

콜로이드방법을 이용한 친수성-친유성 복합막의 제조와 투과증발에 대한 응용연구

박 준 서

안성산업대학교 화학공학과

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A Colloidal Pathway to Hydrophilic-Hydrophobic Polymer Composites; Preparation of Composites and Studies on the Their Permselectivity to Organic Liquids

Jun Seo Park

Department of Chemical Engineering, Ansung National University, Ansung 456-749, Korea

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요약: 분산상인 친유성 단량체가 연속상인 친수성 단량체에 분산되어 있고 분산상의 부피분율이 0.74이상인 O/W 고농축에멀션을 적당한 조건에서 반응을 시켜서 친수성-친유성 고분자복합재료를 합성하였다. 분산상과 연속상사이의 계면장력에 관한 연구를 통하여 중합시 고농축에멀션의 안정성에 미치는 요인을 조사하였다. 친수성 액체와 친유성 액체사이 계면장력의 차이가 클수록 보다 안정된 고농축에멀션을 얻었다. 두 종류의 계면활성제들을 적절하게 혼합하거나 계면활성제와 긴 사슬을 갖은 알콜과의 혼합으로 기계적으로 강한 계면필름을 형성하여 에멀션의 안정성을 증대시킨다. 분산상인 폴리스티렌과 연속상으로 폴리아크릴아미드로 이루어진 친수성-친유성 복합고분자는 유기혼합물에 높은 선택성을 보였다. 투과증발실험을 한 결과 친수성-친유성 복합막은 톨루엔-시클로헥산 혼합물에서 톨루엔에 대해 선택도는 4.8-8.1를 나타내었으며 혼합물의 온도가 낮거나 혼합물에서 톨루엔의 농도가 높을수록 증가하였다.

ABSTRACT: Hydrophilic-hydrophobic composites were synthesized starting from an oil-in-water (o/w) concentrated emulsion of a hydrophobic monomer dispersed in a continuous phase of hydrophilic monomer. The study on the effect of physico-chemical properties on the stability of the concentrated emulsion during polymerization process is investigated. A higher interfacial tension between hydrophobic monomer of dispersed phase and hydrophilic monomer of continuous phase is crucial for a greater stability of the emulsion with the film forming capability of the surfactant employed. The more stable emulsions can be obtained by employing the less polar hydrophobic monomer and the more polar hydrophilic monomer. Mechanically strong viscoelastic interfacial film of surfactants, achieved using blends of surfactants or mixtures of surfactants and long chained alcohols, increase the stability of emulsion. Composites of hydrophilic-hydrophobic polymers show permselectivity to organic solvents. Composite of polystyrene as a dispersed phase and polyacrylamide as a continuous phase shows higher permselectivity to toluene in the mixture of toluene-cyclohexane.

Keywords: concentrated emulsions, stability, permselectivity, hydrophilic-hydrophobic composites.

INTRODUCTION

Polymer composites, composed of more than two chemically different polymers, often show a synergistic behaviour regarding their mechanical properties such as impact strength¹ and permselectivity to organic solvents.²⁻⁴ Because of the tendency for segregation caused by the incompatibility of polymers, the composites have a multi-phase structure. And their applications of these polymer composites are limited due to the difficulty in controlling their morphology. It is very useful to develop polymer composites whose structures can be more easily controlled and hence can be more uniform. Because of their useful properties, such as permselectivity to organic liquids, the combination of dissimilar polymers by chemical and physical methods has been exploited. The chemical methods include the copolymerization^{5,6} and the interpenetration polymerization⁶ while the physical methods involve mechanical blending of two different polymers.³ The preparation method affects the morphology of the multi-phase polymer composites and plays an important role in their physical properties.

