Colloid Polym Sci 274:1025–1032 (1996)

ORIGINAL CONTRIBUTION

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Microphase separation of PEG-modified urethane acrylate and the swelling behavior of its gels

Received: 7 February 1996
Accepted: 16 April 1996

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Abstract The viscosity of PEG-modified urethane acrylate (PMUA) showed peculiar behavior in the course of soap-free emulsification. Moreover, the viscosity change with added amounts of water was influenced by the reaction molar ratio of polyethylene glycol (PEG). The rate of increase in viscosity slowed and the ratio of increase in viscosity increased as the reaction molar ratio of PEG increased. This peculiar viscosity behavior was due to the microphase separation between hydrophilic and hydrophobic segments of PMUA, and the orientation of polyoxyethylene groups at O/W interface which influenced droplet size of the soap-free PMUA emulsion. The location of polyoxyethylene groups of this resin at O/W interface was confirmed using the adsorption isotherm measurement of PMUA molecules containing polyoxyethylene groups at water/benzene interface. The microphase separation behavior of PMUA between hydrophilic and hydrophobic segments could apply to the preparation of the PMUA gels containing peculiar structure. PMUA gels were prepared using dioxane (UAG) and the swelling behavior of these gels were compared to that of gels prepared using water (UAHG) in the same medium. In the same medium, the swelling behavior of UAHG gels differed from that of UAG gels because of the difference in the microstructure of gel due to the microphase separation between hydrophilic and hydrophobic segments. This phase separation in the course of gelation in water could be confirmed using contact angle measurement.

Key words PEG-modified urethane acrylate – microphase separation – viscosity – interfacial tension – gel – swelling ratio – contact angle measurement

Introduction

Polyurethane (PU) ionomer, self-emulsifiable resin, shows the peculiar viscosity behavior in the course of soap-free emulsification. As water is added to an organic solution of PU ionomer, its viscosity first decreases to a minimum owing to a reduction of the ionic association, and then increased alignment of the hydrophobic chain segment; phase separation starts at this stage. Further addition of water causes the viscosity to increase sharply and pass through two maximum, which was due to the increased number of hydrophobic aggregates and dissociation of hard segment less disordered microionic lattices accompanying an increased association of hydrophobic segments. Additionally, it has been known that the viscosity behavior of PU ionomer in the course of emulsification depends on the structure of hard segment, ionic content and dispersion temperature [1, 2].

In our previous experiments [3], PEG-modified urethane acrylate (PMUA) was synthesized by the reaction of polyethylene glycol (PEG) with unreacted isocyanate groups of urethane acrylate and used as a core polymer of the core-shell composite latex.

PMUA, used in this study, can be soap-free emulsified, because this resin has a hydrophilic segment (polyoxyethylene group) and hydrophobic segment in the same molecule, which acted as a polymeric surfactant [4, 5]. Accordingly, it can be thought that PMUA shows peculiar viscosity behavior like PU ionomer do in the process of soap-free emulsification. PMUA has relatively simple molecular structure compared to PU ionomer (PMUA did not contain hard segment) and has the hydrophilic group (polyoxyethylene group) incorporated into molecular backbone not as a pendant group, but as a terminal group. Thus it was thought that the viscosity behavior of PMUA in the course of emulsification was more or less different compared with that of PU ionomer.

The object of this study is the preparation of PMUA gels containing peculiar structure using the microphase separation between hydrophilic and hydrophobic segments. It has been generally known that polyurethane hydrogels have applications in the biomedical area as a contact lens and surgical implants. Gould and Johnston prepared interpenetrating network of polyurethane and diacrylates in the presence of hydrophilic polyurethane [6, 7]. Additionally, Lai and Baccei prepared polyurethane hydrogel by UV curing of mixture comprised of hydrophobic urethane diacrylate and hydrophilic monomers [8, 9].

When polyurethane gels containing peculiar microstructure were prepared using PMUA, the preparation method was very similar to that of the soap-free emulsion polymerization. The soap-free emulsions of PMUA were prepared, and then gelation was carried out in a test tube or molded shape. Therefore, it can be thought that both of emulsion polymerization and droplet coalescence occur simultaneously in the course of gelation, so gels containing peculiar microstructure due to the microphase separation can be prepared by this procedure [10].

