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Synthesis of new pH-sensitive polyurethane gels using polyethylene glycol modified urethane acrylate and urethane acrylate anionomer

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Abstract : New type of amphiphilic pH-sensitive polyurethane networks, derived from the mixture of polyethylene glycol-modified urethane acrylates (PMUA) and urethane acrylate anionomer (UAA), were prepared and their swelling behaviors were evaluated. Three kinds of polymerization methods were employed in the synthesis of polyurethane networks. Polyurethane networks prepared by a process similar to that of soap-free emulsion polymerization (UAHG) showed the highest swelling ratio and pH-sensitivity. Additionally, four kinds of UAHG gels were prepared at different composition of UAA. As the composition ratio of UAA to PMUA increased, swelling of UAHG gels in alkali pH buffer solution and their pH-sensitivity greatly increased. Additionally, swelling of UAHG gels changed reversibly with the change of pH.

Introduction

Polyurethane hydrogels are claimed to have applications in the biomedical area as 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].

In our previous paper[5-7], the amphiphilic polyurethane gels could be prepared using polyethylene glycol-modified urethane acrylate (PMUA) by two methods. When PMUA gels were prepared using soap-free emulsion of PMUA, droplet coalescence and gelation occurred at the same time, then PMUA gels containing microphase separated structures formed. The structure of these gels was similar to the microstructure of PMUA emulsion, which is formed by the microphase separation between hydrophilic and hydrophobic segments in the preparation of soap-free emulsions. PMUA gels swelled in water and organic solvent, and showed different swelling behaviors in both solvents. Additionally, as the composition ratio of water to PMUA increased in the preparation of gels, swelling in water increased, but swelling in organic solvent slightly decreased. These results indicated that the amphiphilicity of PMUA gels changed with the composition ratio of water to PMUA, because the degree of microphase separation varied with the addition amount of water. In the case of PMUA gels prepared with dioxane, however, these gels showed very small swelling ratio in water and greater swelling ratio in dioxane. Therefore, it could be concluded that the

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hydrophilicity or amphiphilicity of PMUA was maximized by the new gelation method similar to soap-free emulsion polymerization.

Generally, pH-sensitive hydrogels are prepared by the polymerization of hydrophilic ionic monomers such as acrylic acids, methacrylic acid, sodium styrene sulfonate, aminoethyl methacrylate, and vinylpyridine[8-11]. However, the object of this study is the preparation of new pH-sensitive polyurethane (PU) gels using PMUA and urethane acrylate anionomer (UAA) instead of conventional hydrophilic monomers[8-11]. Waterborne coatings have been widely utilized recently in industrial coatings, which has made it possible to control pollution, to reduce risks of fire, and to improve aspects of occupational health and safety. Therefore, UAA resin used in this study has been widely applied as water-dispersible UV curing resin, because these resins can be emulsified without the use of an external surfactant[12-13]. The application of PMUA resin as an water-dispersible coating materials was reported in our previous reports[14-15].

To maximize the hydrophilicity and pH-sensitivity of PU gels prepared with PMUA/UAA mixtures, the method used in the preparation of PMUA gels will be also employed in this study. The gelation of PMUA and UAA mixtures were carried out by a process similar to the preparation method of PMUA gels. In order to investigate the pH-sensitivity of these gels, swelling in different pH buffer solutions will be measured.

Experimental

Materials

In the synthesis of PMUA and UAA, poly(tetramethylene glycol (PTMG, Mw = 1000, Hyosung BASF), 2,4-toluene diisocyanate (TDI, Junsei Chemical Co.), 2-hydroxyethyl methacrylate (2-HEMA, Aldrich Chemical Co.), polyethylene glycol (PEG, Mw =600, Junsei Chemical Co.), and dimethylolpropionic acid (DMPA, Shinyo Chemicals) were used. 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. N-methyl-2-pyrrolidone (NMP, Junsei Chemical Co.) as the dissolution agent of DMPA and the agent of reducing the viscosity of synthesized resin was used.

For neutralizing carboxyl groups, triethyl amine (TEA, Waco pure Chemical Co.) was used. (1-Hydroxycyclohexyl) phenylmethanone (Irgacure 184, Ciba-Geigy Chemical Co.) and tert-butyl benzoate (Junsei Chemical Co.) were used as photoinitiator and thermal initiator, respectively.

