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ORIGINAL CONTRIBUTION

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Preparation of PEG-modified urethane acrylate emulsion and its emulsion polymerization

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Abstract In order to improve stability and reduce droplet size, the PEG-modified urethane acrylates were synthesized by the reaction of polyethylene glycol (PEG) with residual isocyanate groups of urethane acrylate to incorporate hydrophilic groups into the molecular ends. The droplet sizes of the PEG-modified urethane acrylate emulsions were much smaller than those of unmodified urethane acrylate emulsions at the same surfactant composition, and the droplet sizes of these emulsions were significantly effected not by surfactant compositions and types, but by the reaction molar ratio of PEG, because the urethane acrylate containing polyoxyethylene groups as terminal groups aided the interfacial activity of surfactant molecules and acted as a polymeric surfactant. The actions of PEG-modified urethane acrylate were confirmed by the investigation of adsorption of urethane acrylate in a water/benzene interface.

For polymerization of emulsions, the stability of emulsion in the process of emulsion polymerization was changed by the type of surfactant or initiator. In the case of emulsion polymerization with a water soluble initiator ($K_2S_2O_8$), the emulsions prepared using TWEEN 60 were broken in the process of polymerization. However, polymerization of these emulsions could be carried out using an oil soluble initiator (AIBN). The conversion of emulsion polymerization changed with the type of urethane acrylates, that is, the reaction molar ratio of PEG to 2-HEMA.

Key words PEG-modified urethane acrylate – emulsion – droplet size – emulsion polymerization – interfacial tension – microsuspension polymerization

Introduction

Recently, in order to improve impact-resistance of thermosetting or thermoplastic having inherent brittleness, core-shell composite latexes have been widely used [1–2]. Core-shell latexes used as impact-modifiers generally were comprised of two or more radially alternating rubbery and glassy polymer layers, the center always being of rubber polymer such as polybutadiene, polybutylacrylate, or SBR, and the outer layer being of glassy polymer [3–5]. We, however, tried to prepare polyurethane-polymethyl methacrylate (PMMA) core-shell latex instead of the previously mentioned rubbery polymers core-shell latexes [6–7].

Polyurethane emulsions generally were prepared using a method in which polyurethane prepolymers containing hydrophilic pendant groups are emulsified first and chain extension follows to increase the molecular weight of prepolymer [8–11]. However in our experiments, for the preparation of polyurethane emulsion, we have employed a method where urethane acrylates were prepared to be emulsified and the emulsion polymerization followed to obtain cross-linked polyurethane latexes.

According to the results of our previous papers [6–7], the impact strength of the blend of PMMA/core-shell latex prepared using the above-mentioned method was unsatisfactory. Moreover, considerable amounts of surfactants were needed to prepare the urethane acrylate emulsion. Therefore, in order to improve the efficiency of polyurethane/PMMA core-shell latex as an impact modifier by controlling particle size, and to reduce the amounts of surfactant used in preparation of urethane acrylate emulsion, we attempted to introduce hydrophilic groups into molecular ends to improve water dispersibility of urethane acrylate.

A special treatment or structural modification for prepolymer or oligomer to improve water-dispersibility has been done generally by incorporating hydrophilic groups into the molecular backbone. These hydrophilic groups always existed as pendant groups, especially, for ionic functional groups, the neutralization process of prepolymer had to be done. To begin with, moreover, in the case of preparation of polyurethane emulsion containing nonionic hydrophilic groups as pendant groups, the synthesis of prepolymers having isocyanate end groups and polyoxyethylene pendant groups at one molecule must be carried out using complicated reaction processes [8–11].

In this experiment, the PEG-modified urethane acrylates containing hydrophilic groups (polyoxyethylene groups) and vinyl groups, not as pendants but at both ends, were synthesized by the reaction of polyethylene glycol (PEG) with residual isocyanate groups of urethane acrylate. Then these urethane acrylates could be emulsified by a very small amount of surfactant. Particularly, a neutralization process was not needed, because this hydrophilic group was a nonionic group. These materials have hydrophilic groups and lipophilic groups at one molecule, thus these molecules act as a polymeric surfactant, which aids activity of surfactants.