The microstructure of gels was confirmed by the swelling behavior of gels in water and organic solvent medium (Dioxane), because the swelling behavior is greatly influenced by the structure of gels. Additionally, in order to support our postulation for the structure of gels, swelling behavior of PMUA gels prepared using dioxane will be compared to those of gels prepared using water in the same medium.

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 polyethylene glycol (PEG, $Mw = 600$, Junsei Chemical Co.) were used. Benzene and dioxane (Junsei Chemical Co.) was stored in a refrigerator and used as received. Potassium persulfate (KPS, Wako Pure Chemicals Co.) and 2,2-azobisisobutyronitrile (AIBN, Junsei Chemical Co.) was recrystallized from DDI water and absolute ethanol respectively.

Synthesis of urethane acrylate (UA) and PMUAs

The UA and PMUA were synthesized by two- or three-step processes. The molar ratio of reactants was summarized in Table 1 and the molecular structure of PMUA and unmodified urethane acrylate (UA) was illustrated in our previous paper [5, 11]. These reactions were carried out in a 4-neck glass reactor equipped with stirrer, thermometer, reflux condenser and inlet system for N_2 gas. Detailed reaction procedure was reported in our previous paper [5, 11].

In order to exclude the effect of surfactant on emulsion viscosity, all PMUA emulsions were prepared using a phase inversion emulsification process without using an external surfactant. An 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 stirring. Water initially was added very slowly until a gel formed, then the last remaining water was added gradually to reduce viscosity.

Preparation of PMUA gel

Cylindrical gels were prepared for swelling measurements. The mixtures of PMUA with solvent (dioxane or DDI

Table 1 The molar ratio of reagents in the synthesis of PEG-modified urethane acrylate

Symbols	Reagents	Molar ratio
UA*	PTMG/TDI/2-HEMA	1/2/2
PMUA1	PTMG/TDI/2-HEMA/PEG 600	1/2/1.85/0.15
PMUA2	PTMG/TDI/2-HEMA/PEG 600	1/2/1.70/0.30
PMUA3	PTMG/TDI/2-HEMA/PEG 600	1/2/1.50/0.50
PMUA4	PTMG/TDI/2-HEMA/PEG 600	1/2/1.20/0.80

UA*: unmodified urethane acrylate.

Table 2 Gelation recipe of PMUA gels

Recipe	PMUA (g)		DDI water (g)	Dioxane (g)	KPS (g)	AIBN (g)	Symbol
A	PMUA2	5	$5 \sim 30$	–	0.05	–	UAHG2
	PMUA3	5	$5 \sim 30$	–	0.05	–	UAHG3
	PMUA4	5	$5 \sim 30$	–	0.05	–	UAHG4
B	PMUA4	5	–	$5 \sim 30$	–	0.05	UAG

water) including AIBN or KPS were transferred into a test tube (inner diameter was 1.5 cm) to carry out gelation. After gelation was complete, all the samples were taken out of the test tube, fully washed with a large amount of DDI water and methanol, and cut into suitable lengths. These gels were dried at convection oven for 24 h and put into dioxane or water to be swelled for 24 h. When PMUA gel (UAG) was prepared by dioxane, PMUA dissolved completely in dioxane and the composition of resin to dioxane was varied 1:1 to 1:6. In case gels were prepared by water (UAHG), to begin with, the soap-free emulsions of PMUA were prepared at different water contents, then these emulsions were poured into test tube to carry out gelation. The composition of water or dioxane in the gelation of PMUA are illustrated in Table 2.

Measurement

The droplet sizes of emulsions were measured using Brookhaven Laser Light Scattering Instrument (BI 9000AT, 2M198631 PM-tube, Ar-Ne laser). The viscosity changes with water concentration were measured using Brookfiled Synchrolectric Viscometer with spindle LVT no. 1–4.

