

Novel Amphiphilic Polyurethane Networks: Gelation Mechanism and Swelling Behaviors

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ABSTRACT: Amphiphilic polyurethane gels can be prepared using poly(ethylene glycol)-modified urethane acrylate (PMUA) through two types of methods. When PMUA gels were prepared at an aqueous phase, droplet coalescence and gelation occurred at the same time, so the microstructure of these gels (UAHG) was similar to that of PMUA emulsion which was formed by the microphase separation between hydrophilic and hydrophobic domains. In the case of UAHG gels, as the composition ratio of water to PMUA increased, swelling in water increased, but swelling in dioxane was slightly decreased. For the other kind of PMUA gels prepared using dioxane through a conventional gelation process (UADG), swelling in dioxane greatly increased with increasing of the composition ratio of dioxane; however, swelling of these gels in water was very low. The difference in swelling behavior between UAHG and UADG gels was due to the difference of microstructures between these gels which also influenced the mechanical properties. Additionally, the microstructures of UADG and UAHG gels were able to be confirmed using scanning electron microscopy (SEM) and contact angle measurement.

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INTRODUCTION

Recently, the modification of water-soluble polymer with hydrophobic moieties has been widely reported. These polymers play a very important role in an array of current interfacial technologies, including flotation, flocculation, wetting, biomedical, and pharmaceutical applications.

Hydrophobically modified hydrogels or so-called amphiphilic networks which exhibit a hydrophilic/hydrophobic heterophase structure in aqueous media have received attention on account of their potentially important and fundamentally interesting properties.^{1–3} Their unique morpho-

logical features greatly influence their properties compared to conventional hydrogels. In particular, the heterophasic gel structure should provide versatile controlled delivery features for hydrophilic, hydrophobic, and amphiphilic agents, enhanced biocompatibility due to hydrophobic/hydrophilic balance, and improved mechanical strength. According to Yu and Grainger's report,⁴ amphiphilic thermosensitive gels prepared using *N*-isopropylacrylamide and *N*-alkylacrylamide through micellar polymerization showed interesting thermosensitive matrix swelling behaviors in water as well as amphiphilic diffusion kinetics.

Polyurethane hydrogels, generally, are prepared using the interpenetrating network of polyurethane and diacrylates in the presence of hydrophilic polyurethane and UV curing of a mixture comprising hydrophobic urethane diacrylate and hydrophilic monomers.^{5–8} In our previous experiments,^{9,10} poly(ethylene glycol)-modified ure-

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thane acrylates (PMUA) were prepared using the incorporation polyoxyethylene groups into urethane acrylate, and the amphiphilic properties of these molecules were confirmed by investigation of the viscosity behavior in the course of soap-free emulsification and adsorption behavior at the water/benzene interface.

The ultimate goal of this study was the preparation of new amphiphilic polyurethane networks based on PMUA containing hydrophilic and hydrophobic segments in the same molecule. In this study, a novel polymerization technique, similar to that of soap-free emulsion polymerization, was used to synthesize amphiphilic PMUA networks using a water-soluble initiator in aqueous media. Additionally, to confirm the gelation mechanism occurring in the course of preparation of UAHG gels, the rapid droplet coalescence and polymerization of PMUA emulsion were investigated using the measurement of the change of the size of droplets of PMUA emulsions and the adsorption behavior of PMUA as a function of temperature.

In this study, eight kinds of PMUA were synthesized using five kinds of poly(ethylene glycol) (PEG) having different molecular weights in order to investigate the effect of the chain length of polyoxyethylene on the amphiphilicity and the mechanism of PMUA network formation. Furthermore, to confirm the amphiphilicity of PMUA gels, the swelling ratio behavior of amphiphilic PMUA gels in water and benzene dioxane and the mechanical properties of PMUA gels were investigated.

EXPERIMENTAL

Materials

In the synthesis of PMUA, poly(tetramethylene glycol) (PTMG, MW = 1000, Hyosung BASF), 2,4-toluene diisocyanate (TDI, Junsei Chemical Co.), 2-hydroxyethyl methacrylate (2-HEMA, Aldrich Chemical Co.), and poly(ethylene glycol) (PEG, MW = 200, 400, 600, 1000, 2000, 4000, and 6000, Junsei Chemical Co.) were used. Benzene and dioxane (Junsei Chemical Co.) were stored in a refrigerator and used as received. Potassium persulfate (KPS, Wako Pure Chemicals Co.) and 2,2-azobisisobutyronitrile (AIBN, Junsei Chemical Co.) were recrystallized from DDI water and absolute ethanol, respectively. Benzophenone (Janssen) as a photoinitiator, triethylamine (TEA,

Junsei Chemical Co.), and *t*-butyl hydroperoxide (Junsei Chemical Co.) were used in the UV curing of PMUA.

Synthesis of PMUAs

All kinds of PMUA were synthesized by three-step processes. The molar ratio of the reactants are summarized in Table I and the molecular structure of PMUA was illustrated in our previous articles.^{9,10} These reactions were carried out in a four-necked glass reactor equipped with a stirrer, thermometer, reflux condenser, and inlet system for N₂ gas. The detailed reaction mechanism was also reported in our previous articles.^{9,10}

All PMUA emulsions were prepared using a phase-inversion emulsification process without the use of an external surfactant. PMUA (10 g) was placed in a 100 mL beaker and heated to 50°C to reduce viscosity, then cooled to 35°C while vigorously stirred. Water was first added very slowly until a gel-like phase formed; then, the remaining water was added gradually to reduce viscosity.