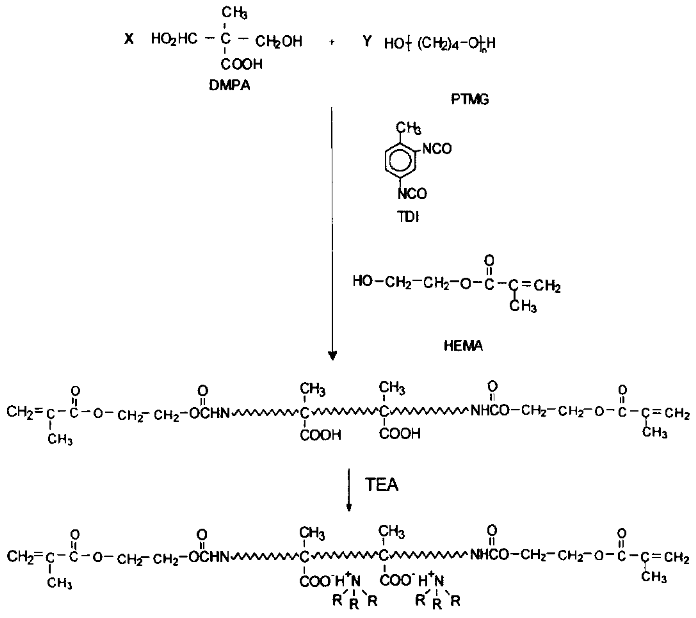
Synthesis of PMUA and UAA

PMUA was synthesized by three step processes. The molar ratio of reactants is summarized in Table 1. These reactions were carried out in a 4-necked glass reactor equipped with stirrer, thermometer, reflux condenser and inlet system for N_2 gas. The procedure and structure of PMUA were presented in our previous paper in detail[5-7]. According to our previous experimental results[6], PMUA synthesized at the molar ratio of 1.2:8 HEMA:PEG showed the greatest swelling ratio in water, so this kind of PMUA is used in this study.

UAA was synthesized by four step processes[13-14]. PTMG, DMPA and NMP (18wt%) as solvent were charged into 500ml 4-necked kettle with stirrer, thermometer, reflux condenser and inlet system for N_2 gas. This mixture was heated to 70°C slowly with N_2 purging and stirring until the DMPA dissolved completely. After the solution was clear, it was cooled to 30°C, then TDI was dropped into the reactor so that the isocyanate group of TDI reacts with the hydroxy group of PTMG and DMPA. Then this mixture was stirred and reacted at 70°C for 5 hours. After 5 hours, the system was cooled to 30°C, then HEMA was dropped into the reactor for the introduction of vinyl group. The mixture was heated to 70°C slowly, stirred and reacted for 4 hours. For neutralizing this resin, TEA was added at room temperature with stirring for 30 minutes. The structure of UAA is represented Scheme 1. UAA was widely used as a water-dispersible UV curing resin, so coating properties and water-dispersibility of this resin were reported in our previous papers[14-15]. Four kinds of UAA were synthesized and used in our previous experiments. Among them, UAA synthesized at the molar ratio of 0.7:0.3 DMPA:PTMG showed the best coating properties and the smallest droplet size, so this kind of UAA was selected and used in this study.

Table 1. Molar ratio of reagents in the synthesis of PMUA and UAA

Symbol	Reagents	Stoichiometry
PMUA	PTMG / TDI / 2-HEMA / PEG600	1 / 2 / 1.2 / 0.8
UAA	DMPA / PTMG / TDI / 2-HEMA	0.7 / 0.3 / 1.5 / 1.5



Scheme 1. The structure of UAA

All of emulsions were prepared using a phase inversion emulsification process without the use of external surfactant. PMUA or the PMUA/UAA mixtures (10g) was placed in a 100ml beaker and heated to 45°C to reduce viscosity, then it was cooled to 35°C while vigorously stirring. Water was added initially very slowly until a gel-like emulsion formed, then the remaining water was added gradually to reduce the viscosity. According to our previous experiments[5-7, 16], the droplet size of PMUA and UAA soap-free emulsions is 50-58nm.

