Hydrophobic and hydrophilic interpenetrating polymer networks composed of polystyrene and poly(2-hydroxyethyl methacrylate): 1. PS–PHEMA sequential IPNs synthesized in the presence of a common solvent

Satoshi Murayama, Shin-ichi Kuroda and Zenjiro Osawa*
Department of Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376, Japan
(Received 3 September 1992; revised 29 October 1992)

Interpenetrating polymer networks (IPNs) composed of hydrophobic polystyrene (PS) and hydrophilic poly(2-hydroxyethyl methacrylate) (PHEMA) were synthesized by a sequential IPN method, and they showed a microphase-separated structure. A common solvent, dimethylformamide, which swells the polymer I network and dissolves monomer II, was used to impregnate monomer II into the network of polymer I. The content of polymer II in the IPNs became large when the crosslink density of polymer I was low and that of polymer II was high. It was found that certain monomer II concentration in the swelling agent existed that maximized the polymer II fraction in the IPN. Contact angle and Fourier-transform infra-red measurements revealed that the polymer II content decreased gradually towards the surface of the IPNs. The gradient composition observed in the IPNs was explained by the polymerization inhibition by oxygen and the thermodynamic effect.

(Keywords: hydrophobic–hydrophilic interpenetrating polymer network; polystyrene; poly(2-hydroxyethyl methacrylate); common solvent; gradient composition)

INTRODUCTION

Polymer alloys composed of hydrophobic–hydrophilic components have received attention owing to their potential applicability as biomedical materials[1,2], membranes for separation[3,4] or selective adsorbents[5–8]. These polymer alloys have been prepared, in general, in the form of random, graft, or block copolymers in order to prevent large phase separation due to the incompatibility of the hydrophobic and hydrophilic components.

As for the biomedical applications of polymer materials, it is known that multicomponent polymers that have a microphase-separated structure exhibit good blood compatibility. Block copolymers composed of hydrophobic and hydrophilic polymers[9–11], of crystalline and non-crystalline polymers[12,13], or segmented polyurethanes[14–16] have been investigated extensively and used practically. However, it has recently been revealed that the state of multicomponent polymers is changeable depending on the environment. For example, the hydrophobic moieties of graft and/or block copolymers of hydrophobic–hydrophilic components expand at an interface to air, and so do the hydrophilic domains at an interface to water[17–21]. From the practical point of view, it is preferred that the phase structure is stable for a long period regardless of the circumstances.

The interpenetrating polymer network (IPN) is defined as a kind of polymer blend composed of two (or more) polymers in network form[22]. In analogy with other polymer alloys, IPNs often exhibit phase separation, but the structure of an IPN is frozen in by physical interlocking between the component polymers, and in favourable cases is composed of bicontinuous domains[23]. IPNs are, therefore, expected to be polymer alloys composed of highly incompatible polymer pairs with stable structure.

Simultaneous IPNs (simIPNs) and sequential IPNs (seqIPNs) are typical IPNs classified by polymerization method. Generally, a simIPN composed of highly incompatible polymer pairs has relatively large phase-separated structures, because phase separation occurs before the networks are completely formed[24]. Kim *et al.* have studied hydrophobic and hydrophilic simIPNs composed of polystyrene and polyurethane[25–28]. They concluded that a small domain size of the order of 10 nm could be obtained by applying a high pressure (10^4 kg cm^{-2}) or by lowering the polymerization temperature (0°C). As regards seqIPNs, control of the phase separation structure could be achieved more precisely than for simIPNs by varying the network structure of polymer I and the synthesis conditions of polymer II. However, polymer I could not be swollen with monomer II in the case of the combination of hydrophobic and hydrophilic polymers, regardless of whether polymer I is hydrophobic or hydrophilic. Hence, a common solvent is required, which is able to swell the

*To whom correspondence should be addressed

0032-3861/93/132845-08

polymer I network and to dissolve monomer II[24].

In this paper, IPNs composed of hydrophobic polystyrene (PS) and hydrophilic poly(2-hydroxyethyl methacrylate) (PHEMA) were synthesized by sequential polymerization using a common solvent and characterized.

EXPERIMENTAL

MATERIALS

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. 2-Hydroxyethyl methacrylate (HEMA) and ethylene glycol dimethacrylate (EGDMA) were distilled under reduced pressure. Azobisisobutyronitrile (AIBN) was recrystallized from methanol. *N,N*-Dimethylformamide (DMF) was dried over 4 Å molecular sieves for 24 h and distilled under reduced pressure.

SYNTHESES

Preparation of polymer I

Crosslinked polystyrene (PS). A pair of glass plates ($120 \times 120\ mm^2$) having a poly(tetrafluoroethylene) (PTFE) spacer (0.8 mm thick) were clipped together. Styrene monomer containing 1.0 or 4.0 mol% DVB, as a crosslinker, and 0.1 mol% AIBN, as an initiator, was poured into the space between the glass plates. The mixture was heated at 70°C for 4 h at first, then 90°C for 3 h, and finally 130°C for 24 h to form a crosslinked PS plate. The PS plate obtained was extracted to remove impurities such as unreacted monomer in a Soxhlet extractor with toluene for 24 h, and dried at 130°C for 24 h *in vacuo*.

Crosslinked poly(2-hydroxyethyl methacrylate) (PHEMA). Crosslinked PHEMA plates were similarly prepared by the procedure described in the preparation of the crosslinked PS. Since PHEMA tends to adhere tightly to a glass plate owing to its high hydrophilicity, PTFE sheets were used instead of glass plates. HEMA monomer containing 0 or 1.0 mol% EGDMA, as a crosslinker, and 0.1 mol% AIBN was poured into the space between the PTFE sheets backed by glass plates. HEMA forms an infinite network even without any crosslinker because the alkyl alcohol group of HEMA is easily subject to chain transfer during polymerization[29]. The HEMA monomer was heated at 70°C for 4 h at first, then 90°C for 3 h, and finally 130°C for 24 h to form a crosslinked PHEMA plate. After Soxhlet extraction with methanol, the plates were dried at 130°C for 24 h *in vacuo*.