Preparation of PMUA Gel

Cylindrical and sheet types of gels were prepared for swelling and mechanical strength measurements. The mixtures of PMUA with solvent (dioxane or DDI water) including AIBN or KPS were transferred into a test tube (inner diameter of 1.5 cm) or a mold (10 × 10 × 0.2 cm) to carry out the gelation. After gelation was completed, all the samples were taken out of the test tube or the mold, thoroughly washed with a large amount of DDI water and methanol, and cut into suitable lengths. These gels were dried in a convection oven for 24 h and then put into dioxane or water for swelling for 24 h. When PMUA gel (UADG) was prepared using dioxane, PMUA dissolved completely in dioxane while the composition of resin to dioxane was varied from 1 : 1 to 1 : 6. In the case where PMUA gels were prepared using water (UAHG), the soap-free emulsions of PMUA were first prepared at different water contents; then, these emulsions were poured into a test tube to carry out gelation. The recipe and procedure for the preparation of two kinds of PMUA gels are illustrated at Table II and Scheme 1, respectively.

Additionally, UV-cured gel (UAVG) was prepared using a conventional curing process and the reagents used in this process are summarized in

Table I The Molar Ratio of Reagents in the Synthesis of PMUA 600 and of PMUA Using Different PEG

Symbols	Reagents	Molar Ratio
(a) PMUA 600		
PMUA600-I	PTMG/TDI/2-HEMA/PEG 600	1/2/1.70/0.30
PMUA600-II	PTMG/TDI/2-HEMA/PEG 600	1/2/1.50/0.50
PMUA600-III	PTMG/TDI/2-HEMA/PEG 600	1/2/1.20/0.80
(b) PMUA Using Different PEG		
PMUA200I	PTMG/TDI/2-HEMA/PEG 200	1/2/1.85/0.15
PMUA400	PTMG/TDI/2-HEMA/PEG 400	1/2/1.85/0.15
PMUA600-III	PTMG/TDI/2-HEMA/PEG 600	1/2/1.85/0.15
PMUA1000	PTMG/TDI/2-HEMA/PEG 1000	1/2/1.85/0.15
PMUA2000	PTMG/TDI/2-HEMA/PEG 2000	1/2/1.85/0.15
PMUA4000	PTMG/TDI/2-HEMA/PEG 4000	1/2/1.85/0.15

Table III. UV irradiation was performed using a UV lamp (450 W, Ace Glass Co.) for 5 min.¹¹

Measurement

The size of the droplets of emulsions was measured using a Brookhaven laser light scattering instrument (BI 9000AT, 2MI98631 PM-tube, Ar—Ne laser). To investigate the adsorption behavior of PMUA at the water/benzene interface, PMUA was first dissolved in benzene; then, this solution was brought into contact with water to form an interface. The interfacial tension of water/benzene was measured by the Du Nouy-ring method (Fisher Scientific Co. surface tensiometer-21).

The swelling ratio of PMUA gels was determined using the gravimetric method. If M_3 is the weight of the sample swollen by the solvent and M_1 is the weight of the dried sample, the swelling ratio is $(M_3 - M_1)/M_1$. The contact angle (θ) of

PMUA gels to water was measured using an Erma contact angle measurement, Model G-1.

Cross sections of PMUA gels were analyzed by scanning electron microscopy (Philips C. XL-30). The conventional secondary electron imaging technique was used. Samples were coated with a thin layer of gold-palladium to reduce any buildup on the fracture surface.

The tensile strength and elongation of PMUA gels were measured with a Hounsfield Model Instron at room temperature using a crosshead speed of 5 mm min⁻¹ and load cell capacity of 50 kgf. All measurements were the average of five runs.

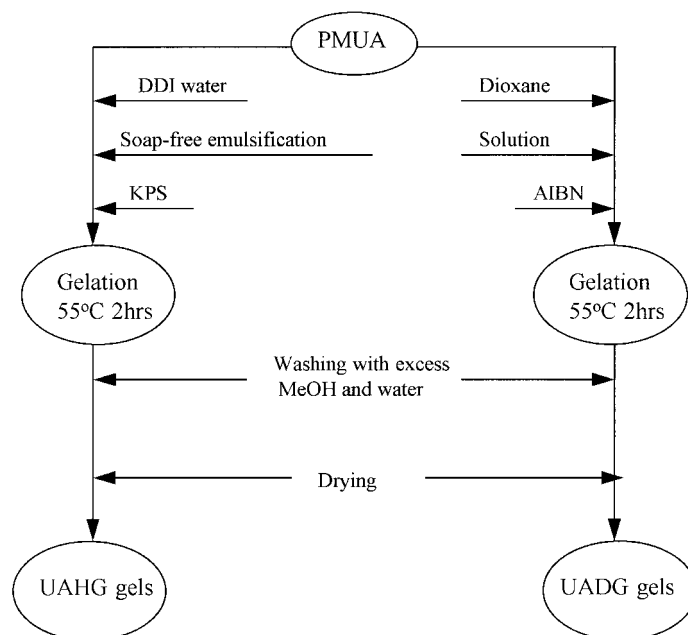
RESULTS AND DISCUSSION

Gelation Mechanism of PMUA Networks in Aqueous Medium

When PMUA gels were prepared using water (UAHG), first of all, PMUA was emulsified with-

Table II Recipe for the Preparation of PMUA Gels

Recipe	PMUA	DDI Water	Dioxane	KPS	AIBN	Symbol	
A	PMUA600-I	10 g	10–50 g	—	0.3 g	—	UAHG600-I
	PMUA600-II	10 g	10–50 g	—	0.3 g	—	UAHG600-II
	PMUA600-III	10 g	10–50 g	—	0.3 g	—	UAHG600-III
	PMUA1000	10 g	10–50 g	—	0.3 g	—	UAHG1000
B	PMUA600-III	10 g	—	10–50 g	—	0.3 g	UADG



Scheme 1 The preparation procedure of PMUA gels.