Table 1 The synthesis composition of urethane acrylates

Symbols	Reagents	Stoichiometry
UA*	PTMG/TDI/2-HEMA	1 / 2 / 2
UA1	PTMG/TDI/2-HEMA/PEG600	1 / 2 / 1.85 / 0.15
UA2	PTMG/TDI/2-HEMA/PEG600	1 / 2 / 1.7 / 0.3
UA3	PTMG/TDI/2-HEMA/PEG600	1 / 2 / 1.5 / 0.5
UA4	PTMG/TDI/2-HEMA/PEG600	1 / 2 / 1.2 / 0.8
UA5	PTMG/TDI/2-HEMA/PEG200	1 / 2 / 1.5 / 0.5
UA6	PTMG/TDI/2-HEMA/PEG1500	1 / 2 / 1.5 / 0.5

* UA represents unmodified urethane acrylate.

Accordingly, this paper examines droplet sizes and centrifugal stability changes of urethane acrylate emulsions are affected by surfactant compositions and types. Moreover, it shows that the droplet sizes of urethane acrylate emulsions changes with the reaction molar ratio of PEG. The polymerizations of these emulsions were used to prepare polyurethane acrylate latexes with different initiators and surfactant types.

Experiments

Materials

In the synthesis of PEG-modified urethane acrylates, poly(tetramethylene glycol, $M_w = 1000$) (PTMG, Hyosung BASF), 2,4-toluene diisocynate (TDI, Junsei Chemical Co.), 2-hydroxy ethylmethacrylate(2-HEMA, Aldrich Chemical Co.), and polyethylene glycol (PEG, $M_w = 600$, Junsei Chemical Co.) were used.

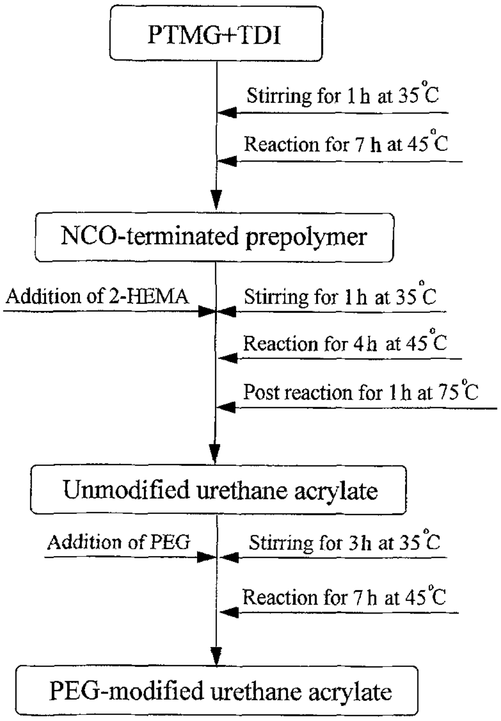
Ionic surfactant, sodium lauryl sulfate (SLS, Shinyo Pure Chemical Co.) and nonionic surfactant, TWEEN 60, 20 and SPAN 60, 20 (Shinyo Pure Chemical Co.) were used as a surfactant and stearyl alcohol, cetyl alcohol and hexadecane were employed as a cosurfactant in the preparation of urethane acrylate emulsions.

Synthesis of urethane acrylate and PEG-modified urethane acrylates

The urethane acrylate and PEG-modified urethane acrylates were synthesized by two or three step processes. The molar ratio of reactants was summarized in Table 1 and the reaction procedure for the preparation of PEG-modified urethane acrylate and unmodified urethane acrylate was illustrated in Scheme 1. These reactions were carried out in a four-neck glass reactor equipped with stirrer, thermometer, reflux condenser and inlet system for N_2 gas.

In the first step, TDI was poured into the four-neck glass reactor at N_2 atmosphere. Then PTMG was dropped into the reactor at 35 °C and reaction temperature was raised to 45 °C so that the isocyanate group of TDI reacted with the hydroxy group of PTMG. This temperature was maintained for 7 h to retain an acceptable rate of reaction and then the temperature was raised slowly to reduce isocyanate levels. The change of NCO value during the reaction was determined using the dibutylamine back titration method to find the end point of reaction [12].

