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Swelling behavior of novel polyurethane hydro-xerogels

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SUMMARY

Polyurethane hydro-xerogels derived from PEG-modified urethane acrylates (PMUA), containing hydrophilic segment (polyoxyethylene groups) and hydrophobic segment at the same molecule, were prepared and their swelling behaviors were evaluated.

Hydro-xerogels of PMUA were prepared using gelation process of PMUA emulsions. these gels could be swelled at both of water and dioxane, moreover, the swelling ratio of these gels at dioxane and water were changed with composition ratio of water to PMUA in the preparation of gel. In aqueous medium, swelling ratio of these gels increased with the increase in composition ratio of water to PMUA. However, in organic medium (Dioxane), swelling ratio decreased as the composition ratio of water increased. Additionally, as the reaction molar ratio of PEG to 2-HEMA increased, swelling ratio of gels at water increased. These results were due to microstructure of PMUA gels, which was formed by phase separation between hydrophilic and hydrophobic segments in the course of gelation.

INTRODUCTION

Polyurethane hydrogels are claimed to have applications in the biomedical area as a contact lens and surgical implants. Gould and Johnston prepared the interpenetrating network of polyurethane and diacrylates in the presence of hydrophilic polyurethane. Additionally, Lai and Baccei prepared polyurethane hydrogel by UV curing of mixture comprised of hydrophobic urethane diacrylate and hydrophilic monomers (1-4).

However, in this study, we intended to prepare a novel polyurethane gel using PEG-modified urethane acrylate (PMUA) containing hydrophilic segment (polyoxyethylene groups) and hydrophobic segment at the same molecule, which was used as a core polymer of impact modifier for PMMA and epoxy resin in our previous experiment (5-6). Additionally, this resin could be formulated and emulsified to be used as a water dispersible UV curable formulation (7).

PMUA shows phase separation behavior in the process of emulsification, that is, the hydrophilic segment (polyoxyethylene group) became orient to water phase and the hydrophobic segment comprised of vinyl groups and hydrocarbon chains became

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aggregate in the course of emulsification (5). Therefore, we thought that gels containing peculiar structure could be prepared using amphiphilic property of PMUA, so we try to prepare PMUA gels using water.

Generally, the preparation of gel is carried out using good solvent and the procedure of gelation is like that of solution polymerization. However, PMUA is not dissolved but just dispersed in water where phase separation between hydrophilic and hydrophobic segments occur. Moreover, the procedure of preparing PMUA gels is very similar to that of emulsion polymerization. For typical emulsion polymerization, emulsion droplets generally are not broken and aggregated in the course of emulsion polymerization. In case of soap-free emulsion of PMUA, emulsion are broken and aggregation of droplets happen fast in the course of emulsion polymerization, which is attributed to the decrease in hydrophilicity of polyoxyethylene groups with the increase of temperature (8-9). Accordingly, it can be thought that both of emulsion polymerization and droplet coalescence occur simultaneously in the course of gelation, so gels containing microstructure similar to that of emulsion can be prepared by this procedure. Then, in order to confirm microstructure of PMUA gels, we will observe swelling behavior of gels in water and organic solvent medium (dioxane), because swelling behavior of gels is greatly influenced by its structure. Additionally, in order to support our postulation for structure of gels, we prepared PMUA gels using dioxane and intend to compare swelling behavior of these gels to that of gels prepared using water in the same medium.