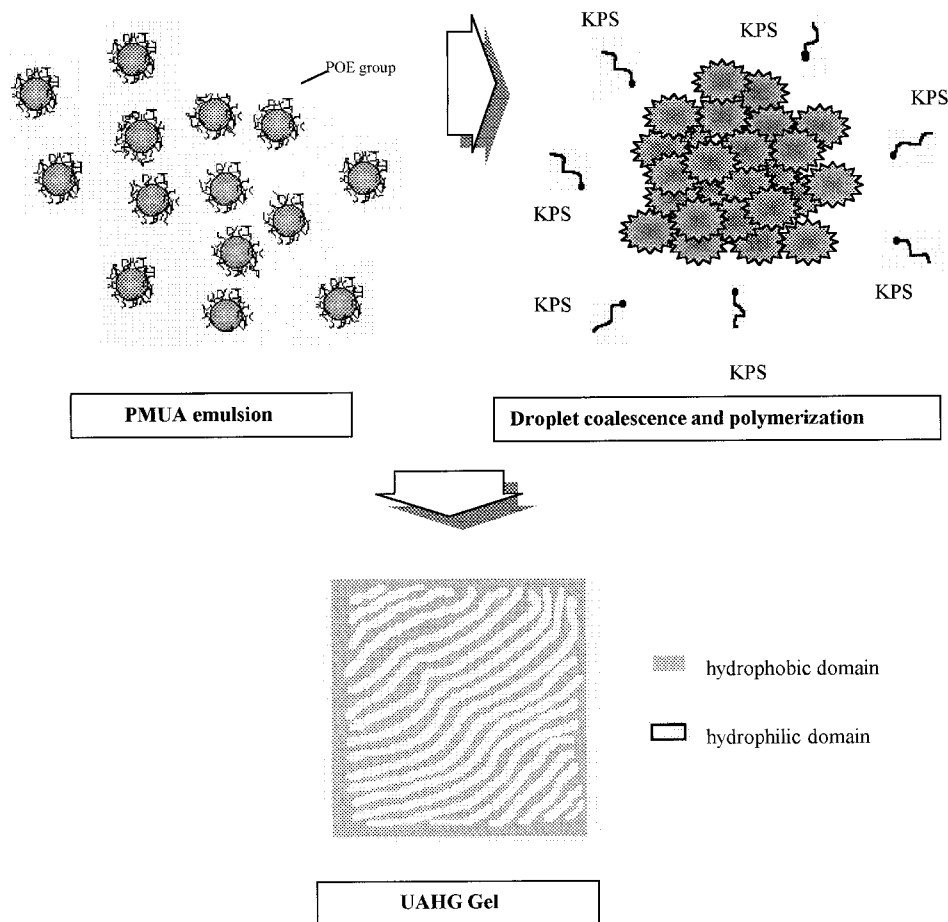
out the use of an external surfactant; then, this emulsion was poured into a test tube or a mold to carry out gelation using the water-soluble initiator, KPS (Scheme 1). Generally, when emulsion polymerization is carried out using a water-soluble initiator, initiator radicals penetrate into the monomer droplet to initiate and propagate polymerization.¹²⁻¹⁷ Emulsion polymerization can be done without the breakdown of droplets. According to our previous experiment,¹⁰ however, when soap-free emulsions of PMUA were polymerized with a water-soluble initiator, these emulsions were broken in the process of emulsion polymerization, because the hydrophilicity of polyoxyethylene groups decreased with increase of the temperature and the initiator radicals penetrated into emulsion droplets which were unstabilized by the increasing temperature. Therefore, in

the case where UAHG gels are prepared using soap-free PMUA emulsions containing KPS, droplet coalescence and polymerization of PMUA emulsions happen at the same time in the course of gelation with increase of the temperature, so it can be thought that UAHG gels which maintain the microphase separation between hydrophilic and hydrophobic segments are obtained.

According to our previous articles,^{10,11} in the process of soap-free emulsification of PMUA, polyoxyethylene chains orient into the water phase while hydrophobic segments aggregate to form their domains such that the microphase separation between hydrophilic and hydrophobic segments of PMUA occurs. This microphase separation behavior was confirmed using the measurement of viscosity change with the addition of water. In the case of gelation of PMUA emulsions

Table III Recipe of the Preparation of UAVG Gel

Symbol	PMUA	Benzophenone	<i>t</i> -Butyl Hydroperoxide	Triethylamine	
UAVG200	PMUA200	10 g	0.3 g	0.2 g	0.1 g
UAVG400	PMUA600	10 g	0.3 g	0.2 g	0.1 g
UAVG600	PMUA600-III	10 g	0.3 g	0.2 g	0.1 g
UAVG1000	PMUA1000	10 g	0.3 g	0.2 g	0.1 g
UAVG2000	PMUA2000	10 g	0.3 g	0.2 g	0.1 g
UAVG4000	PMUA4000	10 g	0.3 g	0.2 g	0.1 g



Scheme 2 Schematic presentation of the formation of UAHG gels.

containing a microphase-separated microstructure, droplet coalescence and polymerization of PMUA emulsion happen simultaneously, so microphase separation between both segments can be maintained (Scheme 2).

Rapid droplet coalescence which happens in the course of the gelation of PMUA emulsion is due to the decrease in the hydrophilicity of polyoxyethylene groups of PMUA with the increase of temperature and the penetration of initiator radicals into oil droplets. Therefore, to confirm the hydrophilicity change of PMUA with temperature, the adsorption behavior of PMUA at the water/benzene interface at different temperatures was observed and is illustrated in Figure 1.

If the hydrophilicity of PMUA decreases with increase of temperature due to the decrease in hydrophilicity of the polyoxyethylene group,¹⁸ the number of molecules locating at the water/benzene interface decreases, so the interfacial tension will increase. As expected, interfacial tension in-

creases with increasing temperature. For PMUA-600-I, 600-II, and 600-III solutions, interfacial tension increases significantly around 48°C.

Additionally, the changes of the size of droplets of PMUA emulsions containing KPS with temperature were investigated using a laser light-scattering apparatus and are illustrated in Figure 2. As the temperature increases, the size of the droplets of PMUA emulsions containing KPS increases discontinuously. For the PMUA600-III emulsion, the size of the droplets increases more than six times, compared to the initial droplet size, with increase of temperature, which makes it possible to maintain the gel shape of PMUA after gelation.