In order to investigate the adsorption isotherm of PMUA at water/benzene interface, PMUA and UA dissolved in benzene, then this solution was brought into contact with water to form interface. The interfacial tension of water/benzene was measured by Du Nouy ring method (Fisher Scientific Co. Surface tensiomat-21).

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

Contact angle (θ) of urethane acrylate to water was measured using Erma contact angle measurement, Model G-1.

Results and discussion

Viscosity behavior of PMUA in the process of soap-free emulsification

The viscosity of pure PMUA decreased with increase of shear rate (shear-thinning behavior), and the viscosity of PMUA emulsion also showed clear shear thinning behavior at very low water concentration. As the water concentration increased, the viscosity increased and showed a large shear thinning behavior. However, at certain water concentrations, the viscosity decreased (phase inversion point) and showed nearly Newtonian behavior. However, when viscosity change of PMUA emulsions was measured with shear rate, it was very difficult to investigate detailed viscosity changes that occurred in the process of emulsification, because the viscosities of PMUA emulsions were nearly same at high shear rate. Therefore, the viscosity change with water concentration was measured at constant shear rate ($5.1\ s^{-1}$). The results are illustrated at Fig. 1.

At the early stage of addition of water, the viscosity first showed a decrease, then increased again with the addition of water. With further addition of water, the viscosity started to increase again, and all types of PMUA showed similar viscosity behavior with the increase of water concentration.

According to Pal and Otsubo [12, 13], for concentrated emulsions, their viscosities increased with the increase of concentration of surfactant and showed non-Newtonian flow behavior. It was suggested that these results were due to the interconnected network structure. At high surfactant concentrations, the aggregates of droplets formed an interconnected network structure, which caused the viscosity to increase. In the case of PU ionomer [1, 2], the increase in viscosity with addition of water was owing to the increased association of hydrophobic segments. Therefore, for PMUA, the microphase separation between hydrophilic and hydrophobic segments occurred in the course of emulsification, so polyoxyethylene groups

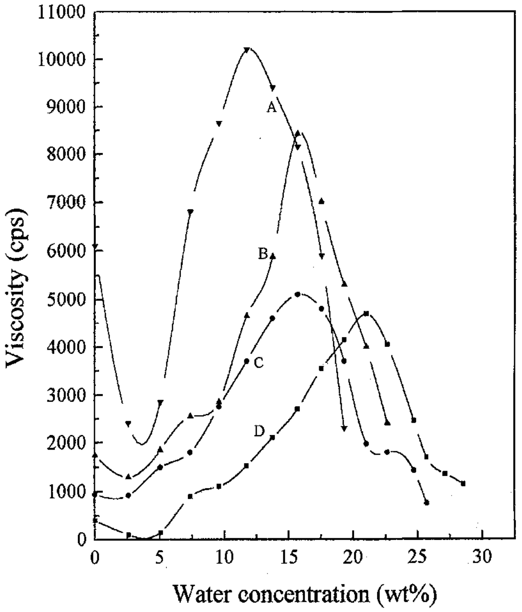

Fig. 1 Viscosity plotted against water concentration at the same shear rate (-▼- = PMUA1, -▲- = PMUA2, -●- = PMUA3, -■- = PMUA4)

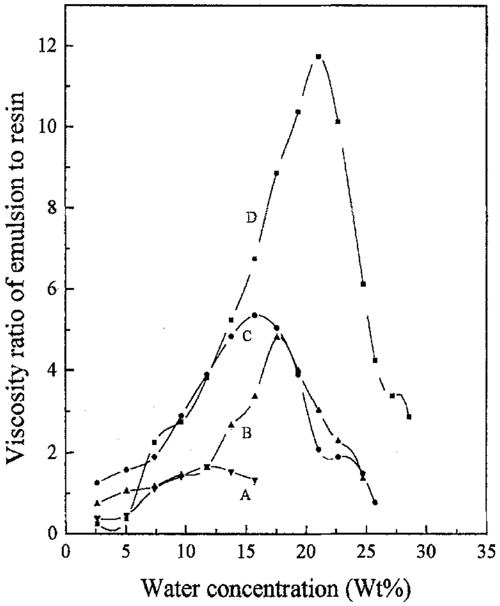

Fig. 2 Viscosity ratio of emulsion to resin plotted against water concentration (-▼- = PMUA1, -▲- = PMUA2, -●- = PMUA3, -■- = PMUA4)

oriented into water phase and associated at O/W interface, which caused the viscosity to increase with the addition of water. Additionally, hydrophobic segments aggregated to form the hydrophobic inner core.