In the second step, 2-HEMA was added slowly into the kettle to react with residual isocyanate group at 45 °C for 4 h, which introduced reactive vinyl groups into the molecular end. The raising of the reaction temperature to



Scheme 1 Reaction scheme for the synthesis of PEG-modified urethane acrylate and unmodified urethane acrylate

75 °C was needed to eliminate unreacted isocyanates. For PEG-modified urethane acrylates, the end point of this step was that the NCO value was not changed with reaction time. However, in the case of unmodified acrylate, the end point of reaction was determined by the disappearance of 2270 cm^{-1} corresponding to NCO stretching.

Unmodified urethane acrylate was prepared by a two-step reaction, but PEG-modified urethane acrylates were synthesized by three consecutive reactions. The first and second steps were the same process as the synthesis process of unmodified urethane acrylate. In the third step, PEG was poured into the kettle to react with the last residual isocyanate. This process made it possible to introduce polyoxyethylene groups into the molecular ends, where hydrophilic groups and reactive vinyl groups existed in the one molecule. The reaction end point of this step was determined by the disappearance of 2270 cm^{-1} corresponding to NCO stretching.

Emulsion preparation and measurement of droplet size

All urethane acrylate emulsions were prepared using a phase inversion emulsification process. SLS and cetyl, stearyl alcohol and mixed nonionic surfactants comprised of TWEEN 60, 20 and SPAN 60, 20 were used.

An oil solution (10 g) containing surfactant mixtures was placed in a 100 ml beaker and heated to 60 °C to melt, then cooled at 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.

The droplet sizes of emulsions were measured by an Ostuka Electronic, Laser Particle Analyzer, LPA-3000/3100 (droplet size $< 1\ \mu m$) and ELZONE 620 PC (droplet size $> 1\ \mu m$).

Adsorption isotherm of PEG-modified urethane acrylates at water/benzene interface

In order to investigate the adsorption isotherm of PEG-modified urethane acrylates in water/benzene interface, the same amount of PEG-modified urethane acrylates and unmodified urethane acrylate 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 Nöuy ring method (Fisher Scientific Co. Surface tensiomat-21).

Emulsion polymerization and measurement of conversion

The emulsion polymerization was carried out in a four-neck glass kettle, equipped with a stirrer, thermometer, reflux condenser, and inlet system for N_2 gas. The kettle was placed in thermostat-controlled oil bath, in which the polymerization temperature was kept at 55 °C ± 0.5 °C.

In the case where a water-soluble initiator, $K_2S_2O_8$, were used, the urethane acrylate emulsions (100 g) were prepared in a 100 ml beaker then were poured into the reaction kettle prior to emulsion polymerization and the initiator ($K_2S_2O_8$) was then added into the aqueous phase. The system temperature was gradually raised to 55 °C over the course of 1 h while slowly stirring at 200 rpm.

In the case of the oil-soluble initiator, AIBN, the initiator was dissolved in oil phase at 45 °C, whether containing surfactants or not, prior to emulsification. The water was added slowly into this mixture at 35 °C into a 100 ml beaker while stirring vigorously and the emulsion that formed was poured into the reaction kettle. The temperature of the kettle was raised to 55 °C over the course of 1 hr while slowly stirring at 200 rpm.

The polymerized urethane acrylate emulsions were introduced into the absolute methanol. The polymerized urethane acrylates were precipitated and the filtered sample was dried for 24 h in a vacuum oven. The conversion of urethane acrylate therefore was determined using following equation:

$$\text{Conversion(wt\%)} = \frac{W_d}{W_t \times \text{TSC}} \times 100 , \qquad (1)$$

where, W_t = collected sample weight (g), W_d = sample weight after washing and drying (g), TSC = theoretical solid content value per gram of collected sample at 100% conversion.

Results and discussion

The emulsion prepared by using mixed nonionic surfactants

For O/W emulsions of unmodified urethane acrylate (UA), which does not contain hydrophilic groups at molecular ends, the order of centrifugal stability was TWEEN 60-SPAN 60 > TWEEN 60-SPAN 20 > TWEEN 20-SPAN 60. The relatively stable emulsion was formed at HLB 11 of TWEEN 60-SPAN 60. However, the centrifugal stabilities and droplet sizes of these urethane acrylate emulsions formed by these surfactant systems were unsatisfactory compared with commercially available emulsions.