Network synthesis

The solutions of PMUA and UAA mixtures were transferred into a mold (10X10X0.5 cm) to carry out gelation. After gelation was complete, the samples were taken out of the mold, fully washed with a large amount of DDI water and methanol, and cut into suitable lengths. The gels were dried in a convection oven for 24 hours and placed into water to be swelled for 6 hours. When PMUA gel (UADG4-4) was prepared by dioxane, PMUA dissolved completely in dioxane and the composition of resin to dioxane was 6:1 - 1:1.5. In case gels were prepared with water (UAHG4-4), to begin with, the soap-free emulsions of PMUA were prepared at 6:1 - 1:1.5 composition ratio of PMUA to DDI water, then these emulsions were poured into a mold to carry out the gelation. The recipe and procedure for the preparation of UADG and UAHG gels are illustrated at Table 2, and Scheme 2, respectively. Additionally, UV cured gel (UAVG) was prepared by conventional curing and the reagents used are summarized in Table 3. The systems were irradiated by UV-lamp (450W, Ace glass Co,.) for 5 minutes[14-15].

Table 2. Recipe for the preparation of UAHG and UADG gels

Recipe	PMUA/UAA	DDI water	Dioxane	KPS	AIBN	Symbol
A	10g	15g	-	0.005g	-	UAHG4-0
	8g / 2g	15g	-	0.005g	-	UAHG4-1
	5g / 5g	15g	-	0.005g	-	UAHG4-2
	4g / 6g	15g	-	0.005g	-	UAHG4-3
	2g / 8g	1.67 - 15g	-	0.005g	-	UAHG4-4
B	2g / 8g	-	1.67-15g	-	0.005g	UADG4-4

Table 3. Recipe for the preparation of UAVG gel

PMUA / UAA = 2g / 8g
Benzophenone = 0.3g
t-butyl hydroperoxide = 0.2g
Triethyl amine = 0.1g

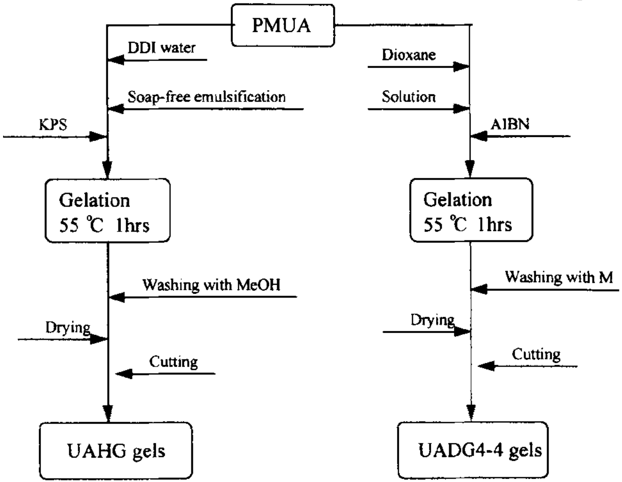
Swelling Measurement

UAHG, UADG, and UAVG gels in triplicate were immersed in pH buffer solution at 37°C. Standard pH buffer solutions (pH 3, 4, 5, 7, 9, and 11, Shinyo Pure Chemicals Co., LTD) were used to investigate the pH dependence of swelling of these networks. The swelling ratio of these samples was determined by 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 $(M_3-M_1)/M_1$

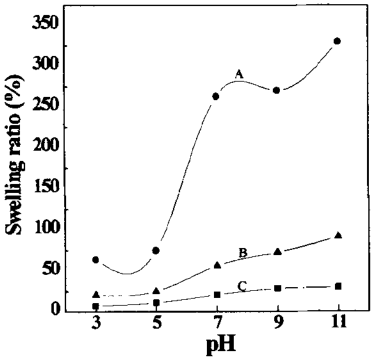
Results and Discussion

Fig. 1 shows the equilibrium swelling behavior for UAHG4-4, UADG4-4, and UAVG gels prepared by different procedures, measured as a function of pH at 37°C. The swelling ratio of

UAVG gel (Curve C) is very low and independent of pH. For UADG4-4 gel (Curve B) prepared with dioxane, the swelling ratio is higher than that of UAVG gel and slightly dependent on pH. UAHG4-4 gel (Curve A), however, shows the highest swelling ratio and pH sensitivity. Even though three kinds of PU gels are prepared by the same kind of PMUA/UAA mixture, these gels show different swelling behaviors, which are due to the difference of microstructure between UAHG4-4, UADG4-4, and UAVG gels.