For PMUA1, the smallest PEG reaction molar ratio, the emulsion viscosity was higher than any other emulsions at the same water concentration, and it showed maximum value at lower water concentration than other PMUA emulsions. PMUA1 had smaller numbers of molecules containing polyoxyethylene groups than other resins, so the ratio of hydrophilic segment solubilizing water to hydrophobic segment was relatively low. Therefore, for PMUA1, the phase separation between hydrophilic and hydrophobic segments occurred faster than other PMUA with the addition of water, so the increase in viscosity of PMUA1 was faster than any other PMUA in the course of emulsification. For PMUA4, the increase of viscosity with the addition of water was slower than the other PMUA, because PMUA4 had largest amount of molecules containing polyoxyethylene groups owing to the highest reaction molar ratio of PEG. As the reaction molar ratio of PEG increased, the number of molecules containing polyoxyethylene group solubilizing water increased and the ratio of hydrophilic segment to hydrophobic segment also increased. Therefore the relatively large amount of water added could be solubilized and the microphase separation between hydrophilic and hydrophobic segments occurred slowly, which caused the viscosity of its emulsion to increase slowly with the addition of water.

For PU ionomer, this resin has two types of hard segment (more disordered hard segment and a less disordered one), and the entrance of water into the less disordered hard segment is more difficult than into the more disordered hard segment. Therefore, in the case of emulsification of PU ionomer, in the first stage, the viscosity increases slightly owing to the increased number of hydrophobic aggregates and passes through a small maximum. In second stage, continuing addition of water causes the viscosity to increase sharply to another maximum, indicating the dissociation of the less disordered microionic hard segments accompanying an increased association of hydrophobic segments, so its viscosity shows two maximum values in the course of emulsification. However, for PMUA, the viscosity showed only one maximum value in the course of soap-free emulsification, because it did not have hard segments and hydrophilic groups existed not as a pedant group but as a terminal group [5, 11].

The ratio of increase in viscosity of PMUA with water concentration is illustrated at Fig. 2. The ratio of increase in viscosity means the ratio of emulsion viscosity to its pure resin at certain water concentrations. For PMUA4 showing the slow increasing rate of viscosity, the ratio of increasing in its viscosity was larger than any other PMUA at the same water concentration. However, PMUA1 showed the smallest increasing ratio of viscosity. These results indicated that the PMUA4 had largest

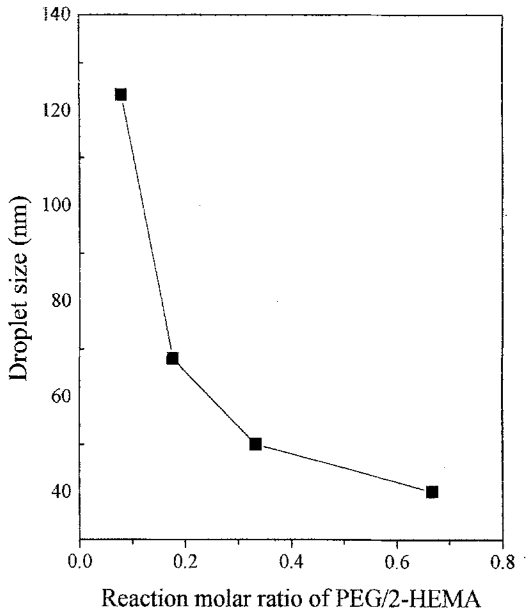

Fig. 3 Droplet size change of PMUA emulsions with the reaction molar ratio of PEG to 2-HEMA