Figure 3 illustrates the changes of the size of droplets of PMUA emulsions with the type of initiator. In the case of PMUA emulsion containing AIBN, the sizes of droplets remain unchanged with increasing temperature, because polymerization of emulsion occurs mainly in the oil droplet. For the PMUA emulsion containing KPS in

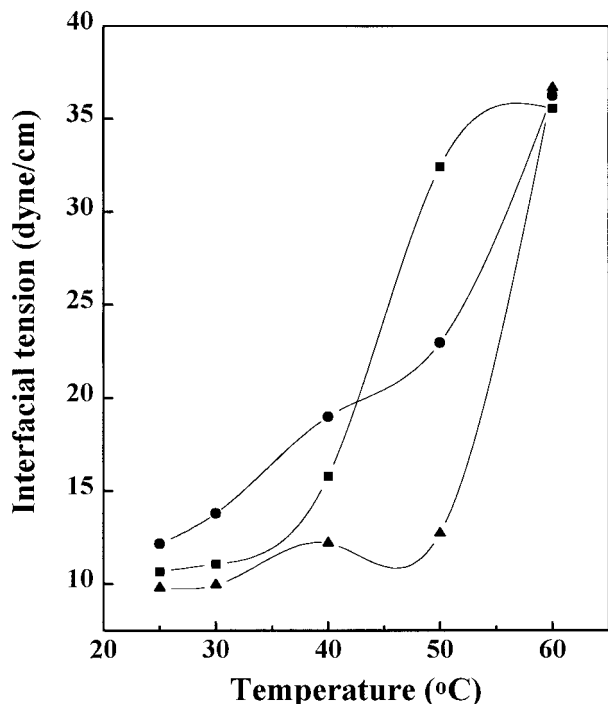


Figure 1 Adsorption behavior change of PMUA with temperature: (—■—) PMUA600-I; (—●—) PMUA600-II; (—▲—) PMUA600-III.

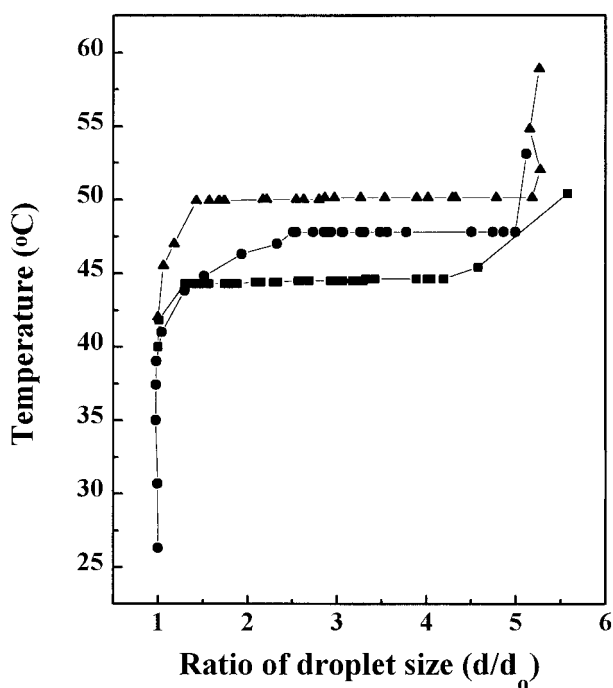


Figure 2 The change of droplet sizes of PMUA emulsions as a function of temperature: (—■—) PMUA600-I; (—●—) PMUA600-II; (—▲—) PMUA600-III.

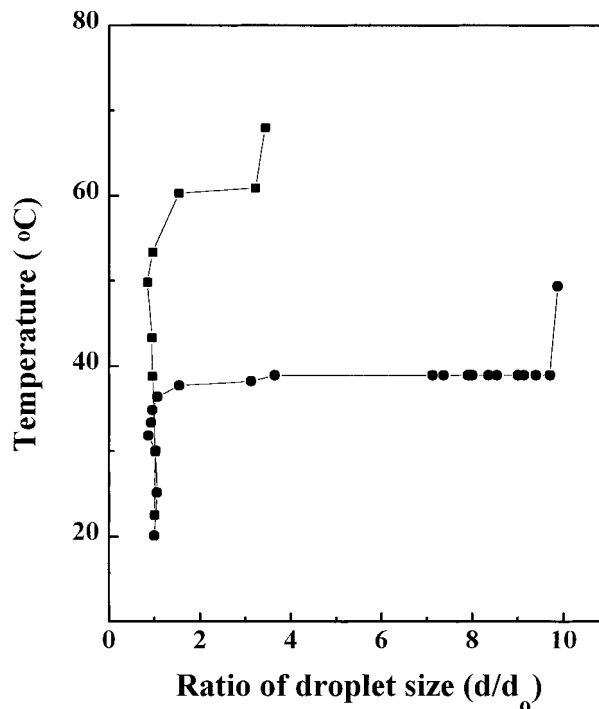
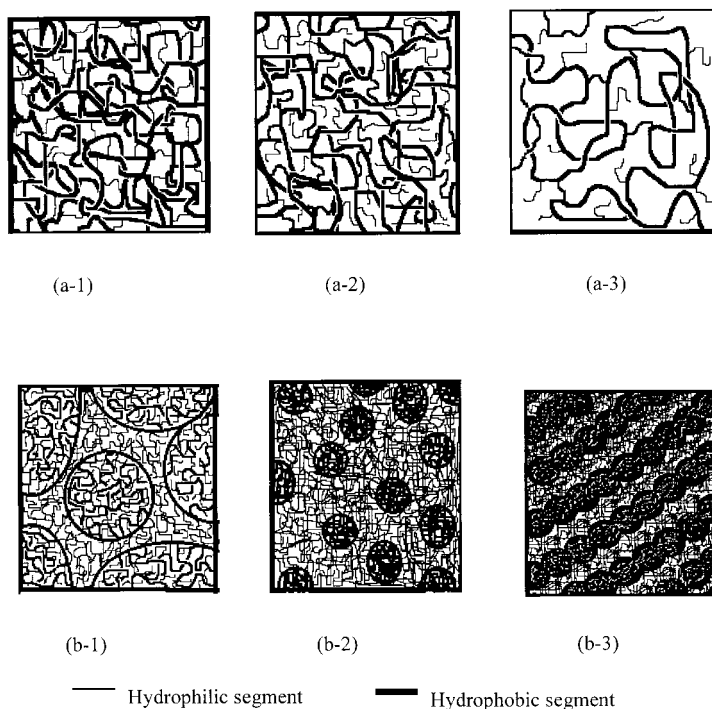


Figure 3 The change of droplet size of PMUA emulsions containing different types of initiator with increase of temperature: (—■—) AIBN; (—●—) KPS.

the aqueous phase, however, the droplet size changed significantly around 43°C. These results indicate that the penetration of radicals from the water phase into emulsion droplets causes the soap-free emulsion of PMUA to be broken while polymerization of PMUA occurs, so PMUA gels could be formed in an aqueous medium using a water-soluble initiator while maintaining a microstructure similar to that of soap-free emulsion [Scheme 3(b)].