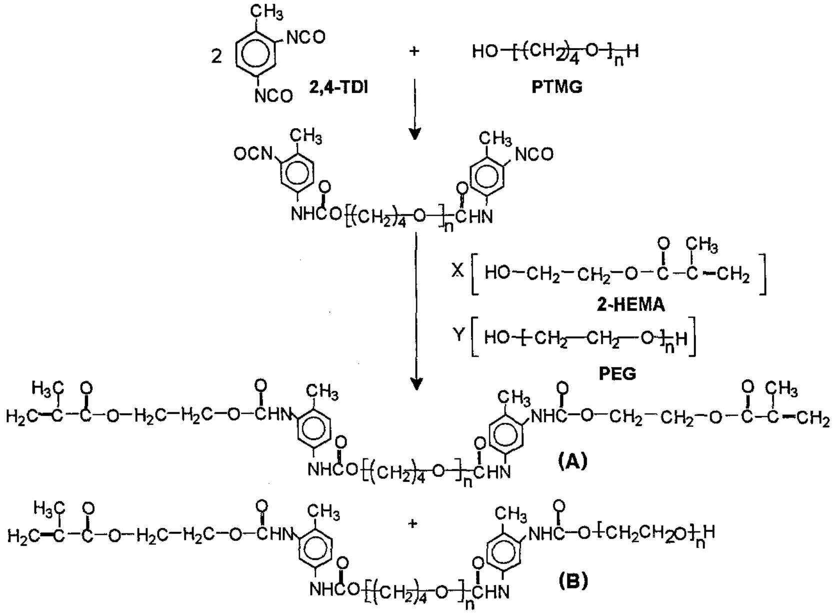
EXPERIMENTAL

Materials

In the synthesis of PEG-modified urethane acrylates, poly(tetramethylene glycol, Mw= 1000) (PTMG, Hyosung BASF), 2,4-toluene diisocynate (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-azobisiso-butyronitrile (AIBN, Junsei Chemical Co.) was recrystallized from DDI (Distilled Deionized) water and absolute ethanol respectively.

Synthesis of PMUA

The PEG-modified urethane acrylate(PMUA)s were synthesized by three step processes. The molar ratio of reactants was summarized in Table 1 and the reaction procedure for the preparation of PMUA was illustrated in Scheme 1. These reactions were carried out in a 4-neck glass reactor equipped with stirrer, thermometer, reflux condenser and inlet system for N_2 gas. The reaction procedure was presented in our previous paper in detail (5, 10). The number of the molecule ((B) type of scheme 1.) containing polyoxyethylene groups in molecular end increase with the increase of molar ratio of PEG. All PMUA emulsions were prepared using a phase inversion emulsification process without using external surfactant. PMUA (10g) was placed in a 100ml beaker and heated to 50°C to reduce viscosity, then cooled to 35°C with vigorously stirring. Water was initially added very slowly until a gel formed, then the last remaining water was added gradually to reduce viscosity.



Scheme 1. The reaction procedure and molecular structure of PMUA

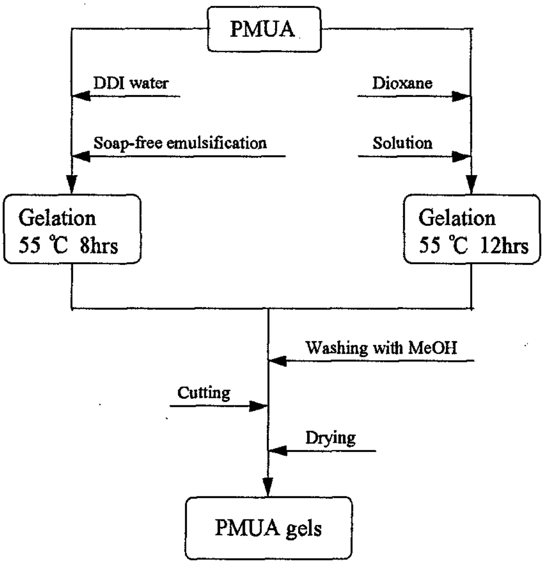
Table. 1. The molar ratio of reagents in the synthesis of PEG-modified urethane acrylate

Symbols	Reagents	Molar ratio
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

Preparation of PMUA gel

Cylindrical gels were prepared for swelling measurements by mixing 10mL of PMUA with dioxane or DDI water including AIBN or KPS, and this solution transferred quickly into a test tube (inner diameter was 1.5cm) to carry out gelation. After gelation was completed, all the samples were taken out of the test tube, fully washed with a large amount of DDI water or methanol, and cut into suitable lengths. These gels were dried at convection oven for 24 hours and put into dioxane or water to be swelled for 24hours. When the gels of PMUA were prepared by dioxane (UAG), this resin was dissolved completely in dioxane and the composition of resin to dioxane was varied 1:1 to 1:6. When 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 solvent composition and procedure of gelation of

PMUA was illustrated at Table 2 and Scheme 2 respectively.



Scheme 2. The procedure for PMUA gel preparation

Table 2. Gelation recipe of PEG-modified urethane acrylates

Recipe	PMUA (g)		DDI water (g)	Dioxane (g)	KPS (g)	AIBN (g)	Symbol
A	PMUA2	5	5 ~ 30	-	0.05	-	UAHG2
	PMUA3	5	5 ~ 30	-	0.05	-	UAHG3
	PMUA4	5	5 ~ 30	-	0.05	-	UAHG4
B	PMUA4	5	-	5 ~ 30	-	0.05	UAG

Measurement

The droplet sizes of emulsions were measured using Brookhaven Laser Light Scattering Instrument (BI 9000AT, BI 200SM, 2MI98631 PM-tube, LEXEL Ar-Ne laser, 514nm).
In order to investigate the adsorption behavior of PMUA in water/benzene interface, PMUA dissolved in benzene, then this solution was brought into contacted 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 urethane acrylate gels was determined using gravimetric method. When 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 of urethane acrylate to water was measured using Erma contact angle measurement, Model G-1.