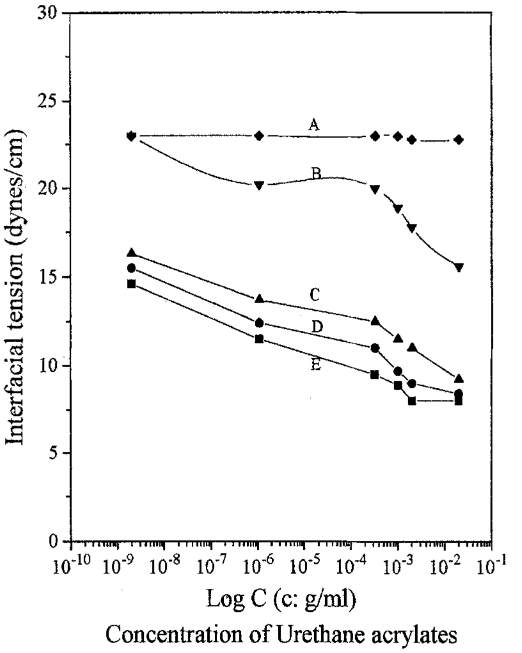

Fig. 4 Adsorption isotherm of PMUA at water/benzene interface (—◆— = UA, —▼— = PMUA1, —▲— = PMUA2, —●— = PMUA3, —■— = PMUA4)

amount of molecules containing polyoxyethylene groups, so the degree of hydration of polyoxyethylene groups with water was relatively large, causing the formation of interconnected network structure at O/W interface.

Figure 3 shows droplet size change of PMUA emulsions with the reaction molar ratio of PEG to 2-HEMA. Droplet sizes of PMUA emulsion decrease as the reaction molar ratio of PEG increase. PMUA4 emulsion shows the smallest droplet size, because PMUA4 has the largest amount of molecules containing polyoxyethylene groups.

In the case of PMUA, the molecules containing polyoxyethylene groups act as a polymeric surfactant while polyoxyethylene groups orienting into water phase, so soap-free emulsion can be formed. Therefore, as the reaction molar ratio of PEG increase, the number of molecules acting as a polymer surfactant increase and the orientation of these molecules into water phase increases, causing the droplet size of PMUA emulsion to decrease. Therefore, the reason that PMUA4 shows the largest increasing ratio of viscosity with the addition of water can be supported by these results.

We tried to determine how many molecules of PMUA locate at O/W interface. PMUA, however, was highly viscous, so it was very difficult to determine that directly. Therefore, in order to examine location of molecules having polyoxyethylene groups at O/W interface, the adsorption isotherm of PMUA at water/benzene interface was measured. Figure 4 illustrates the interfacial tension changes with the concentration of urethane acrylates in benzene. If urethane acrylates containing polyoxyethylene groups could be located and adsorbed at the O/W interface, the interfacial tension of water/benzene would be decreased with the concentration of PMUA in benzene.

Curve A of Fig. 4 indicates the change of interfacial tension of water/benzene containing unmodified urethane acrylate (UA). The interfacial tension was not changed with concentration of urethane acrylates. However, for PMUA (PMUA1–PMUA4), the interfacial tensions (Curve B, C, D, E) decreased as the concentration of urethane acrylates in benzene increased. PMUA4, the highest reaction molar ratio of PEG, showed the lowest interfacial tension (Curve E). These results indicated that the urethane acrylate molecules containing polyoxyethylene groups could locate at the O/W interface and the amount of molecules locating at O/W interface increased with the increase of PEG reaction molar ratio.

Swelling behavior of PMUA gels

When PMUA gels were prepared using water (UAHG), first of all, PMUA was emulsified without using surfactant, then this emulsion was poured into a test tube to carry out gelation. Generally, when emulsion polymerization is carried out using water soluble initiator, initiator radicals penetrate into the monomer droplet to initiate and propagate polymerization. Emulsion polymerization can be done without breakdown of droplets. According to our previous experiment [5, 10], however, when PMUA emulsions prepared using without surfactant were polymerized with water-soluble initiator, these emulsions were broken in the process of emulsion polymerization, because the hydrophilicity of polyoxyethylene groups decreased with the increase of temperature and the initiator radicals penetrate into emulsion droplets unstablized by the raising of temperature. When the soap-free emulsions of PMUAs were polymerized with KPS, these emulsions were broken and droplets aggregated with each other, so gels maintaining peculiar microstructure. In other words, when the temperature of medium increases and initiator radicals penetrate into emulsion droplets, the flocculation and polymerization of PMUA emulsions happen at the same time in the course of gelation, so PMUA gels maintaining the microphase separation between hydrophilic and hydrophobic segments can be formed.