Preparation of the IPNs

IPNs were prepared by a sequential IPN method, i.e. monomer II was permeated into polymer I and polymerized *in situ*. However, HEMA monomer could not swell a crosslinked PS, because PS is a hydrophobic polymer and HEMA is a hydrophilic monomer. Conversely, the crosslinked PHEMA could not be swollen with styrene monomer. Monomer II, therefore, required a common solvent to be incorporated into polymer I. DMF was employed as a common solvent, since it dissolves both styrene and HEMA monomers and swells crosslinked PS and PHEMA.

The designation 'PS←PHEMA IPN' indicates the IPN that contains PS as polymer I and PHEMA as polymer II. Similarly, the designation 'PHEMA←PS IPN' indicates the IPN that contains PHEMA and PS as polymers I and II, respectively.

PS←PHEMA IPNs. HEMA monomer containing 0, 1.0 or 4.0 mol% EGDMA and 0.1 mol% AIBN was mixed with DMF. The concentrations of HEMA monomer were 10, 30 or 50 vol%. The PS plate prepared previously was soaked in the monomer solution and left to swell at 25°C for 24 h. To obtain higher content of the second component, it is preferable to attain a higher degree of swelling. The degree of swelling at high temperature is higher than at low temperature. Though a high temperature is suitable, a temperature higher than 40°C leads to decomposition of AIBN. Consequently, the swelling temperature was maintained at 25°C. Then the swollen PS was placed between the PTFE sheets and heated at 70°C for 4 h at first, then 90°C for 3 h, and finally 130°C for 24 h to form PS←PHEMA IPN. The prepared IPN was extracted in a Soxhlet extractor with toluene for 24 h and dried at 130°C for 24 h *in vacuo*.

PHEMA←PS IPNs. The PHEMA←PS IPNs were similarly prepared by the procedure described for the preparation of PS←PHEMA IPNs. The fraction of DVB was 0 or 1.0 mol%. The concentrations of styrene monomer in DMF were 30, 40, 50 or 60 vol%.

MEASUREMENTS

Degree of swelling for homopolymers

The crosslinked homopolymer plates of PS or PHEMA ($1 \times 2\ cm^2$) were immersed into sample tubes, containing DMF solution of HEMA or styrene. The concentration of monomer in the solution ranged from 0 to 100 vol%. The sample tubes were kept at 25°C. After swelling equilibrium was attained, which took about 24 h, the swollen gels were taken out of the sample tubes, wiped with a filter paper and weighed. The degree of swelling was defined as the weight ratio of swollen gel and that of dried polymer.

Monomer unit composition

Monomer unit compositions of the IPNs were determined by means of *FT*i.r. spectroscopy. The specimens for the measurements were prepared by the KBr method. About 2 mg of 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 an *FT*i.r. spectrometer (Jasco, FT/IR-8000). The ratio of the two optical densities that are characteristic of PS ($698\ cm^{-1}$) and PHEMA ($1728\ cm^{-1}$) was converted into the mole fraction of the monomer units of the two polymers in the IPN using the individual molar absorptivities at the two absorptions.

Transmission electron microscopy (TEM)

The IPNs were cut into thin sections by an ultramicrotome (JEOL, JUM-7) to which an artificial sapphire knife (Sunkay Laboratories Inc., Crystome ASM-45) was attached. These specimens of 0.1 nm thickness were treated with osmium tetraoxide vapour

in order to stain selectively the hydrophilic microdomains of PHEMA. The microphase-separated structures were observed by a transmission electron microscope (JEOL, JEM-200CX) at 80 kV of accelerating voltage.

Dynamic viscoelasticity

The dynamic viscoelastic measurements were made by a dynamic viscoelastic meter (Toyoseiki, Rheolograph Solid) from room temperature to 180°C at a heating rate of 2°C min^{-1}.

Scanning electron microscopy (SEM)

The sample plates of the homopolymers and the IPNs were cooled in liquid nitrogen and were fractured into two pieces. The fracture surface was coated with Au (5 nm) using a quick autocoater (JEOL, JFC-1500) and observed by a scanning electron microscope (JEOL, JSM-820).

Depth profile

In order to clarify the changes in the hydrophilicity and the monomer unit composition from the surface to the inner region, contact angle of water and *FT*i.r. measurements were carried out for the surface of the as-prepared IPN and the IPN that was ground to the required thickness. The contact angle of water was measured with a sessile drop contact angle meter (Kyowa Interface Science, CA-D). Monomer unit composition was determined by *FT*i.r. with a micro KBr method using about 1 mg of KBr powder. First, the measurements were carried out for the as-prepared IPN surface. Then, the surface layer was removed by a cutter knife until the prescribed thickness of the IPN was attained. The new surface was polished by sandpaper and finished by a cloth woven with ultrafine fibres (Toray, Toraysee). The thickness of the IPN that remained was measured by a micrometer. The grinding and measurements were repeated until the middle layer of the IPN was exposed.

Designation of the samples

The components of polymer I are designated SX*n* ($n=1$, 4) or HX*n* ($n=0$, 1), where S and H represents PS and PHEMA, respectively, and X*n* represents the mole percentage of the crosslinker. The designation of polymer II is the same as above. Swelling conditions are represented by the figure at the end of sample name. This figure describes the concentration of monomer II in DMF. For example, the IPN 'SX1←HX0–30' consists of PS containing 1 mol% of DVB and PHEMA with no EGDMA, and was prepared from PS that was soaked in DMF solution containing 30 vol% of HEMA monomer.