The polymer composite investigated in the present paper is a new type of polymer composite in which we refer to as the hydrophilic-hydrophobic polymer composite. This composite is synthesized starting from a concentrated emulsion of a hydrophobic monomer dispersed in a continuous phase of a hydrophilic monomer. In the concentrated emulsion the volume fraction of the dispersed phase is larger than 0.74, which represents the volume fraction of the most compact arrangement of spheres, and can be as large as 0.995.^{7,8} In concentrated emulsions, the spheroidal globules of the conventional emulsions are replaced by polyhedral shape globules separated by thin films of the

continuous phase. The thin films form a network, which is similar to that in a foam, and the stability of the concentrated emulsions is ensured by the adsorption of the surfactant from the continuous phase to the globule and film interface. The concentrated emulsions, which have the appearance of gels, are prepared at room temperature. Suitable initiators are introduced to both the continuous phase and the dispersed phase, respectively. Polymer composites are synthesized by heating the emulsions at appropriate polymerization temperature. The microstructure of composites, thus obtained, can be controlled by changing the size of the globules of the concentrated emulsions. The concentrated emulsions, which are generated and stable at room temperature, may become unstable at the polymerization temperature. In order to prepare polymer composites, the concentrated emulsion has to form and remain stable at the polymerization temperature.

The first objective of this paper is to investigate the factors which influence the formation and the stability of the concentrated emulsions at polymerization temperatures in order to identify the factors which ensure their stability. The second objective includes the permselectivity of the composites which are obtained subsequently. Stability of emulsions refers to the resistance to the formation of the colliding droplets responsible for the phase separation of emulsions. And the film forming capability of the surfactant which is adsorbed on the surface of the globules can play an important role in the coalescence process. Double layer repulsive forces, steric repulsion as well as van der Waals attractive forces among the adsorbed surfactant molecules have influences on the rate of coalescence. The mechanical properties of this interfacial film depend upon the cohesive force among the adsorbed surfactant molecules and upon the

electrostatic repulsion among the charged head groups, or steric repulsion among the charged head groups, or steric repulsion among the polar head groups of the nonionic surfactants.⁹⁻¹¹ There might be mechanism by which the larger droplets grow in size at the expense of the smaller ones which decrease in size. The stability of the concentrated emulsions can be affected by the chemical natures of the hydrophilic monomers of the dispersed phase and the hydrophobic monomers of the continuous phase, the type and concentration of surfactants, the viscosity of the continuous phase, and the temperature of polymerization.^{8,12} Selective permeation through polymeric composite membranes has been applied for the separation of organic mixtures and close boiling liquids including azeotropic mixtures.¹³⁻¹⁵ Their permeation process includes selective absorption, molecular diffusion, and evaporation.^{4,14} A highly soluble polymer can be prevented from being dissolved by its entanglement in the composite with another polymer.¹⁶ This allows a significant swelling of the composites and hence this composites can be applied for the membrane for the purpose of selective permeation of liquid mixtures.

In this paper, studies on the stability of the concentrated emulsions and the microstructure and the permselectivity of the composites synthesized from the concentrated emulsion are conducted.

EXPERIMENTAL

Materials. Chemicals purchased for the test of the stability of the concentrated emulsions were used as received. Inhibitors in monomers used for the synthesis of composites were removed before use. Water was deionized and double-distilled. The styrene monomers (Aldrich) were washed with excess amount of aqueous solution of 10% of

sodium hydroxide and deionized water several times and then vacuumed distilled. Acrylamide (Aldrich) was recrystallized from methanol solution. Cyclohexane and toluene, ethanol, methylene chloride, benzene, ethyl benzene, n-butyl methacrylate, butyl acrylate, ethyl acrylate, methyl methacrylate, and vinyl acetate were purchased from Aldrich and used as received. Azobisisobutyronitrile (AIBN, Fluka), potassium persulfate (Alfa) were recrystallized from methanol solution. Surfactant of sodium dodecyl sulfate (SDS, Aldrich), Tween 20 (polyoxyethylene(20) sorbitan laurate) (Fluka), Tween 40 (polyoxyethylene(20) sorbitan monopalmitate) (Fluka), Tween 60 (polyoxyethylene(20) sorbitan monostearate) (Fluka), and Span 20 (sorbitan monolaurate, Fluka) were used as received. Cetyl alcohol (CA, Aldrich) and oleyl alcohol (OA, Aldrich) were used as received.