In order to support our postulation for the microstructure of PMUA gels, another type of PMUA gels (UAG) was prepared using dioxane. Both segments of PMUA dissolve in dioxane, so microphase separation between both segments did not occur in the course of gelation. Thus, it could be thought that UAG gels contained different microstructure from that of UAHG gels. The schematic presentation for the microstructure of PMUA gels is illustrated in Fig. 5. In the case of UAG gels (B-1, 2, 3 and 4), homogeneous network structure was formed, because both segments can be dissolved in dioxane used in the gelation. For UAHG gels (A-1, 2, 3 and 4), however, hydrophilic segments (polyoxyethylene groups) were hydrated with water while hydrophobic segments aggregate with each other in the course of gelation, which make it possible to maintain peculiar structure of UAHG gel.

Swelling ratios of PMUA gels in the organic solvent medium (dioxane) were measured and illustrated in Fig. 6. For UAG gels prepared using dioxane, the swelling ratio increased with the increase in the composition ratio of dioxane to PMUA (Curve A of Fig. 6). However, in the case of UAHG gels, the swelling ratio decreased as the composition ratio of water to PMUA increased (Curve B, C and D of Fig. 6). These results were attributed to the difference in the microstructure for two types of gels (UAG and UAHG). When UAG gels were prepared by using recipe B (Table 2), both of hydrophilic and hydrophobic segments of PMUA were able to dissolve in dioxane, so the chain entanglement decreased as the composition ratio of dioxane to PMUA increased (B-1, 2, 3 and 4 of Fig. 5), which caused the swelling ratio of UAG to increase.

However, in the case of UAHG gels prepared using water (Recipe A of Table 2), only hydrophilic segment of PMUA could dissolve or oriented at water phase, so the microphase separation occurred in the process of gelation. Furthermore, the orientation of polyoxyethylene groups into water phase and the aggregation of hydrophobic segments were increased with the increase in the composition ratio of water to PMUA in the preparation of gels,