RESULTS AND DISCUSSION

Control of the amount of monomer II fed into polymer I by swelling

Figure 1a shows the degree of swelling for PS homopolymers as a function of the HEMA monomer fraction in the DMF solution, and *Figure 1b* shows the degree of swelling for PHEMA homopolymers as a function of the styrene monomer fraction in the DMF solution. In both cases, the degree of swelling decreases with increase in the fraction of monomer II, and polymer I is not swollen at all with pure monomer II. It is clear that the mixed solvent composed of DMF and

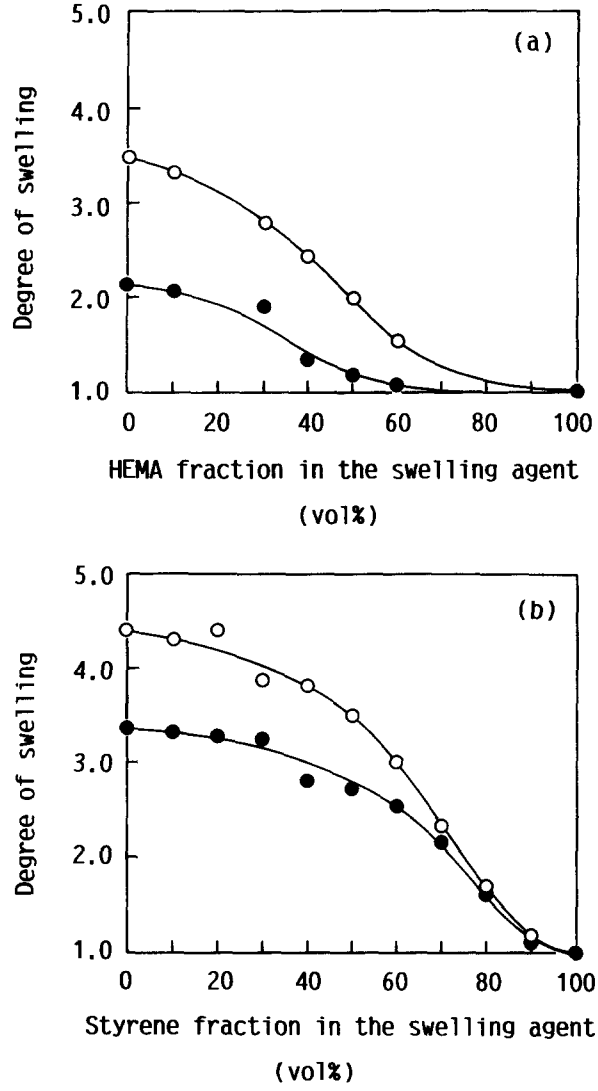

Figure 1 Degree of swelling for (a) PS swollen with HEMA/DMF, (○) SX1, (●) SX4, and for (b) PHEMA swollen with styrene/DMF, (○) HX0, (●) HX1

monomer II becomes poorer for swelling of polymer I with increasing monomer II concentration. Furthermore, the degree of swelling is also affected by the crosslink density of the homopolymers. These results suggest that a common solvent for polymer I and monomer II is required to synthesize the seqIPN consisting of hydrophilic and hydrophobic polymers.

Figure 2 shows the monomer II content in the swollen gel, for the two cases. These values were calculated from the degree of swelling shown in *Figure 1*, and represent the mole fraction of monomer II per monomer unit of polymer I. The maximum content of the HEMA fraction in a swollen PS network is obtained when the swelling agent contains 30–40 vol% of HEMA. The content of styrene fraction in a swollen PHEMA network is maximum when the styrene fraction in the swelling agent is 50–60 vol%. From the results mentioned above, the composition of the two polymers in an IPN could be controlled by the fraction of monomer II in the swelling agent and the crosslink density of polymer I.

Monomer unit compositions for the IPNs

Representative *FT*i.r. spectra of a PS←PHEMA IPN and a PHEMA←PS IPN are shown in *Figures 3a*

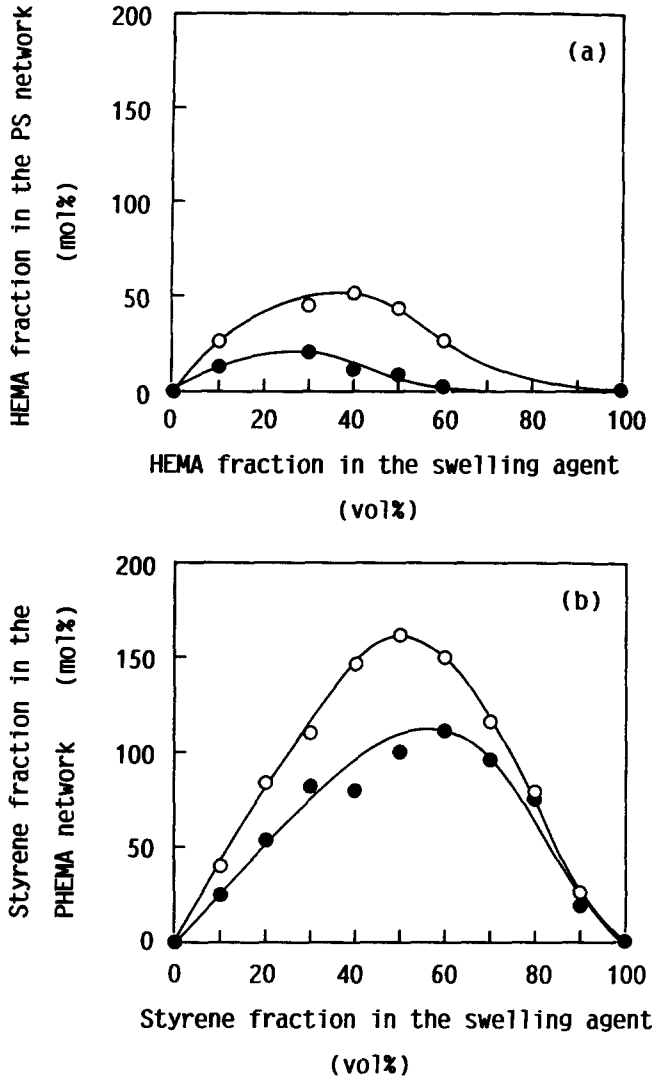

Figure 2 Contents of (a) HEMA monomer in PS gel, (○) SX1, (●) SX4, and of (b) styrene monomer in PHEMA gel, (○) HX0, (●) HX1, calculated from the value of degree of swelling