Preparation of the Concentrated Emulsion. A small amount of aqueous solution of hydrophilic monomer (acrylamide) containing water soluble initiator (potassium persulfate) and surfactant was placed in a 250 mL three-neck flask equipped with a mechanical stirrer and an addition funnel. Hydrophobic monomer (styrene) containing an oil-soluble initiator (AIBN) was placed in the addition funnel. Initiator was not added for the emulsion stability test and surfactant was dissolved completely prior to emulsification. The preparation of emulsion was carried out by drop-wise addition of the hydrophobic liquid mixture to the pre-emulsified aqueous hydrophilic solution at room temperature.

Test of the Concentrated Emulsion Stability. The concentrated emulsions prepared at room temperature and free of initiator were stored in the 50 °C controlled water bath for 24 hours. The stability of emulsion was characterized by weighing the amount of bulk phases separated from the emulsion.

Preparation of the Polymer Composites and Composites Strips. The concentrated emulsions, which contain styrene (27 g) and initiator (AIBN, 0.02 g/g styrene) as dispersed phase, aqueous acrylamide solution (1.0 g acrylamide/10 g water) as continuous phase, and Tween 20 (1 mL) as surfactant, were packed in test tubes by mild centrifugation. The prepared concentrated emulsions were placed on the glass plates (12 × 12 cm), which were cleaned with detergent and dried at 120 °C for 5 hours. The emulsions between the glass plates were squeezed slowly to avoid trapping of air bubbles. The glass plates were placed in an oven at 50 °C for 24 hours. The polymer strips (200 μ m, 30 mm × 60 mm), thus obtained, were dried at 80 °C in a convection oven for 2 days before use.

Swelling and Absorption Experiments. Polymer composites strips were dried at 80 °C for 5 days and immersed in various organic solvents for various lengths of time. And then their weights were measured with a Mettler balance. The weights of the strips remained constant after 3 days. It is assumed that the latter values are the maximum solubility of the polymer composites which also represents the value of swelling.

Measurement of the Interfacial Tension. The drop weight method with the correction of Harkins¹⁷ were employed to measure interfacial tension of two different liquids at room temperature. The density of the liquids was measured by using Mohr's Mechanical Balance (Fisher Science).

Pervaporation Experiments. After the composite strips were soaked for 1 hour in test liquids, they were inserted into the pervaporation cell. The strips were supported on a sintered-glass disk in the pervaporation cell. Feed solutions were placed in the upstream compartment of the pervaporation cell and the downstream compartment was evacuated to vacuum. The upstream com-

partment was temperature controlled. The permeate was collected in the cold trap which was immersed in liquid nitrogen. The permeate was analyzed by HPLC. A Bondapack C₁₈ column was used and a methanol-water solution (50/50 volume %) was used as the mobile phase. Benzene was used as the standard. The selectivity $\alpha_{T,C}$ is defined by

$$\alpha_{T,C} = \frac{W_T^P \times W_C^F}{W_T^F \times W_C^P}$$

where W_T^F , W_T^P , W_C^F , and W_C^P denote the weight fractions of the component T and C in the feed and permeate, respectively.

Transmission Electron Microscopy. The samples of polymer composites were cooled to -120 °C and sectioned by an ultramicrotome (Reichert-Jung Ultracut 43-E, Cambridge Instruments) which was equipped with FC-4D ultramicrotomy stage. The thin sections (ca. 900 Å) thus obtained were mounted on copper grids under vacuum overnight, before micrographs with a transmission electron microscope (Hitachi HS-8, Hitachi Instruments) were taken.