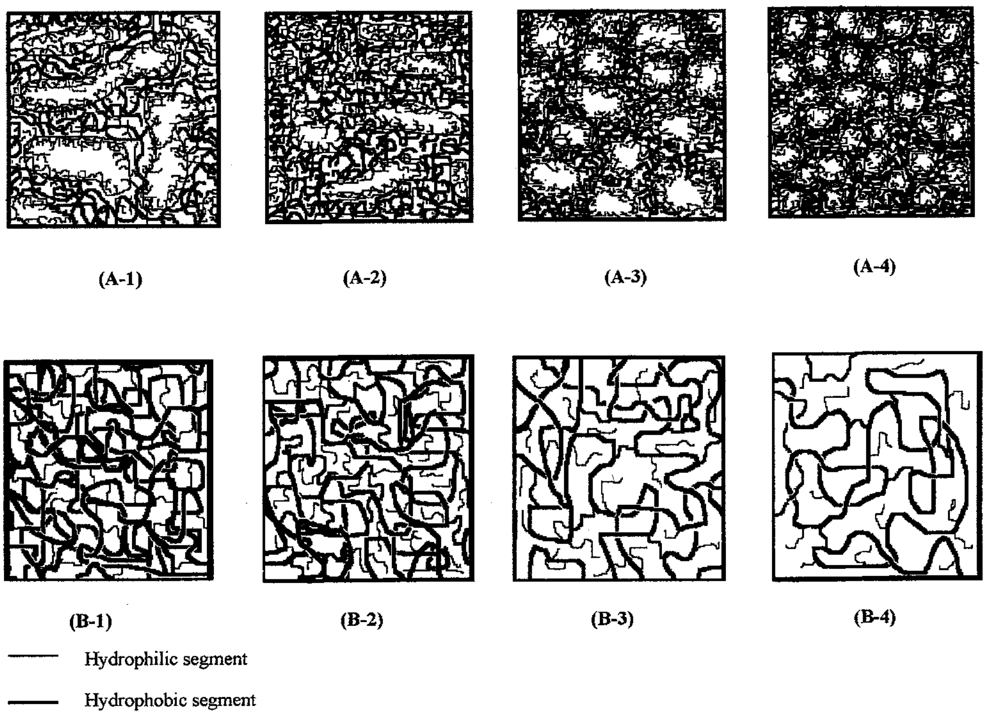

Fig. 5 Schematic representation of microstructure of PMUA gels; (A): UAHG gels prepared using different water concentration, (B): UAG gels prepared using different dioxane concentration

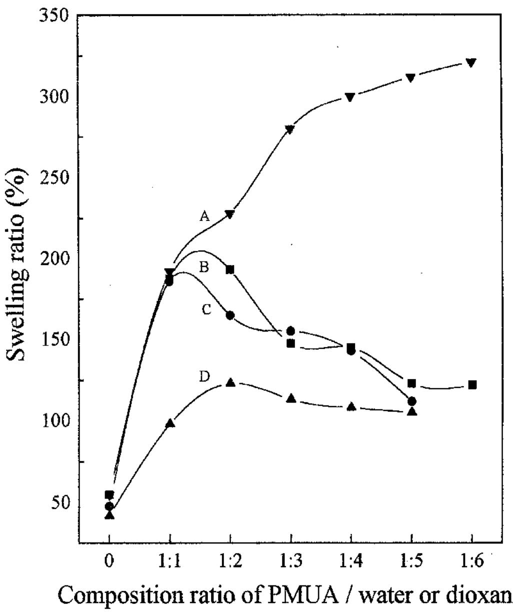

Fig. 6 Swelling ratio of PMUA gels at organic solvent medium (dioxane), PMUA gels were prepared using the different composition ratio of PMUA to water to dioxane (-▼- : UAG gel prepared using dioxane, -■- : UAHG4, -●- : UAHG3, -▲- : UAHG2)

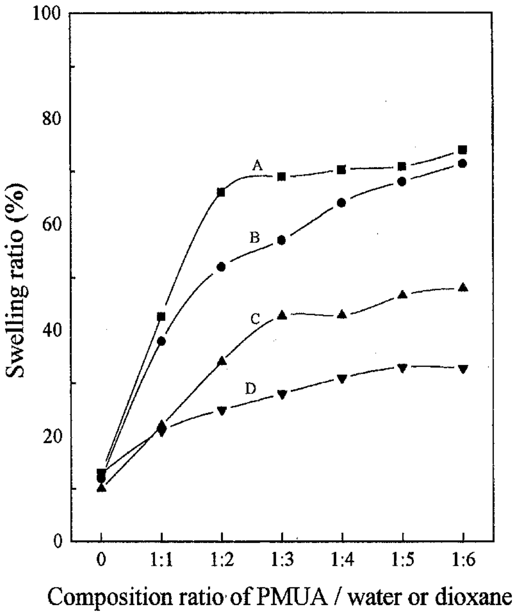

Fig. 7 Swelling ratio of PMUA gels at aqueous medium (water), PMUA gels were prepared using the different composition ratio of PMUA to water or dioxane (-■- : UAHG4, -●- : UAHG3, -▲- : UAHG2, -▼- : UAG gels prepared using dioxane)

which caused the chain entanglement of hydrophobic segments to increase and the swelling of hydrophobic segments by dioxane to restrain (A-1, 2, 3 and 4 of Fig. 5).

When UAHG and UAG gels were swelled in the aqueous medium (DDI water), the swelling ratio of UAHG gels increased as the composition ratio of water to PMUA increased (Curve A, B, and C of Fig. 7). Moreover, the swelling ratio of these gels was larger than that of UAG gel (Curve D). In the case of UAG gels prepared using different dioxane composition, the swelling ratios of these gels were increased slightly with the increase in the composition ratio of dioxane. As the composition ratio of water to PMUA increased in the preparation of UAHG gel, the numbers of polyoxyethylene groups orienting to water phase increase, which cause swelling of UAHG gel to increase.