and *3b*, respectively. Among the characteristic absorption peaks of PS and PHEMA, the two peaks at 698 cm^{-1} (due to ring deformation vibration of the monosubstituted benzene) and 1728 cm^{-1} (due to C=O stretching vibration of the ester groups) were used to estimate the concentration of PS and PHEMA in the IPN. The optical density ratios of the two peaks were converted into mole fractions of the monomer units by using their molar absorptivities. The molar absorptivity of PS at 698 cm^{-1} was 9.3 $m^2 mol^{-1}$, and that of PHEMA at 1728 cm^{-1} was 8.0 $m^2 mol^{-1}$, which were evaluated for the corresponding homopolymers by the KBr method.

The dependence of monomer II concentration in the swelling solution on polymer II fraction in the IPN is illustrated in *Figure 4*. *Figures 4a* and *4b* show the mole fractions of PHEMA in the PS←PHEMA IPNs and those of PS in the PHEMA←PS IPNs, respectively. It is obvious that the polymer II contents in the IPNs based on weakly crosslinked polymer I (SX1 or HX0) are higher than those in the IPNs based on highly crosslinked polymer I (SX4 or HX1). The results should be readily expected from *Figure 2*; namely, the IPN based on the highly crosslinked polymer I is swollen to a low extent by the monomer II solution, leading to the low polymer II content in the IPN formed.

The polymer II content in the IPN was strongly affected by the monomer II concentration in the DMF solution. As shown in *Figure 4a*, maximum PHEMA contents in the PS←PHEMA IPNs are observed when the HEMA monomer concentration is 30 vol%. On the other hand, when the styrene monomer concentration is 50 vol%, PS contents in the PHEMA←PS IPNs are maximum except HX1–SX0 (see *Figure 4b*). These results reflect the monomer II content in the swollen gel shown in *Figure 2*.

The polymer II contents also varied according to the presence of crosslinked structure (see *Figures 4a* and *4b*). The uncrosslinked polymer II gave a lower content of polymer II in the IPNs than the crosslinked one. This result implies that the rates of removal and gelation of monomer II affect the content of polymer II. The monomer II that contains the crosslinker forms a gel rapidly compared with that which does not contain crosslinker. And the monomer II is removed gradually from the gel by evaporation or by exclusion due to the gel's shrinkage during polymerization. Gelation and removal of monomer II are thought to be competitive processes for determining the polymer II content in the IPN, and hence monomer II containing no crosslinker was lost from the swollen polymer I to a larger extent than that containing the crosslinker.

Mole fraction of polymer II can be controlled in the range of 0 to 50 mol% in both cases of PS←PHEMA and PHEMA←PS IPNs. Consequently, an IPN with any composition can be prepared when one chooses the kind of polymer I, the crosslink density of polymers I and II, and the concentration of monomer II in the DMF solution. The effects of the gelation rate on the composition, the morphology and the viscoelastic