To investigate the effect of chain length of polyoxyethylene groups on the formation of UAHG gels, six kinds of PMUA were prepared using different kinds of PEG (Tables I and II). Figure 4 illustrates the size change of the droplets of PMUA emulsions containing different chain lengths of polyoxyethylene as a function of temperature. PMUA200 and PMUA400 cannot be soap-free emulsified, so the changes of droplet size of these emulsion were not measured. The sizes of droplets of PMUA600-III and PMUA1000 emulsions are changed greatly with increase of temperature. In the case where KPS is added at these emulsions, the change of the size of droplets is greater at lower temperature than that of emulsions without KPS. For PMUA2000 and 4000



Scheme 3 Schematic presentation of the microstructures of UAHG and UADG gels.

emulsions, the sizes of droplets of these emulsions remain unchanged with increase of temperature, indicating that the hydrophilicity of these PMUA does not decrease at higher temperature and that droplet coalescence accompanied with polymerization does not happen. Therefore, it can be concluded that this kind of PMUA gels could be prepared using only PMUA600-III and 1000 through the above-mentioned process.

The swelling behavior of UAHG gels prepared at different composition ratios of water in aqueous medium was measured and is illustrated in Figure 5. As the composition ratio of water increases in the preparation of UAHG gels, the swelling ratio in water increases. These results are due to the phase-separated microstructure of UAHG gels. As the composition ratio of water to PMUA increases, the microphase separation between hydrophilic and hydrophobic segments increases, so the numbers of polyoxyethylene groups orienting to the water phase increase, which causes the swelling of UAHG gels in water to increase [Scheme 3(b)]. Therefore, it can be thought that the degree of microphase separation between hydrophilic and hydrophobic segments of PMUA gels greatly influences the swelling in water. Additionally, UAHG600-III shows higher swelling in

water than that of UAHG600-I and II. These results are due to the differences in the number of molecules containing polyoxyethylene groups between three kinds of PMUA600 which cause gels to be swelled by the hydration with water. UAHG600-III gels are prepared using PMUA600-III, which has the largest number of polyoxyethylene chains, so the amount of hydrophilic domains of UAHG600-III is larger than that of other UAHG gels.

According to Gould and Johnston's reports,^{5,6} polyurethane hydrogels can be obtained using UV curing of the mixture comprising hydrophilic urethane acrylate and hydrophilic monomer. Five kinds of PMUA used in this study can be polymerized by UV curing, because these molecules contain reactive vinyl groups as end groups. Thus, five kinds of UAVG gels were prepared using PMUA200, 400, 2000, and 4000, which could not be used in the gelation process employed in the preparation of UAHG600 gels (Table III) and swelled in water.

Figure 6 shows the swelling ratio of UAVG and UAHG600-III gels in water as a function of temperature. For UAVG gels, the swelling ratio of these gels increases with increase of the chain length of polyoxyethylene and UAVG4000 shows

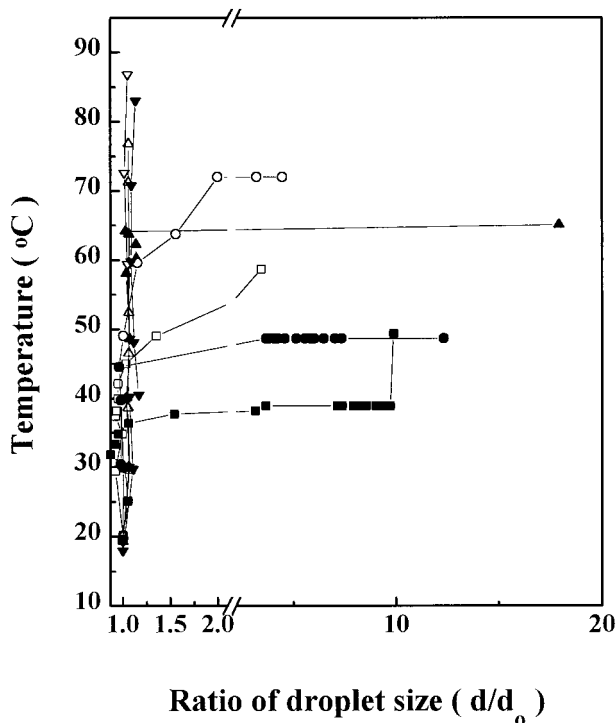


Figure 4 The change of droplet size of PMUA600-III, 1000, 2000, and 4000 emulsions as a function of temperature: (—□—) PMUA600-III emulsion; (—■—) PMUA600-III emulsion, 0.5 wt % KPS; (—○—) PMUA1000 emulsion; (—●—) PMUA1000 emulsion, 0.5 wt % KPS; (—△—) PMUA2000 emulsion; (—▲—) PMUA2000 emulsion, 0.5 wt % KPS; (—▽—) PMUA4000 emulsion; (—▼—) PMUA4000 emulsion, 0.5 wt % KPS.

the highest swelling in water. These results are attributed to the increase of hydrophilicity of PMUA with increase of the chain length of polyoxyethylene of PMUA. However, UAHG600-III gels containing smaller polyoxyethylene chains show a higher swelling ratio than those of UAVG2000 and 4000 gels which have a larger chain length of polyoxyethylene. These results are due to the microphase-separated microstructure of UAHG-600-III gels. In other words, when UAHG600-III gel is prepared using the above-mentioned method, similar to that of soap-free emulsion polymerization, microphase separation between polyoxyethylene chains and hydrophobic segments occurs, which causes the hydrophilicity of UAHG-600-III gels to be maximized. Therefore, even though UAVG2000 and 4000 have longer polyoxyethylene chains than those of UAHG600-

III, the swelling of UAHG600-III in water is higher than in UAVG gels.