RESULTS AND DISCUSSION

Gelation mechanism of PEG-modified urethane acrylate

PMUA used in this study have hydrophilic and hydrophobic segment at the one molecule, so these resin can be emulsified without using external surfactant because this resin can act as a polymeric surfactant. Therefore, when PMUA gels were prepared using water, first of all, PMUA were emulsified without surfactant, then emulsion, mixed with water soluble initiator (KPS), poured into a mold. Gelation was carried out at 55°C for 3 hours. This procedure is very similar to that of emulsion polymerization. For typical emulsion polymerization, breakdown and coalescence of emulsion droplets don't occur in the course of emulsion polymerization. However, soap-free emulsion of PMUA were broken around the initiation temperature of KPS and aggregated each other, which cause PMUA emulsion to form gel. In other words, droplet coalescence and polymerization of PMUA by KPS occur simultaneously in the course of gelation.

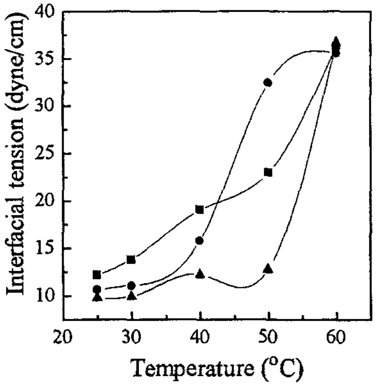


Fig. 1. Adsorption behavior change of PMUA with temperature (-▲-PMUA4, -■-PMUA3, -◆- PMUA2)

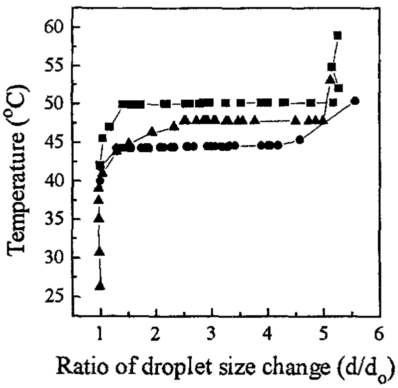


Fig. 2. Droplet size change of PMUA emulsions with temperature (-■- PMUA4, -▲- PMUA3, -◆- PMUA2)

Droplet coalescence is due to the decrease in hydrophilicity of polyoxyethylene groups with the increase of temperature, which cause the number of molecules locating O/W interface to decrease. Therefore, in order to confirm interfacial activity change with temperature, the adsorption behavior of PMUA in water/benzene interface at different temperature was observed and illustrated in Fig. 1.

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

Additionally, in order to observe droplet coalescence with the increase of temperature, it was investigated that droplet size changes of PMUA emulsions with temperature by laser dynamic light scattering, and these results were illustrated at Fig. 2. As temperature increase, droplet size of PMUA emulsions increase discontinuously. For PMUA4 emulsion, droplet size increased more than 6 times compared to initial droplet size with the increase of temperature, which makes it possible to maintain gel shape of PMUA after gelation.

Swelling behavior of PMUA gels

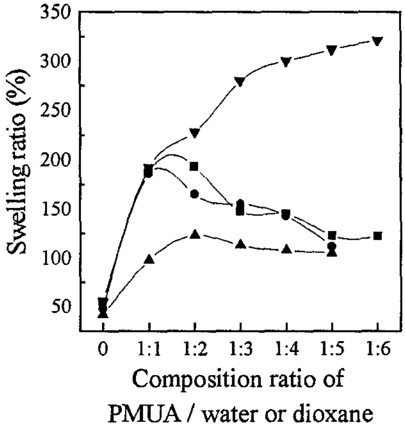


Fig. 3. The swelling ratio change of PMUA gels with the composition ratio of water or dioxane at organic medium (Dio xane) (-▼- UAG, -■-UAHG4, -▲- UAHG3, -◆- UAHG2)

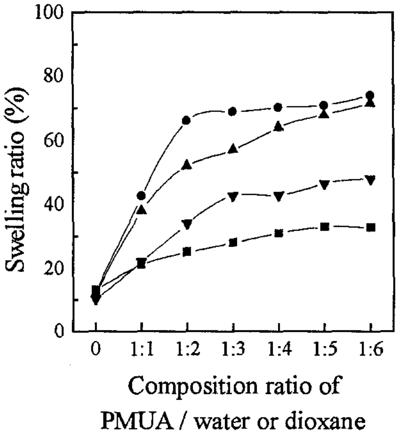


Fig. 4. The swelling ratio change of PMUA gels with the composition ratio of water or dioxane at aqueous medium (Water) (-●- UAHG4, -▲- UAHG3, -▼- UAHG2, -■- UAG)