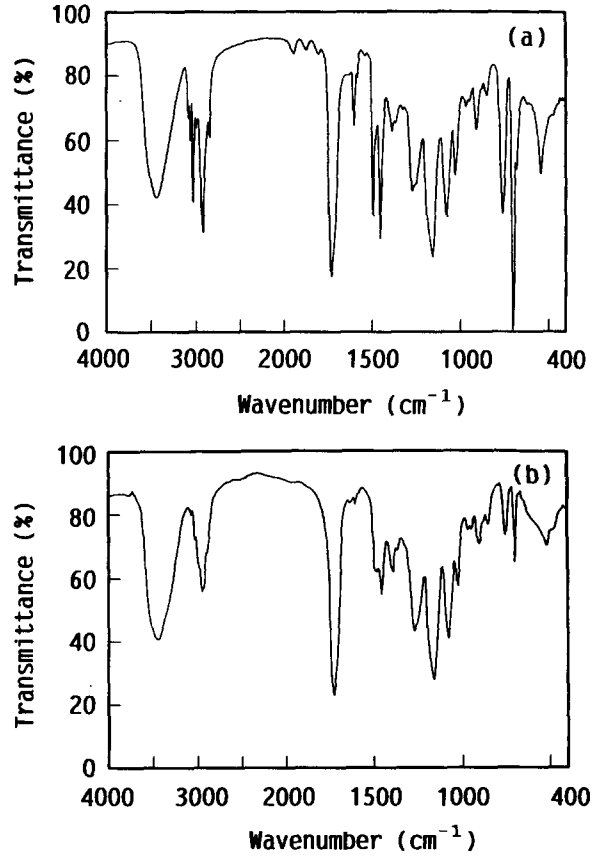

Figure 3 *FT*i.r. spectra of (a) PS←PHEMA IPN and (b) PHEMA←PS IPN

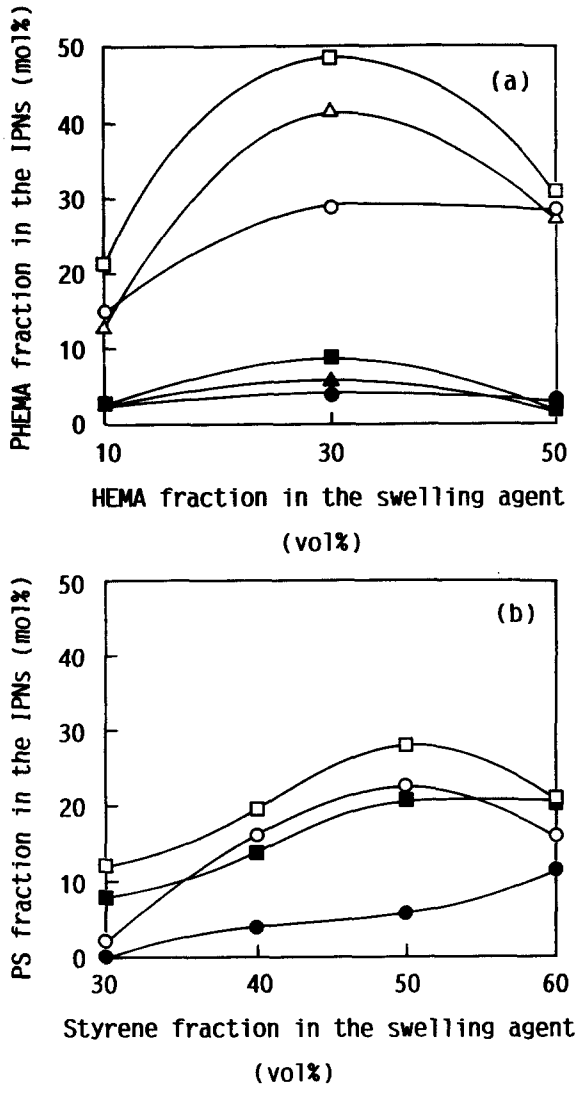

Figure 4 Monomer unit fraction of (a) PHEMA in PS←PHEMA IPNs, (○) SX1–HX0, (□) SX1–HX1, (△) SX1–HX4, (●) SX4–HX0, (■) SX4–HX1, (▲) SX4–HX4, and of (b) PS in PHEMA←PS IPNs, (○) HX0–SX0, (□) HX0–SX1, (●) HX1–SX0, (■) HX1–SX1

properties of the IPNs formed will be reported in detail in later sections.

It should be noted here that there is a limitation on the polymer II content in the IPN due to the swelling capacity of the polymer I network. It is generally assumed in the commonly prepared IPNs, especially in simIPNs, that the component polymers' compositions are equal to the compositions of the monomers charged in the mould[22]. The morphology of the polymer formed is, however, able to show a large, discontinuous phase separation when an excess amount of monomer II is in the feed.

Evidence of IPN formation

Figure 5 shows the TEM photograph of a representative PS←PHEMA IPN (SX1←HX4-30). As osmium tetraoxide vapour stains selectively the PHEMA domain, the black area is the PHEMA domain and the white is PS. The photograph represents the inner region of the IPN plate. The PS←PHEMA IPN has microphase-separated structure, the domain size of which is of the order of 10 nm. As regards the PHEMA←PS IPN, microphase-separated structure of the order of 10 nm was not observed. Probably, the domain size of PHEMA←PS IPN was not larger than that of PS←PHEMA IPN. Such a fine domain size is one piece of evidence that these samples consisting of hydrophobic and hydrophilic polymers are not simple polymer blends but IPNs, because polymer blends of such a combination should have larger domain size[30].

The results of the dynamic viscoelastic measurements also supported IPN formation. The temperature dependence of the mechanical loss tangent (tan δ) of SX1, HX1 and SX1←HX4-30 are shown in *Figure 6*. The tan δ curve of SX1←HX4-30 has a broad peak in the α dispersion regions of PS and PHEMA homopolymers. There seem to be some interactions between PHEMA and PS domains[31].

Depth profile of the IPNs

SEM photographs of the fracture surfaces of the homopolymers and the IPNs are shown in *Figure 7*. In the PS homopolymer, there is no difference between the fracture surfaces of the outside (*Figure 7a*) and the inner region (not shown). The surfaces are uneven, but the roughness is very small. The surface of the PHEMA homopolymer is similar to that of PS, and the outside