RESULTS AND DISCUSSION

Effect of the Nature of Hydrophobic Liquids of the Dispersed Phase on the Stability of the Concentrated Emulsion. The stability of the concentrated emulsions prepared employing hydrophobic liquids and water (at 50 °C, in the absence of initiator) and their interfacial tensions (at 25 °C, in the absence of surfactant) can be correlated as shown in Fig. 1. The result indicates that the stability of emulsion increases with increase of the interfacial tension. The hydrophobic liquids with high polarity, for which the interfacial tension at 25 °C is less than 38 dyn/cm, produce less stable concentrated emul-

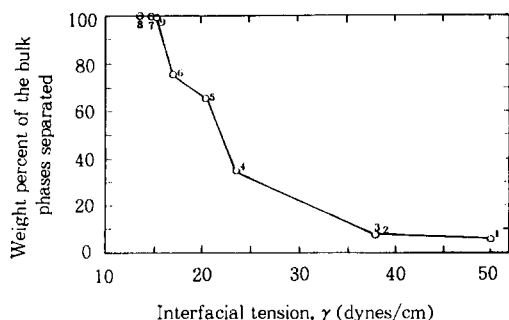


Figure 1. Weight percent of bulk phases separated from the concentrated emulsion at 50 °C plotted against the interfacial tension between hydrophobic liquid and water at room temperature. The concentrated emulsions, which had a volume fraction of the dispersed phase of 0.9, were prepared by using hydrophobic liquid as dispersed phase, water as continuous phase, and SDS (0.347 mol/L water) as surfactant. The hydrophobic liquids were decane(1), ethyl benzene(2), styrene(3), n-butyl methacrylate(4), butyl acrylate(5), ethyl methacrylate(6), vinyl acetate(7), ethyl acrylate(8), and methyl methacrylate(9), respectively.

sions. Phase separation in the concentrated emulsion, which indicates a measure of instability, can occur because of the coalescence of the globules of the dispersed phase by the molecular diffusion between globules. The latter process can be called as the Ostward ripening process, in which large globules grow in size at the expense of the small globules.

Effect of the Nature of the Hydrophilic Liquids of the Continuous Phase on the Stability of the Concentrated Emulsion. Fig. 2 shows that the stability of the concentrated emulsions of styrene and aqueous acrylamide solution and their interfacial tensions. The concentrated emulsions were prepared by employing two kinds of surfactants, Span 20 (sorbitan monooleate, non-ionic surfactant) and SDS (ionic surfactant). As the concentration of acrylamide in aqueous solution of the continuous phase increases, the interfacial tensions between styrene and the aqueous solutions decrease and the emulsion prepared with

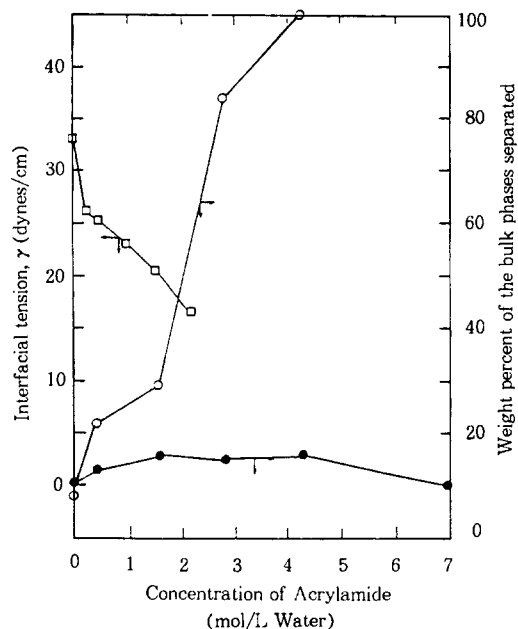


Figure 2. Weight percent of bulk phases separated from the concentrated emulsion at 50 °C and for 24 hours and the interfacial tension at 25 °C plotted against the concentration of aqueous acrylamide solution. The concentrated emulsions, which had a volume fraction of dispersed phase of 0.9, were prepared by employing styrene as dispersed phase and aqueous acrylamide solution as continuous phase, respectively. ○ and ● denote the emulsions prepared by employing SDS (0.347 mol/L water) and Span 20 (0.289 mol/L water) as surfactant, respectively. (□) Denotes interfacial tension between styrene and aqueous acrylamide solution.