Amphiphilic Property of UAHG and UADG Networks

The swelling ratios of UAHG and UADG gels in the organic solvent media (dioxane and benzene) were measured and are illustrated in Figure 7. For UADG gels prepared using dioxane, the swelling ratio increases in organic solvent mediums with increase in the composition ratio of dioxane to PMUA (curves A and B of Fig. 7). Contrarily, the swelling ratio of UAHG600-III decreases as the composition ratio of water to PMUA increases (curves C and D of Fig. 7). Additionally, the swelling ratio of UAHG gels is lower than that of UADG gels. These results are attributed to the difference in the microstructure of UADG and UAHG gels.

When UADG gels are prepared using recipe B (Table II), both hydrophilic and hydrophobic segments of PMUA can dissolve in solvents, so the chain entanglement decreases as the composition ratio of solvents to PMUA increases, which causes the swelling ratio of these gels in organic solvents to increase [Scheme 3(a)].

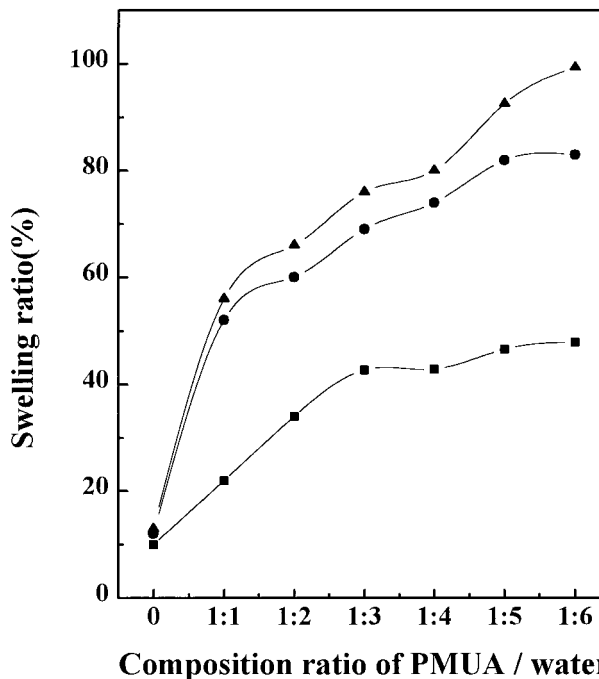


Figure 5 The change of swelling ratio of UAHG gels in water as a function of composition ratio of water to PMUA: (—■—) UAHG600-I; (—●—) UAHG600-II; (—▲—) UAHG600-III.

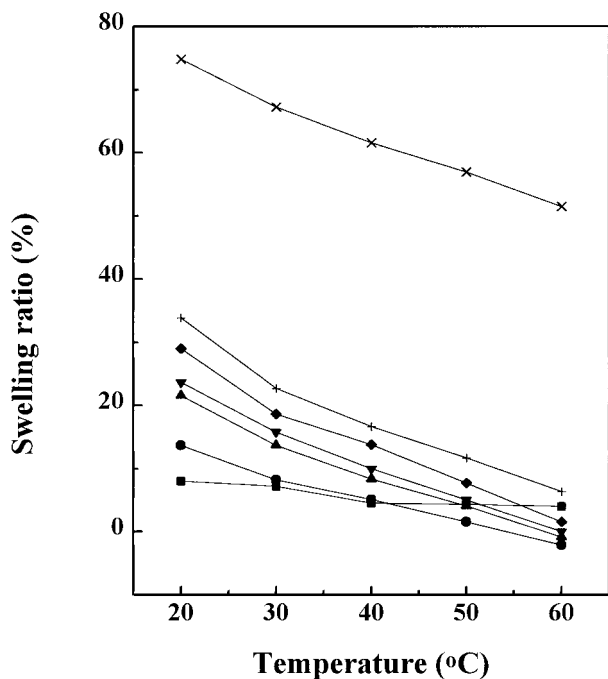


Figure 6 The change of swelling ratio of UAAG and UAHG600-III gels: (—■—) PMUA200; (—●—) PMUA400; (—▲—) PMUA600-III; (—▼—) PMUA1000; (—◆—) PMUA2000; (—+—) PMUA4000; (—×—) UAHG600-III gel.

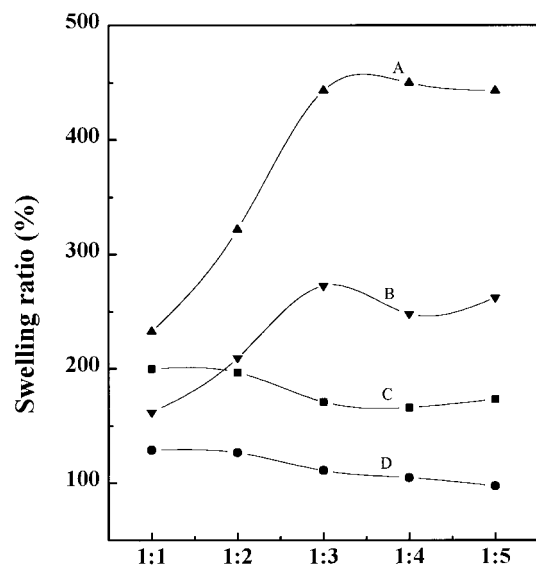


Figure 7 The change of swelling ratio of UAHG and UADG gels in dioxane and benzene: (—■—) UAHG in dioxane; (—●—) UAHG in benzene; (—▲—) UADG in dioxane; (—▼—) UADG in benzene.