Scheme 2. Procedure of preparation of UADG and UAHG gels



g. 1 Swelling ratio change of UAHG, UA DG, and UAVG gels as a function of pH (-■- UAVG, -●- UADG, -▲-UAHG)

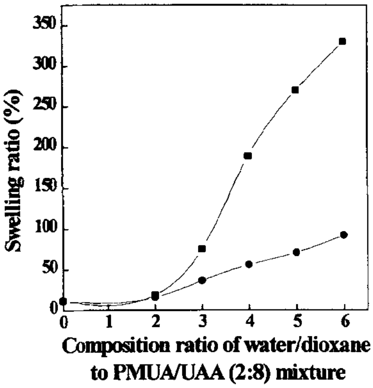
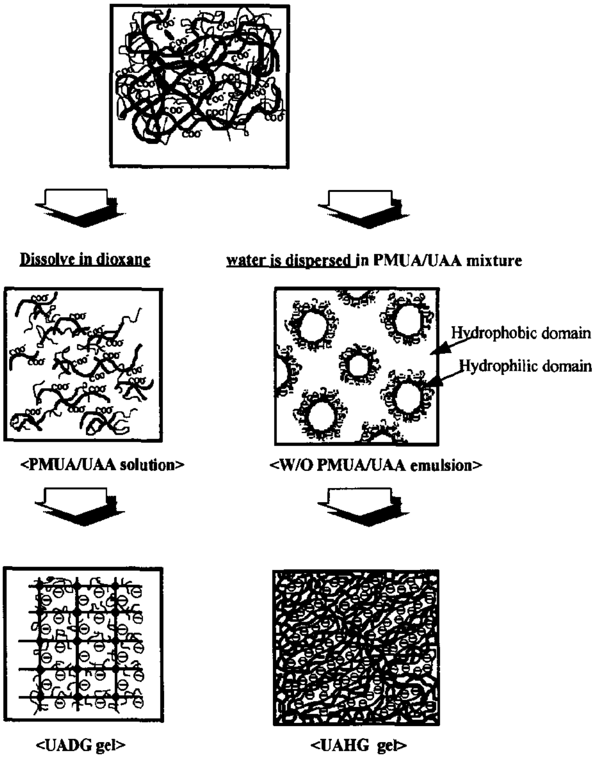


Fig. 2 the change of swelling of UADG4-4 and UAHG4-4 gels in pH 11 as a function of composition ratio of water or dioxane in the preparation of gels (-■- UAHG4-4, -●- UADG4-4)



(a) (b)

Scheme 3. Schematic presentation of microstructure of UADG and UAHG gels

In the case of preparation of UAHG 4-4 gel, to begin with, the soap-free emulsification of PMUA and UAA mixtures was carried out. In the course of emulsification of these mixtures, microphase separation between hydrophilic and hydrophobic segments occurs, so hydrophilic segments comprised of polyoxyethylene and carboxylate anions orient toward the water phase to form domains while the hydrophobic segments also aggregate to form the other domains (Scheme 3 (b)). When the gelation of PMUA/UAA W/O emulsion was carried out with KPS, initiator radicals formed in the aqueous phase penetrated into oil droplets, then gelation occurs while the microphase-separated structure of this emulsion is maintained. In other words, the microphase-separated structure can be maintained after gelation and the microstructure of this gels is very similar to that of soap-free emulsion of PMUA/UAA mixtures. As the external pH increases, the ionic repulsion between charged groups of hydrophilic domains significantly increases, so large volume change occurs. This microphase separation between both segments causes the hydrophilicity of UAHG to be maximized, so the swelling in water and pH sensitivity of UAHG gel are higher than any other gels prepared by different methods. However, for the preparation of UADG4-4 gel, microphase separation does not occur during gelation, because both segments of UAA and PMUA dissolve in dioxane. Negatively charged groups of UADG gel don't form their domains and attach to the networks as pendant groups, so the volume change owing to the ionic repulsion is small relative to UAHG4-4 gel (Scheme 3(a)).