SDS becomes unstable. But the stability of the concentrated emulsions prepared using Span 20 does not decrease with increasing acrylamide concentration in the aqueous phase. These phenomena might be attributed to the interactions between the sorbitan ring of the surfactant and acrylamide at the interface.

Effect of the Surfactant and its Concentration on the Stability of the Concentrated Emulsion. In Fig. 3, the interfacial tension between styrene and aqueous ionic surfactant solution of SDS and the stability of the concentrated emulsion are plotted against the logarithm of the

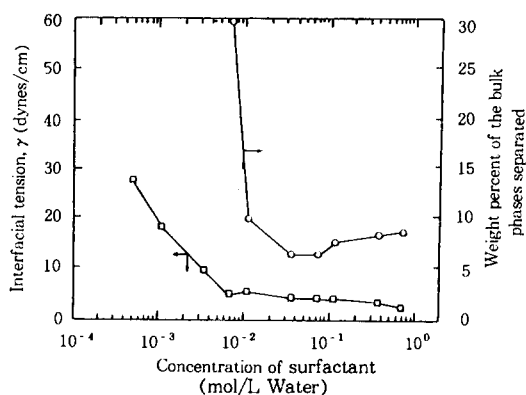


Figure 3. Weight percent of bulk phases separated from the concentrated emulsion at 50 °C and for 24 hours and the interfacial tension at 25 °C plotted against the concentration of aqueous SDS solution. The concentrated emulsions, which had a volume fraction of dispersed phase of 0.9, were prepared by employing styrene as dispersed phase, water as continuous phase, and SDS as surfactant. ○ and □ denote the stability of emulsion and interfacial tension, respectively.

concentration of surfactant. The concentrated emulsions were prepared using styrene as the hydrophobic liquid and water as the hydrophilic liquid at room temperature. The break observed in the curve of the interfacial tensions between styrene and surfactant solutions occurs when the concentration of surfactant equals the critical micelle concentration (CMC), the minimum concentration at which surfactant form a micelle. Fig. 3 indicates that the stability of emulsion increases with increasing surfactant concentration until the equilibrium concentration of the surfactant in the continuous phase reaches the CMC. When the concentration of the surfactant is below CMC, the emulsion formed at room temperature is unstable and separates into two phases in a short time. Above the CMC, the interfacial tension remains essentially constant, since only the adsorption of the monomeric form of the surfactant contributes to the decrease in the interfacial tension and any further addition of surfactant above the CMC increases the number of micelles. There are no

Table 1. Effect of the HLB of the Surfactant on the Stability of Concentrated Emulsion

surfactant (HLB value)	weight fraction of bulk phases separated from concentrated emulsions* for 24 hours at 50 °C
Tween 60 (14.9)	0.080
Tween 40 (15.5)	0.075
Tween 20 (16.6)	0.069
SDS (30)	0.091

* The concentrated emulsion contains styrene as dispersed phase and water as continuous phase and the volume fraction of dispersed phase is 0.9. The concentration of Tweens and SDS were 0.08 mol/L and 0.35 mol/L, respectively

changes of the stability of the concentrated emulsion above CMC. As the concentration of surfactant becomes larger than 2.0 mol/L, there is no formation of concentrated emulsions. This is due to the high viscosity of the continuous phase, which prevents the corporation of the dispersed phase into the continuous phase.

Effect of the Surfactant Blends on the Stability of the Concentrated Emulsion.

Table 1 presents that the concentrated emulsions can be generated by nonionic surfactants with high hydrophilic-lipophilic balance (HLB) values and ionic surfactant of SDS, which are water soluble.