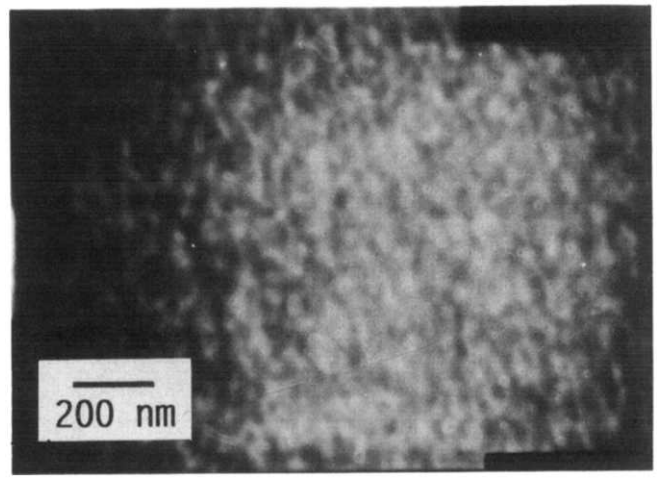

Figure 5 TEM photograph of PS←PHEMA IPN

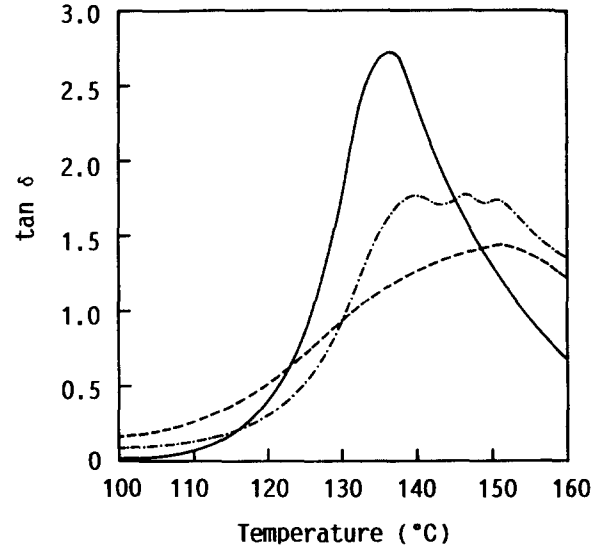

Figure 6 Tan δ curves of (——) SX1, (– – –) HX1 and (–·–·–) SX1←HX4-30

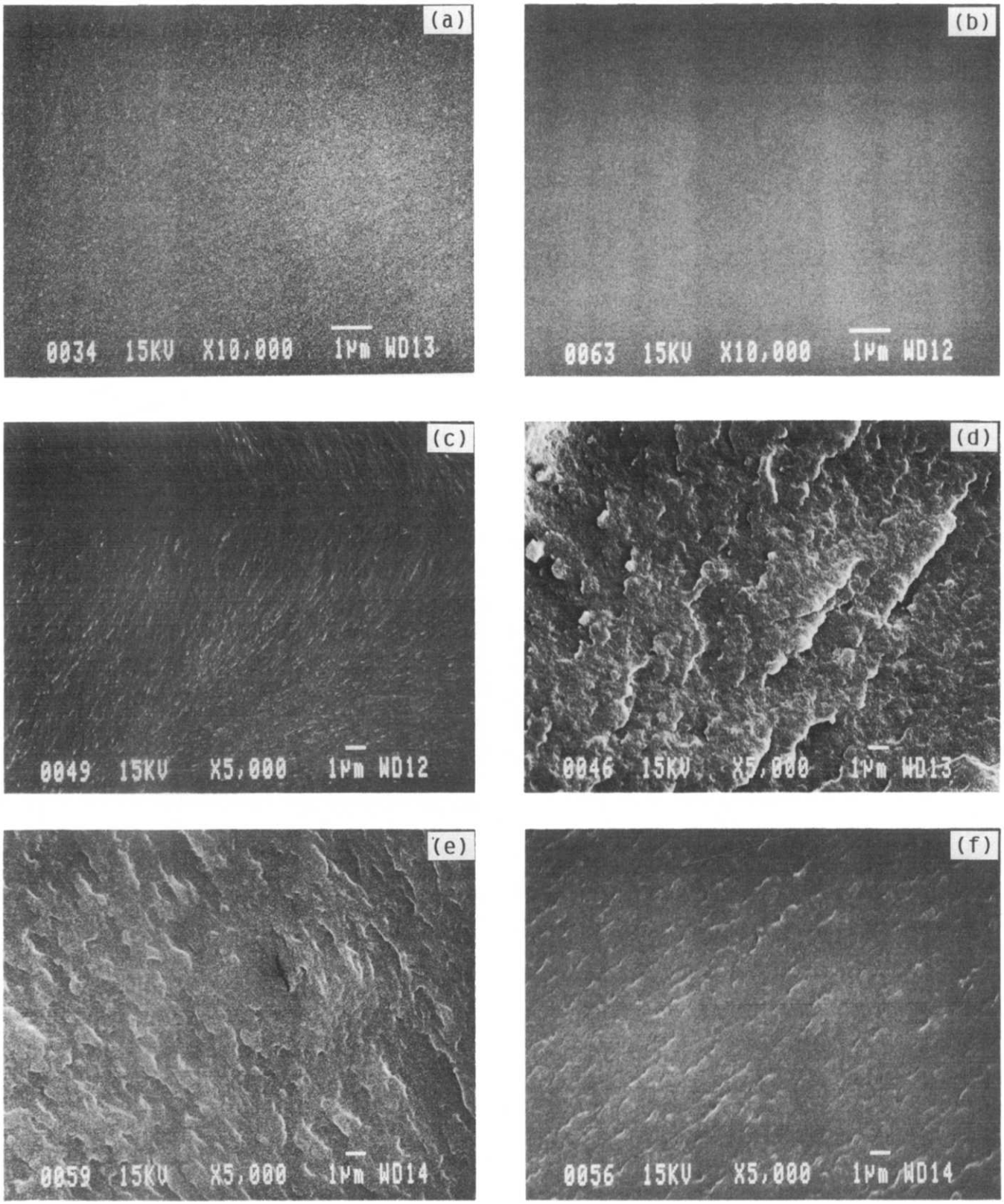

Figure 7 SEM photographs of fracture surfaces of (a) outside region of PS, (b) outside region of PHEMA, (c) outside and (d) inner region of PS←PHEMA IPN and (e) outside and (f) inner region of PHEMA←PS IPN

(*Figure 7b*) and the inner region (not shown) have the same fracture surface.

Figures 7c and *7d* show the fracture surfaces of the outside and the inner region of a PS←PHEMA IPN, respectively. The surface of the inner region is very rough and there are small dimples on the surface. On the other hand, there is no small dimple on the surface of the outside region. *Figures 7e* and *7f* show the fracture surfaces of the outside and the inner region of a PHEMA←PS IPN, respectively. In contrast to the PS←PHEMA IPN, the fracture surface of the inner region of the PHEMA←PS IPN is rough compared with the outside region. The results suggest that the composition of the two components differs between the