First, swelling ratios of two types of PMUA gels (UAG and UAHG) at dioxane were measured and illustrated in Fig. 3. For PMUA gels prepared using dioxane (UAG), the swelling ratio increased with the increase of dioxane composition in organic solvent medium, but the swelling ratio of gels (UAHG) prepared using water decreased with the increase of water composition. These results were attributed to the difference in microstructure of PMUA gels prepared using water or dioxane. When UAG gels were prepared using dioxane, both of hydrophilic and hydrophobic segment of PMUA could dissolve in dioxane, so the chain entanglement decreased as composition ratio of dioxane to PMUA increased.

However, when gel was prepared by water, only hydrophilic segment of PMUA could dissolve or oriented at water phase, so phase separation occurred in the process of gelation. The hydrophilic segments oriented at water phase and aggregated with each other, and the hydrophobic segments aggregate each other and formed hydrophobic core, then the chain entanglement of hydrophobic segment increased with the increase of composition ratio of water to PMUA.

The swelling behaviors of UAHG and UAG gels in water were measured and its results was represented at Fig. 4. In the case of UAHG, these gels could be swelled about 70% at water. The swelling ratio increased as the ratio of water to PMUA increased and was larger than that of UAG gels prepared using dioxane. Moreover, when gels prepared at different dioxane composition were swelled at water, swelling ratios of UAG gels were nearly constant, as the composition ratio of dioxane to PMUA increased in the preparation of gel. Therefore, it can be concluded that the microstructure of UAHG is different from that of UAG and the increase in swelling ratio of UAHG with the increase of water composition is due to the increase in the orientation of polyoxyethylene group of PMUA to water phase. In other words, as the composition ratio of water to PMUA increases in the prepration of gel, the number of polyoxyethylene groups orienting to water phase increase due to microphase separation between hydrophilic and hydrophobic groups, which cause swelling of UAHG to increase in water medium. However, in the case of UAG gels prepared using dioxane, the orientation of polyoxyethylene groups to water phase is slightly changed by the change of composition ratio of dioxane, because hydrophilic and hydrophobic segments can be dissolved at dioxane. The microphase separation between segments did not occurred in the course of gelation, which made difficult swelling of the polyoxethylene groups with water.

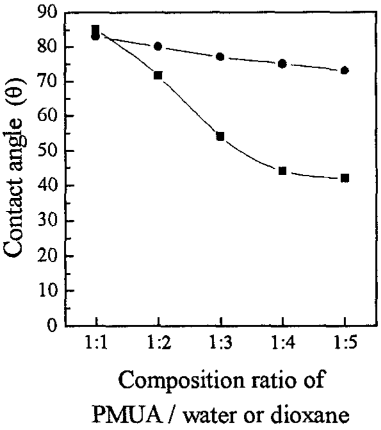


Fig. 5. The contact angle (θ) change of UAHG and UAG gel with the composition ratio of water or dioxane (-●- UAHG3 , -■- UAG)

Additionally, in order to confirm the orientation of polyoxyethylene groups into outer layer, the surface hydrophilicity of gels were investigated using contact angle measurement and these results were illustrated in Fig. 5. The contact angles of UAG gels were decreased slightly, but that of UAHG gels were changed with the composition ratio of water to PMUA, so it can be concluded that in the case of UAHG gels, the orientation of polyoxyethylene groups increased with the ratio of water to resin due to microphase separation between hydrophilic and hydrophobic segments, but for UAG gels, the orientation of polyoxyethylene groups did not change with the composition ratio of dioxane to resin.

CONCLUSIONS

PMUA gels (UAHG), which can be swelled at both of organic solvent and water, can be prepared using water. Therefore, it could be thought that the structure of these gels was comprised of outer and inner layer and differ from that of gels prepared using conventional method, because microphase separation between hydrophilic and hydrophobic groups occured in the course of gelation. The outer layer was composed of hydrophilic segments (polyoxyethylene groups) and the inner layer was comprised of hydrophobic segments. When these gel were swelled by water, the hydrophilic layer was swelled by water but the hydrophobic layer did not swelled. Additionally, the swelling ratio of UAHG gels can be controlled by the composition ratio of water to PMUA.

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