Fig. 4 shows that the effect of the HLB of surfactant blends on the stability of the concentrated emulsions. It indicates that the stability of the concentrated emulsions prepared using surfactant blends is higher than that of concentrated emulsions prepared with individual surfactants and the emulsions exhibit minimum coalescence at a HLB value of about 12. The increased stability of emulsions can be explained as followings. When two nonionic surfactants are used together, they can cover the interface between hydrophilic liquid and hydrophobic liquid in a more compact manner. Because their shape and area per surfactant molecule are different and hence they can fill better the space. This also increases the mechanical

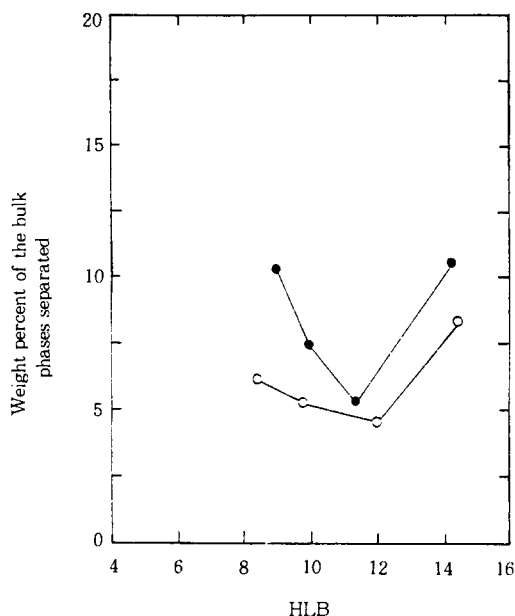


Figure 4. Weight percent of bulk phases separated from the concentrated emulsion at 50 °C and 24 hours plotted against HLB values of surfactant blends. The concentrated emulsions, which had a volume fraction of dispersed phase of 0.9, were prepared by using styrene as dispersed phase and water as continuous phase. ○ and ● denote concentrated emulsions prepared by using surfactant blends of Tween 20-Span 85 and Tween 40-Span 85, respectively. The total concentration of surfactant blend was held constant at 0.065 mol/L water.

properties of interfacial film.

Table 2 shows that a blends of ionic surfactant of SDS and long chain alcohols can affect the stability of the concentrated emulsions. The result indicates that SDS coupled with a long chain alcohol can generate a more stable emulsion than when it is used alone. The presence of the alcohol molecules among those of SDS molecules increases the distance between the charged head groups of SDS molecules and thus decreases the electrostatic repulsion among them. This increases the cohesion of molecules of interface. This cohesion is additionally increased by more compact packing of two different shape surfactants and thus in-

Table 2. Effect of Surfactant and Long Chain Alcohols on the Stability of the Concentrated Emulsion

surfactant compositions	weight fraction of bulk phases separated from concentrated emulsions* at 50 °C and for 24 hours
SDS (0.348 mol/L)	0.091
SDS (0.174 mol/L)/ Cetyl alcohol (0.174 mol/L)	0.080
SDS (0.174 mol/L)/ Oleyl alcohol (0.174 mol/L)	0.063

* The concentrated emulsion contains styrene as dispersed phase and water as continuous phase and the volume fraction of dispersed phase is 0.9.

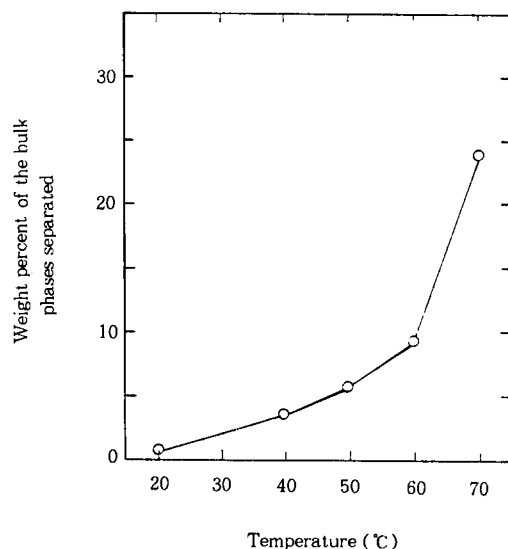


Figure 5. Weight percent of bulk phases separated from the concentrated emulsion at 50 °C and for 24 hours plotted against temperature. The concentrated emulsions, which had a volume fraction of dispersed phase of 0.9, were prepared by employing styrene as dispersed phase, water as continuous phase, and Tween 20 (0.081 mol/L water) as surfactant.

crease the mechanical properties of interface film.