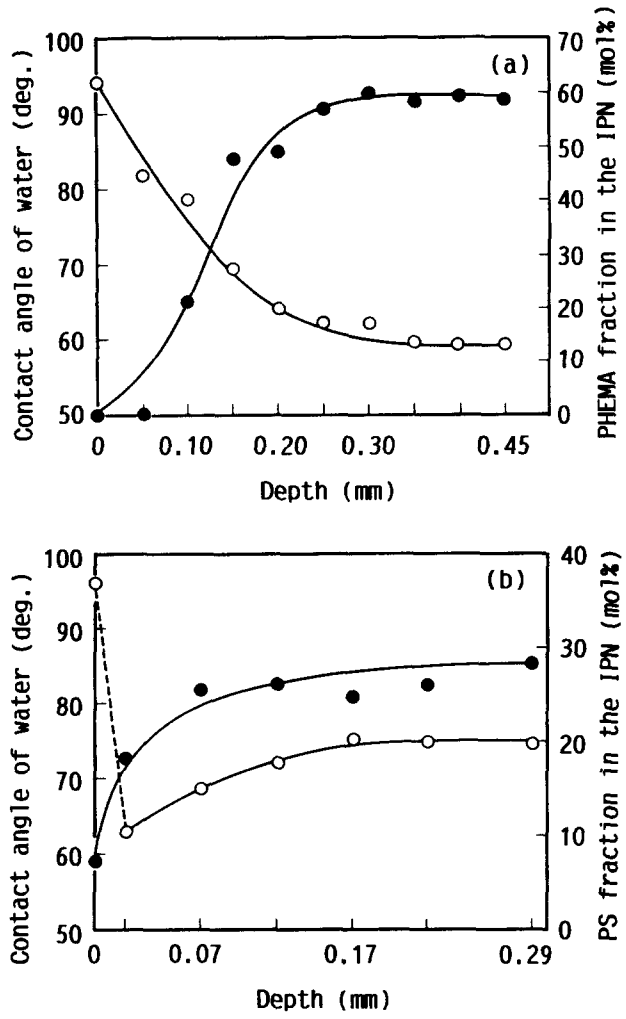

Figure 8 Depth profile of (a) the PS←PHEMA IPN and (b) the PHEMA←PS IPN; (○) contact angle of water, (●) monomer unit fraction of polymer II

outside and the inner region, i.e. a kind of gradient polymer material can be made by the sequential IPN polymerization method using a common solvent.

Figure 8a shows the PHEMA fraction and the contact angle of water as a function of depth from the surface of the PS←PHEMA IPN (0.9 mm thick). The total content of the PHEMA monomer unit in this IPN was about 30 mol%. The content of PHEMA is nearly zero at the surface region. The contact angle at the surface is 94°, which is approximately the same value as for the crosslinked PS (95°, SX1). Consequently, it is apparent that the surface region of the IPN contains PS only.

The content of PHEMA increases with increase in depth from the surface and reaches about 60 mol% at 0.3 mm depth. In the region deeper than 0.3 mm, the PHEMA content is held constant around 60 mol%. On the other hand, the contact angle decreases with increase in depth and is constant around 59° in the inner region of the IPN. The decrease in contact angle could be attributed to the increase in the content of the hydrophilic PHEMA.

Figure 8b shows the PS fraction and the contact angle of water as a function of the depth of PHEMA←PS IPN (0.6 mm thick). The total content of PS monomer unit in this IPN was about 20 mol%. PS content is about 7 mol% at the surface region and increases with increase in depth. In the region deeper than 0.1 mm, PS content is held at 25–30 mol%. The contact angle increases with increase in depth and this value corresponds to the composition of PS and PHEMA. That is, the increase in contact angle results from the increase in the fraction of PS followed by the enlarging of the hydrophobic area.

At the surface of the PHEMA←PS IPN, however, the contact angle is 96°. This value corresponds to that for the crosslinked PS, but the mole fraction of PS is estimated to be about 7 mol% by the *FT*i.r. analysis. Since the contact angle is influenced only by the very surface, but the *FT*i.r. measurement reflects the approximately 1 μm layer near the surface, it was suggested that a very thin layer of PS existed on the surface of the PHEMA←PS IPN. Formation of this layer is ascribed to the use of extremely hydrophobic PTFE sheets during polymerization of the IPNs. It has been found that the chemical composition of a polymer is determined so as to minimize the free energy at the interface to the 'atmosphere' in contact with it when the polymer is formed[32–40]. Since the surface free energy of PTFE is low, PS with a low surface free energy might aggregate on the surface of the IPN.

In both systems of IPNs, the content of polymer II increases gradually with increase in depth from the surface as opposed to the gradient IPN previously reported by Sperling *et al.*[41]. Two factors were regarded as the reason why such a gradient IPN was obtained. First, monomer II in the swollen gel evaporated together with DMF by applied heat during polymerization even after the volume of the gel was nearly fixed. Secondly, oxygen, which diffused into the gel from the surface, inhibited the polymerization of monomer II. In order to clarify the reason, polymerization of polymer II was carried out under N_2 atmosphere. The IPN polymerized in this way was found to have only a slight gradient of composition. The results apparently support the idea that the formation of the gradient IPN is due to polymerization inhibition by diffused oxygen. Detailed studies on the formation mechanism of the gradient IPN will be reported in a subsequent paper.

CONCLUSIONS

Sequential IPNs composed of hydrophobic PS and hydrophilic PHEMA have been successfully prepared using DMF as a common solvent. The polymer II contents in the bulk IPNs could be arbitrarily controlled through the choice of the kind of polymer I, the crosslink densities of polymers I and II, and the concentration of monomer II in the DMF solution.

The IPNs prepared had microphase-separated structures. The tan δ curve of the IPN had a broad peak in the α dispersion region of PS and PHEMA. These observations manifested the presence of an interaction between the two phases. The contact angle and the *FT*i.r. measurements revealed that the polymer II contents decreased gradually on approaching the surface of the IPNs. Polymerization inhibition of monomer II by diffused oxygen from polymer I gel swollen with monomer II and DMF was regarded to be the primary reason for the gradient composition. It was also suggested that the surface composition of an IPN was influenced thermodynamically by the material in contact with the IPN during polymerization.