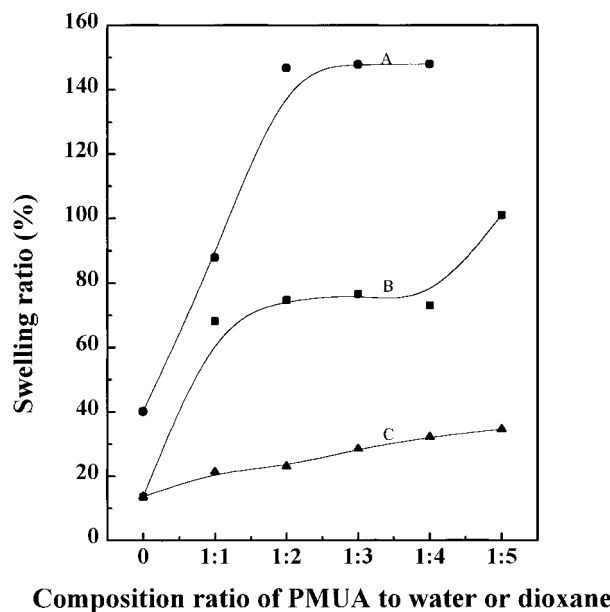
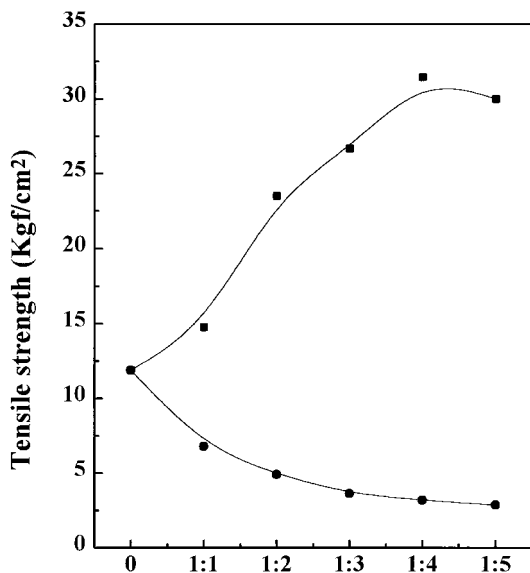


Figure 8 Swelling behavior of UAHG600-III, UAHG1000, and UADG gels in water: (—■—) UAHG600-III; (—●—) UAHG1000; (—▲—) UADG.

However, in the case of UAHG gels prepared using water (Recipe A of Table II), only polyoxyethylene chains of PMUA dissolved or oriented into the water phase, so the microphase separation occurs in the process of emulsification. This microphase separation can be maintained in the course of gelation owing to rapid droplet coalescence and polymerization of PMUA emulsions. Furthermore, the orientation of polyoxyethylene groups into the water phase and the aggregation of hydrophobic segments are increased with increase in the composition ratio of water to PMUA in the preparation of gels, so the chain entanglement of hydrophobic segments is increased by this microphase separation, which causes the swelling of hydrophobic segments by dioxane to be restrained [Scheme 3(b)].

Figure 8 shows the swelling behavior of UAHG600-III, UAHG1000, and UADG gels in water. When UAHG600-III (curve A) and 1000 (curve B) are swelled in the aqueous medium (DDI water), the swelling ratio of these gels increases as the composition ratio of water to PMUA increases. Moreover, the swelling ratio of these gels is larger than that of UADG gels (curve C). In the case of UADG gels prepared using different composition ratios of dioxane to PMUA, the swelling ratios of these gels are increased slightly with



Composition ratio of PMUA to water or dioxane

Figure 9 Tensile strength change of UAHG and UADG gels with the composition ratio of PMUA/water or dioxane: (—■—) UAHG; (—●—) UADG.

increase in the composition ratio of dioxane [Scheme 3(a)].

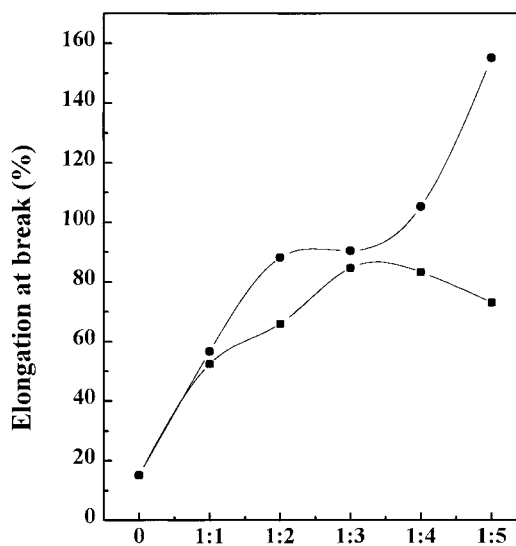
As the composition ratio of water to PMUA increases in the preparation of UAHG gel, the microphase separation between hydrophilic and hydrophobic segments increases, so the numbers of phase-separated hydrophilic domains of UAHG gels increase, which causes the swelling of UAHG gels in water to increase. In other words, the swelling of UAHG gels in water or dioxane significantly depends on the degree of the microphase separation between hydrophilic and hydrophobic segments. However, in the case of UADG gels, both hydrophilic and hydrophobic segments of PMUA dissolve in dioxane, so microphase separation does not occur and polyoxyethylene groups are mixed with hydrophobic segments, which made difficult the swelling of the polyoxyethylene groups in water.