Effect of Temperature on the Stability of Concentrated Emulsion. Fig. 5 indicates that the concentrated emulsions become unstable with increasing temperature. This is due to the mutual

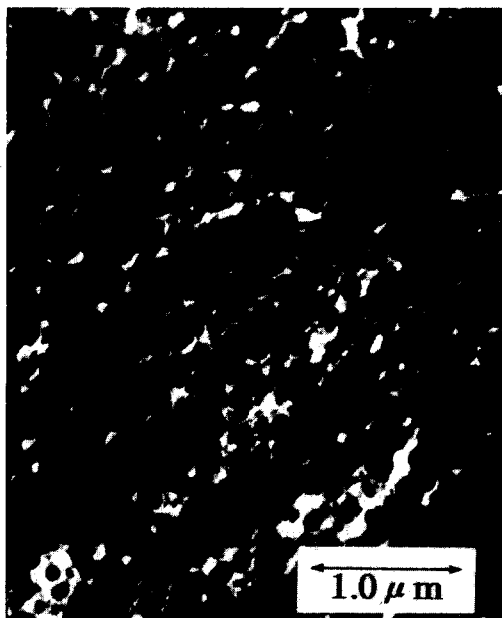


Figure 6. Transmission electron micrograph of hydrophilic-hydrophobic polymer composite. The black spheres are polystyrene and separated by thin film of polyacrylamide. The composite was synthesized starting the concentrated emulsion prepared by using styrene as dispersed phase, acrylamide as continuous phase, and Tween 20 (0.081 mol/L water) as surfactant.

solubilities of the two phases, the solubilities of surfactant, and the interfacial tension. With the increase of temperature the mutual solubilities of two phases increase and the surfactant molecules migrate away from the interface to the bulk liquid phases, thus allowing the globules to coalesce.

Investigation of the Morphology of the Hydrophilic-hydrophobic Composite. Fig. 6 presents that the morphology of the polymer composite examined by employing transmission electron microscopy. The electron micrograph of the composite illustrates that the dispersed phase is composed of sub-micron size polyhedral particles of polystyrene separated by network of thin films of polyacrylamide. The structure of the polymer composites, which is synthesized starting from the concentrated emulsion, can be controlled by con-

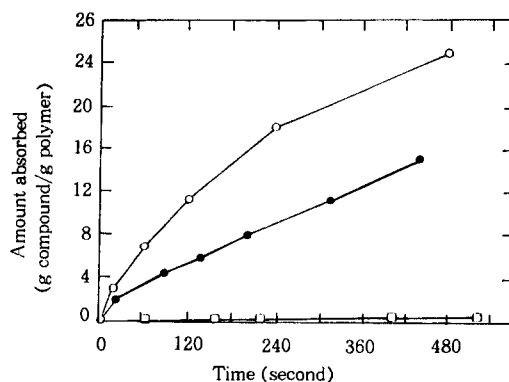


Figure 7. Absorbed amount of liquid per gram of hydrophilic-hydrophobic polymer composite plotted against time at 30 °C. The composite was prepared by the concentrated emulsion employing styrene as dispersed phase and aqueous acrylamide solution as continuous phase. The volume fraction of dispersed phase was 0.9 and SDS(0.081 mol/L) as surfactant. ○, ●, and □ indicate methylene chloride, toluene, and cyclohexane, respectively.

trolling the structure of the concentrated emulsion.

The Test of Swelling of the Composites.

Results of absorption experiment of the hydrophilic-hydrophobic composites strips are plotted in Fig. 7. When methylene chloride, toluene, and cyclohexane are used as test liquids, the absorption of methylene chloride in the composite is the highest. While toluene exhibits high absorption, the absorption of cyclohexane is relatively low. The equilibrium absorption of composites in toluene and cyclohexane, obtained from the swelling experiment at room temperature and for 2 days, are 14.86 and 1.03 g liquid /g polymer, respectively. Fig. 8 presents that the absorption behavior of composites in the binary mixture of toluene and cyclohexane. Amount of the absorption of this composite is larger for higher concentration of toluene.

