements. Considering the results of the depth profile measured by *FT*i.r. and X.p.s., the outermost layer of the IPN polymerized in N_2 was a PS-enriched phase.

It is known that surface enrichment often occurs by the thermodynamical demands in a multicomponent polymer such as a blend polymer and a graft polymer[18–24]. It has been recently revealed that the chemical composition of a polymer plate surface is inclined to be determined so as to minimize the free energy on the interface to the substance with which the plate is in contact during polymerization[25]. The IPNs prepared in this study were in contact with PTFE sheet during polymerization. Since the surface free energy of PTFE sheet is extremely low, PS, which has a surface energy lower than that of PHEMA, was considered to be enriched on the IPN surface. It should be noted here that the IPNs, regardless of whether the polymerization was performed in air or N_2 atmosphere, were not as polymerized but had been subjected to Soxhlet extraction. However, considering that physical interlocking among the component polymers makes the structure of an IPN frozen in, the surface composition is not thought to be changed by extraction. Accordingly, it is considered that the PS-enriched outermost layer was formed during polymerization and was not changed by Soxhlet extraction.

On the other hand, regarding the IPN polymerized in air, the PS contents in the irradiated and the back surface regions (within a depth of 10 nm) are 23.3 and 14.4 mol%, respectively. The result agrees fairly well with the result of depth profiling by *FT*i.r. measurements, i.e. the PS content in the surface region was lower than in the inner region. However, PS contents in the surface regions (within a depth of 1 nm) are 37.7 and 32.1 mol%, respectively, for the irradiated and the back surface regions. The PS contents in the surface regions (within a depth of 1 nm) still seem small considering that the contact angles of water on the surfaces were ~82°. These values are thought to be somewhat unreliable because the unevenness of the surface scatters the experimental data in the case of low take-off angle measurements. Nevertheless, the PS content in the outermost 1 nm is regarded to be higher than the average PS content in the outermost 10 nm layer. Moreover, it should be noted that the wettability of the polymer surface is varied by the orientation of the functional groups[25]. It was reported for PHEMA film that the contact angle of water on the free surface was changed from 0 to 70° depending on the orientation of the hydroxyl and methyl groups[8]. Further investigations should be carried out to determine the composition and the structure at the surface of the IPN plates.

CONCLUSIONS

SIPNs composed of hydrophilic PHEMA and hydrophobic PS have been prepared by photopolymerization using

DMF as a common solvent. The IPNs contained more PS than the IPNs prepared by thermal polymerization, and exhibited a microphase-separated structure of the order of 100 nm. These features were considered to be brought about by preventing the evaporation of the styrene monomer and the solvent (DMF) through polymerization at room temperature.

Gradient compositions were observed in the surface region (within a depth of 0.1 mm) of the irradiated and back surfaces of the IPN prepared in air. When an IPN was polymerized in N_2 atmosphere, however, the gradient compositions were scarcely observed, and the total PS content increased. These findings indicated that the inhibition of polymerization of styrene by oxygen diffused from the swollen PHEMA gel surfaces resulted in the gradient compositions.

X.p.s. and *FT*i.r. analyses revealed that the outermost layers of the IPNs prepared in N_2 atmosphere were PS-enriched. The surface of the IPN was thought to be influenced thermodynamically by the material which was in contact with the IPN during polymerization. That is, the composition and the structure at the surface were suggested to be determined so as to minimize the surface free energy at the interface of the IPN and the highly hydrophobic PTFE sheet.

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