Mechanical Properties and Morphology of UAHG and UADG Gels

Figures 9 and 10 show, respectively, the tensile strength and elongation change of UAHG and UADG gels with the composition ratio of water or dioxane. For UADG gels, as the composition ratio of dioxane increases, tensile strength decreases

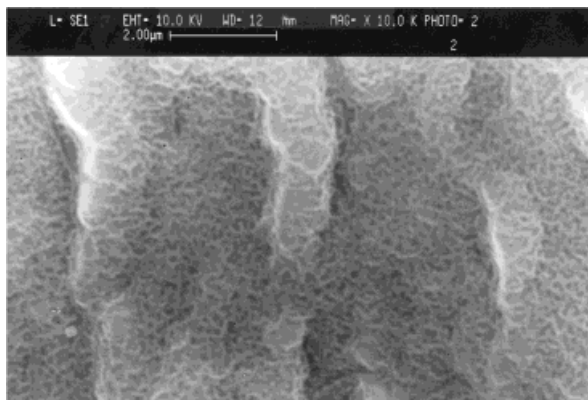
but elongation increases because of the reduction of chain entanglements which create the networks. In the case of UAHG 600-III gels, however, both tensile strength and elongation increase with increase in the composition ratio of water. These results are due to the phase-separated microstructure of UAHG600-III gels causing the chain entanglement of hydrophobic and hydrophilic segments to increase. In other words, in the course of gelation of PMUA in water, polyoxyethylene chains aggregate to form their domains while hydrophobic segments also gather together. Thus, the increase in tensile strength and elongation of UAHG are due to the aggregation of hydrophobic segments and polyoxyethylene chains, respectively. Thus, it can be concluded that the difference of microstructures between UAHG and UADG gels influence their mechanical strength as well as their swelling behavior.

The morphology of UAHG and UADG gels were analyzed using scanning electron microscopy and are illustrated in Figure 11. Even though UAHG and UADG gels were prepared using the same kind of PMUA, swelling behaviors in water and dioxane were varied with the method used in the preparation of these gels. Additionally, mechanical properties of these gels also showed different behaviors, as mentioned above, because the microstructures of these gels are changed with the gelation processes.

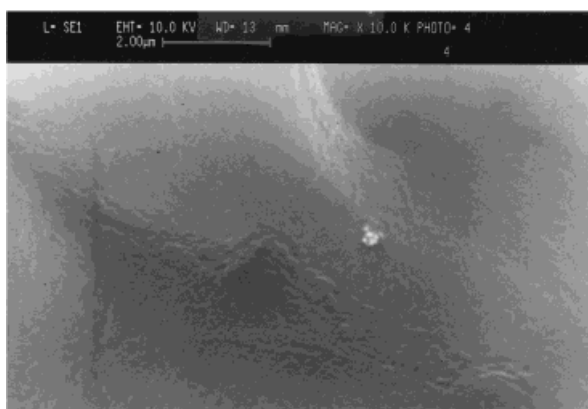


Composition ratio of PMUA to water or dioxane

Figure 10 Elongation change of UAHG and UADG gels with the composition ratio of PMUA/water or dioxane: (—■—) UADG; (—●—) UAHG.



(a)



(b)

Figure 11 SEM microphotographs of UADG and UAHG gels: (a) UAHG gels; (b) UADG gels.

As expected, UADG gels show a homogeneous morphology [Fig. 11(b)] while UAHG gels represent a heterogeneous morphology like a honeycomb [Fig. 11(a)]. It can be thought that the micropores in the UAHG gel networks are formed by the rapid droplet coalescence of PMUA emulsions and the evaporation of water. Therefore, our schematic presentation for the microstructure of UAHG and UADG, Schemes 1 and 2, is confirmed by these results.

Figure 12 illustrates the changes of contact angle (θ) of UADG and UAHG600-III gels to water. The contact angle of UAHG gels decreases with increase of the composition ratio of water, indicating increase in the formation of hydrophilic domains owing to microphase separation. For

UADG gels, however, the contact angle is nearly constant with the change of the composition ratio of dioxane to PMUA, because the hydrophilicity of these gels remain unchanged with the composition ratio of dioxane. Therefore, the differences in microstructure between UADG and UAHG gels can be confirmed by the measurements of SEM and the contact angle.

CONCLUSION

UAHG gels were prepared using a novel gelation technique, similar to that of soap-free emulsion polymerization. These gels contain a similar microstructure to that of the emulsion and could swell in both water and organic solvent. However, even though UAHG and UADG gels were prepared using the same kind of PMUA, these gels show large differences in their swelling behaviors in the same dissolution medium because of differences in the microstructure between UAHG and UADG gels.

According to earlier researchers,^{7,8} hydrophilic polyurethane gels could be obtained by the UV curing of hydrophilic urethane acrylate. However, in the case of UAVG gels prepared with UV irradiation using PMUA, although these gels were pre-

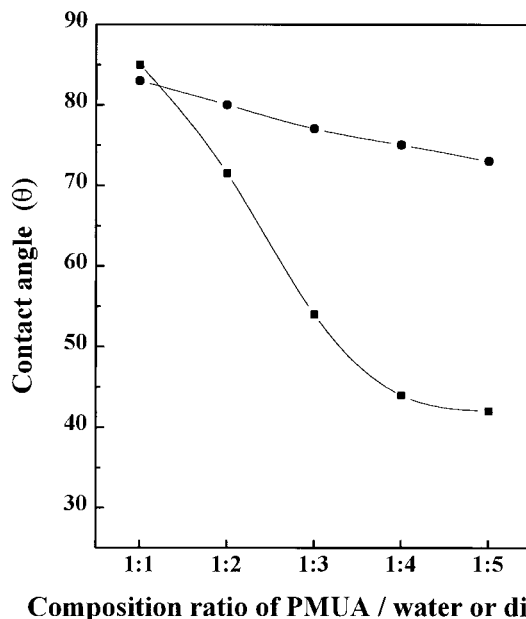


Figure 12 Contact angle (θ) change with composition ratio of PMUA to water or dioxane for its gels: (—■—) UADG gels; (—●—) UAHG600-III gels.

pared with the same kind of PMUA used in the preparation of UAHG and UADG gels, the swellings in dioxane and water were very low, because chain entanglement was very high relative to UAHG and UADG gels. Furthermore, the swelling of UAVG1000, 2000, and 4000 in water is lower than that of UAHG600-III which has the smaller polyoxyethylene chains. Therefore, it can be concluded from these results that microphase separation between polyoxyethylene chains and hydrophobic segments causes the amphiphilicity and hydrophilicity of UAHG gels to be maximized.

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