In other words, the swelling ratios of UAHG gels depended on degree of phase separation between hydrophilic and hydrophobic segments. However, in the case of UAG gels, both hydrophilic and hydrophobic segments of PMUA could dissolve in dioxane, so microphase separation did not occur and polyoxyethylene groups were mixed with hydrophobic segments, which made difficult swelling of the polyoxyethylene groups at water.

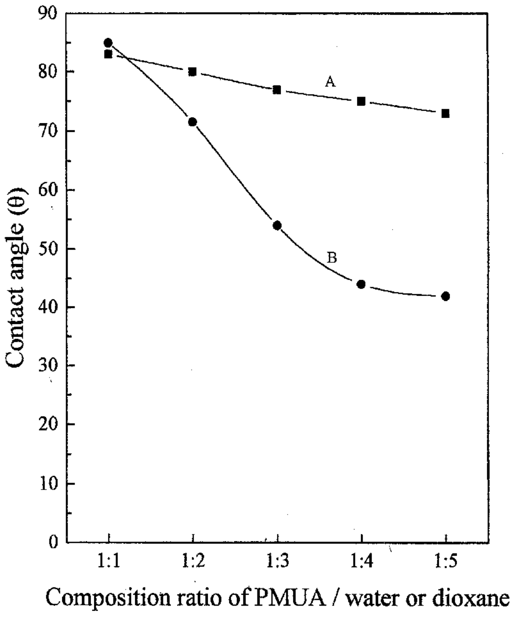

Fig. 8 Contact angle (θ) change with composition ratio of PMUA to water or dioxane for its gels (-■- : UAG gels -●- : UAHG3 gels)

Additionally, the swelling ratio of UAHG4 was larger than that of UAHG3 and UAHG2. These results are due to the difference in the number of molecules containing polyoxyethylene groups which cause gels to be swelled by the hydration with water. The UAHG4 gels were prepared using PMUA4 that had the largest number of molecules containing polyoxyethylene groups, so the amount of hydrophilic segment of UAHG4 was larger than other UAHG gel.

In order to confirm the orientation of polyoxyethylene groups into outer layer, the surface hydrophilicity of gels was investigated using contact angle measurement and its result are represented at Fig. 8. The contact angle (θ) of gels prepared using water were changed with the ratio of water to resin, indicating that the orientation of polyoxyethylene groups to outer layer increased with the ratio of water to resin due to phase separation between hydrophilic and hydrophobic segments. However, the contact angles of gels prepared using dioxane were nearly constant, indicating that the orientation of polyoxyethylene groups did not change with the ratio of dioxane to resin.

Conclusion

The viscosity of PMUA was changed in the process of soap-free emulsification, which was more or less differ from that of PU ionomer. The increasing ratio and rate of viscosity largely depended on the reaction molar ratio of PEG, that is, the number of molecules containing polyoxyethylene groups. The orientation of polyoxyethylene groups owing to the microphase separation between hydrophilic and hydrophobic segments of PMUA caused the peculiar viscosity behavior in the course of emulsification. The degree of orientation of polyoxyethylene groups significantly influenced the droplet size of soap-free PMUA emulsion and was confirmed using the adsorption isotherm measurement of PMUA at water/benzene interface.

UAHG gels containing the peculiar microstructure could be prepared using the microphase separation behavior of PMUA happened in the course of emulsification. PMUA gels prepared using water (UAHG) could be swelled at both water and dioxane, which was due to the microstructure of these gels comprised of outer and inner layers. When UAHG gels were swelled at water, the hydrophilic domains were swelled, but the hydrophobic inner domains did not swell. Additionally, the swelling behavior of UAHG gels was different from that of UAG gels, which was due to the difference in the microstructure of UAG and UAHG. In the near future, we will study the probability of these new gels as a drug delivery system.

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