Permeation Experiments. The permeation of toluene-cyclohexane mixtures through composite strip was investigated in the temperature

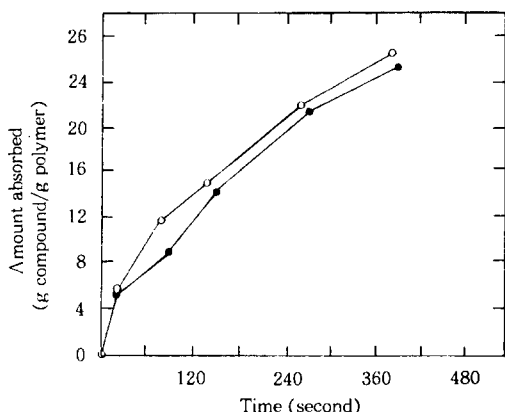


Figure 8. Absorbed amount of liquid from toluene and a mixture of toluene-cyclohexane(1:1 by weight) plotted against time at 30 °C. ○ and ● indicate absorbed amount of liquid from toluene and mixture of toluene-cyclohexane, respectively. The composite was prepared by the concentrated emulsion, which is obtained by using styrene as dispersed phase and aqueous acrylamide solution as continuous phase. The volume fraction of dispersed phase of the concentrated emulsion was 0.9 and SDS (0.081 mol/L) as surfactant.

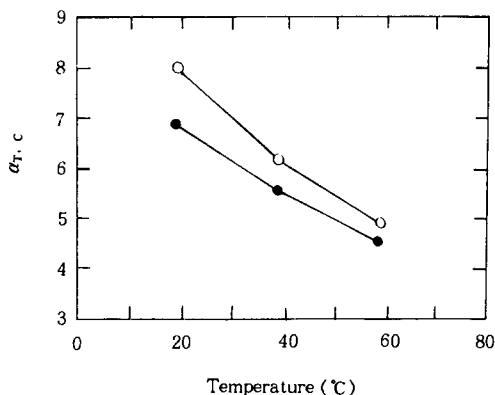


Figure 9. Selectivity for toluene from toluene-cyclohexane mixtures as a function of temperature. ○ and ● denote selectivities obtained from mixture of toluene-cyclohexane (75/25 by weight) and mixture of toluene-cyclohexane (50/50 by weight), respectively.

range of 20–60 °C (Fig. 9). The selectivity of the composites depends on the concentration and temperature of the feed solution. The selec-

tivity of the composites achieved in these experiments were in the range of 4.75–8.10. The selectivity of the composites decreases with temperature, and increases with concentration of toluene in the feed solution.

CONCLUSIONS

A new type of composites, hydrophilic-hydrophobic polymer composites, was synthesized starting from a concentrated emulsion, in which the volume fraction of dispersed phase is greater than 0.74. The concentrated emulsion is composed of styrene as the hydrophobic liquid and aqueous acrylamide as the hydrophilic liquid and stabilized by means of a surfactant soluble in the hydrophilic liquid.

A number of factors are found to be important in the stability of the concentrated emulsions at the polymerization temperature, thus not changing the initial morphology of emulsions. The important factors are the polarity of hydrophobic and hydrophilic liquids and the capability of surfactants and their blends in forming mechanically strong interfacial film at the interface. The lower the polarity of the hydrophobic monomer and the higher polarity of the hydrophilic monomer, the more stable the emulsion. Blends of nonionic surfactants and mixture of ionic surfactant and long chain alcohols are more efficient surfactants than the single surfactant by forming strong viscoelastic interfacial film at the interface. By examining the result of microstructure of composite by the electron microscope and the factors affecting stability of emulsions, it is possible to design the microstructure of the hydrophilic-hydrophobic polymer composites. The hydrophilic-hydrophobic composites shows high permselectivity to organic liquids, such as toluene in the mixture of toluene and cyclohexane. From permselectivity experiment this composites can be applied in the separa-

tion of organic liquid from mixtures.

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