Fig. 2 shows the change of swelling of UADG4-4 and UAHG4-4 gels at pH 11 as a function of composition ratio of water or dioxane. In case of UAHG4-4 gels, swelling in pH 11 increased largely with the increase in the composition ratio of water. For UADG4-4 gels, however, the increase of swelling at pH 11 with the composition ratio of dioxane is smaller than that of UAHG4-4. These results indicate that the hydrophilicity of UAHG4-4 gels increase with the increase of water concentration and the increase of hydrophilicity of UAHG4-4 is larger than that of UADG4-4 gels. These results are due to the difference of the formation of hydrophilic domains between these gels. In other words, for UAHG4-4 gels, as the composition ratio of water to resin increase in the preparation of gels, the degree of microphase separation between hydrophilic and hydrophobic segments increase, thus the numbers of hydrophilic domains in gel matrix increase. In case of UADG4-4 gels, chain entanglements decrease with an increase of composition ratio of dioxane, so chain mobility and penetration of water molecules increase, which increases the swelling of UADG4-4 gels.

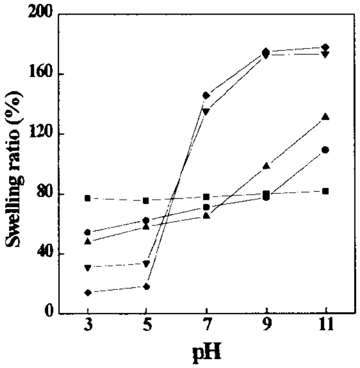


Fig. 3 The change of swelling ratio of UAHG gels with pH conditions (-■-UAHG4, -●-UAHG 4-1, -▲-UAHG4-2, -▼-UAHG 4-3, -◆-UAHG4-4)

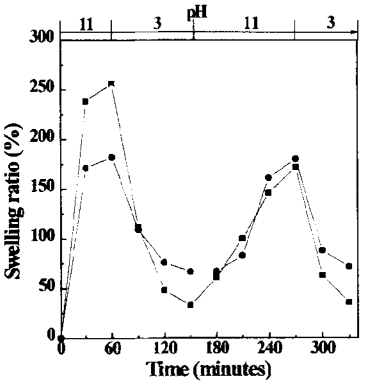


Fig. 4 Swelling dynamic of UAHG4-3 4-4 gels in pH 3 and 11 buffer solution (-■- UAHG4-4, -●- UAHG4-3,)

Fig. 3. illustrates the swelling ratio change of UAHG4-0, 4-1, 4-2, 4-3, and 4-4 gels as a function of pH. Swelling ratio of UAHG4-0 gel remains unchanged with pH, because the hydrophilic segments of this gel are comprised of nonionic group only. For UAHG4-1, 4-2, 4-3, and 4-4 gels, however, their swelling ratio increases with the increase of pH and the composition ratio of UAA. The difference of swelling ratio between low pH and high pH increases with the composition ratio of UAA. These results are attributed to the increase of phase-separated carboxylate anion domains in polyurethane networks.

The dynamic response of swelling to a step change in pH is illustrated in Fig. 4. UAHG4-1, 4-3 and 4-4 gels showing relatively high pH-sensitivity were placed into pH 3 buffer solution for 1 hr and then transferred to pH 11 buffer solution. Later, these gels were placed back into pH 11 solution. Both of UAHG 4-3 and 4-4 gels show reversible swelling with pH. These phenomena are desirable for pH-sensitive controlled release system, because the swelling of these gels can be controlled by change of pH[16]. As expected these gels show reversible swelling with the change of external pH.

Conclusion

New pH-sensitive polyurethane gels, UAHG4-3 and 4-4 gels, can be prepared with the UAA/PMUA mixture by the new gelation method using O/W soap-free emulsions. These gels showed higher swelling in water and pH-sensitivity than UADG and UAVG gels. These results are due to the difference of microstructures of these gels. The microstructure of these gels changes with the synthesis processes of these gels.

It could be thought that the microphase separated UAHG gels comprising hydrophilic and hydrophobic domains maximize the hydrophilicity and pH-sensitivity of UAHG gel, because this microphase separation between segments occurs in the course of gelation. Additionally, the swelling of UAHG gels in pH could be controlled by the composition ratio of water to resins, and UAHG4-4 and 4-3 gels showed reversible swelling with the change of pH.

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