ACKNOWLEDGEMENTS

The authors are grateful to Nippon Polyurethane Industry Co. Ltd for financial support.

REFERENCES

1 Shalaby, S. W., Hoffman, A. S., Ratner, B. D. and Horbett, T. A. (Eds) 'Polymers as Biomaterials', Plenum Press, New York, 1984
2 Sakurai, Y., Akaike, T., Kataoka, K. and Okano, T. 'Biomedical Polymers', Academic Press, New York, 1980
3 Kesting, R. E. 'Synthetic Polymeric Membranes, A Structural Perspective', Wiley, New York, 1985
4 Lee, Y. K. and Kim, S. C. *Polym. Bull.* 1988, **20**, 261
5 Schmitt, A., Varoqui, R., Uniyal, S., Brash, J. L. and Pusiner, C. *J. Colloid Interface Sci.* 1983, **92**, 25
6 Brash, J. L., Uniyal, S., Pusiner, C. and Schmitt, A. *J. Colloid Interface Sci.* 1983, **92**, 28
7 Kataoka, K., Sakurai, Y. and Tsuruta, T. *Makromol. Chem., Chem. Suppl.* 1985, **9**, 53
8 Kataoka, K., Okano, T., Sakurai, Y., Nishiyama, T., Inoue, S., Watanabe, T., Maruyama, A. and Tsuruta, T. *Eur. Polym. J.* 1983, **19**, 979
9 Shimada, M., Miyahara, M., Tahara, H., Shinohara, I., Okano, T., Kataoka, K. and Sakurai, Y. *Polym. J.* 1983, **15**, 649
10 Hirao, A., Kata, H., Yamaguchi, K. and Nakahama, S. *Macromolecules* 1986, **19**, 1294
11 Okano, T., Katayama, M. and Shinohara, I. *J. Appl. Polym. Sci.* 1978, **22**, 369
12 Yui, N., Sanui, K., Ogata, N., Kataoka, K., Okano, T. and Sakurai, Y. *J. Biomed. Mater. Res.* 1986, **20**, 929
13 Yui, N., Kataoka, K. and Sakurai, Y. *Medical Progress Through Technology* 1987, **12**, 221
14 Lyman, D. J., Knutson, K., McNeil, B. and Shibatani, K. *Trans. ASAIO* 1975, **21**, 49
15 Takahara, A., Tashita, J., Kajiyama, T., Takayanagi, M. and MacKnight, W. J. *Polymer* 1985, **26**, 978
16 Takahara, A., Tashita, J., Kajiyama, T., Takayanagi, M. and MacKnight, W. J. *Polymer* 1985, **26**, 987
17 Tezuka, Y., Fukushima, A., Matsui, S. and Imai, K. *J. Colloid Interface Sci.* 1986, **114**, 16
18 Tezuka, Y., Ono, T. and Imai, K. *J. Colloid Interface Sci.* 1990, **136**, 408
19 Tezuka, Y., Kazama, H. and Imai, K. *J. Chem. Soc., Faraday Trans.* 1991, **87**, 147
20 Tezuka, Y., Okabayashi, A. and Imai, K. *J. Colloid Interface Sci.* 1991, **141**, 586
21 Ito, M., Hirao, A., Nakahama, S., Ratner, B. D. and Lewis, K. B. *Polym. Prepr. Japan* 1992, **41**, 1519
22 Sperling, L. H. 'Interprenetrating Polymer Networks and Related Materials', Plenum Press, New York, 1981
23 Lipatov, Y. S. in 'Advances in Interpenetrating Polymer Networks', (Eds D. Klempner and K. C. Frisch), Technomic Publishing, Lancaster, PA, 1989
24 Kim, S. K. and Kim, S. C. *Polym. Bull.* 1990, **23**, 141
25 Lee, D. S. and Kim, S. C. *Macromolecules* 1984, **17**, 2193
26 Lee, D. S. and Kim, S. C. *Macromolecules* 1984, **17**, 2222
27 Lee, J. H. and Kim, S. C. *Macromolecules* 1986, **19**, 644
28 Kim, B. S., Lee D. S. and Kim, S. C. *Macromolecules* 1986, **19**, 2589
29 Gregonis, D. E., Russell, G. A., Andrade, J. D. and deVisser, A. C. *Polymer* 1978, **19**, 1279
30 Yeo, J. K., Sperling, L. H. and Thomas, D. A. *Polymer* 1983, **24**, 307
31 Lipatov, Y. S. *J. Macromol. Sci.-Rev. Macromol. Chem. Phys. (C)* 1990, **30**, 209
32 Ratner, B. D. 'Physicochemical Aspects of Polymer Surfaces' (Ed. K. L. Mittal), Plenum Press, New York, 1983
33 Ray, B. R., Anderson, J. R. and Scholz, J. J. *J. Phys. Chem.* 1958, **62**, 1220
34 Bhatia, Q. S., Pan, D. H. and Koberstein, J. T. *Macromolecules* 1988, **21**, 2166
35 Chaikov, E. L. and Merrill, E. W. *J. Colloid Interface Sci.* 1990, **137**, 340
36 Hirasawa, E. and Ishimoto, R. *J. Adhesion Soc. Japan* 1982, **18**, 247
37 Thomas, H. R. and O'Malley, J. J. *Macromolecules* 1979, **12**, 323
38 Coulon, G., Russell, T. P., Deline, V. R. and Green, P. F. *Macromolecules* 1989, **22**, 2581
39 Kajiyama, T., Teraya, T. and Takahara, A. *Polym. Bull.* 1990, **24**, 331
40 Tsuchida, M. and Osawa, Z. *Polym. Prepr. Japan* 1992, **41**, 1515
41 Sperling, L. H. and Thomas, D. A. US Patent 3833404, 1974