Thus, the PEG-modified urethane acrylates (UA1-UA4) were emulsified by this mixed surfactant (TWEEN 60-SPAN 60, HLB 11-15), and the droplet sizes of PEG-modified urethane acrylate emulsions were investigated and illustrated at Fig. 1. The droplet sizes of UA, UA1, UA2 emulsions were smallest at HLB 11 and 12 respectively. For the emulsions of unmodified urethane acrylate (UA) (Curve A of Fig. 1), the difference in emulsion droplet sizes between HLB 11 and HLB 14.9 (HLB of TWEEN 60 is 14.9) was larger than that of PEG-modified urethane acrylate emulsions (UA1, UA2). The UA1 and UA2 emulsions (Curve B and C of Fig. 1) showed the smallest droplet size at more hydrophilic HLB range than unmodified urethane acrylate (UA), because the PEG-modified urethane acrylate became relatively hydrophilic as the polyoxyethylene groups were introduced into the urethane acrylate molecule ends.

Additionally, at constant HLB range, the droplet size of urethane acrylate emulsion decreased significantly with the introducing polyoxyethylene groups into molecular. In other words, the droplet sizes of PEG-modified urethane acrylates emulsions were much smaller than that of unmodified urethane acrylate emulsions. However, in case of UA2-UA4, droplet sizes of its emulsion were not decreased significantly with the increase of PEG reaction molar ratio (Curve D and E), which was due to the limitation in interfacial area where polyoxyethylene groups located and exerted interfacial activity.

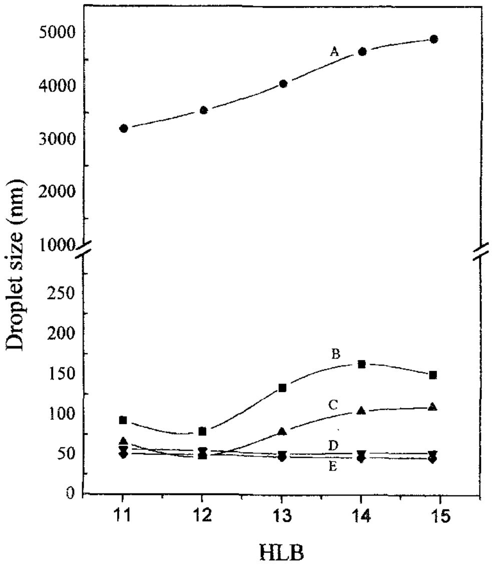


Fig. 1 Droplet size changes of urethane acrylate emulsions with HLB (-●- UA, -■- UA1, -▲- UA2, -▼- UA3, -◆- UA4)

Table 2 The surfactant composition of urethane acrylate emulsions

Urethane acrylate = 10 g
DDI water = 50 g
SLS = 0.15–0.45 g
Cetyl alcohol = 0–0.2 g
Stearyl alcohol = 0–0.1 g

Moreover, it was clear from previous experiments that a stable emulsion of oligomer, such as urethane acrylate or epoxy acrylate, couldn't be formed using monomeric surfactant (SLS) only, even though phase inversion emulsification were employed. The relatively stable emulsion of oligomer could be prepared using a mixture of SLS and co-surfactant (cetyl alcohol, stearyl alcohol or hexadecane) or a mixture of TWEEN 60-SPAN 60 and co-surfactant [6–7]. According to earlier workers and our previous experiments, when the molar ratio of SLS to long-chain alcohol was 1:2 or 1:3, the most stable emulsion could be prepared. Thus, all urethane acrylate emulsions were prepared by these surfactant combinations (Table 2).

Figure 2 shows the droplet size changes with the molar ratio change of SLS to co-surfactant for urethane acrylate emulsions. The unmodified urethane acrylate (UA) emulsion could not be obtained using SLS alone, and the stable and fine droplet emulsion was formed when the molar ratio of SLS to cosurfactant was 1:3 or 1:2 [6], but for PEG-modified urethane acrylates (UA1, UA2), the droplet size was smallest when the molar ratio of SLS to co-surfactant was 1:1. Moreover, stable and fine droplet emulsions could be formed using SLS only.

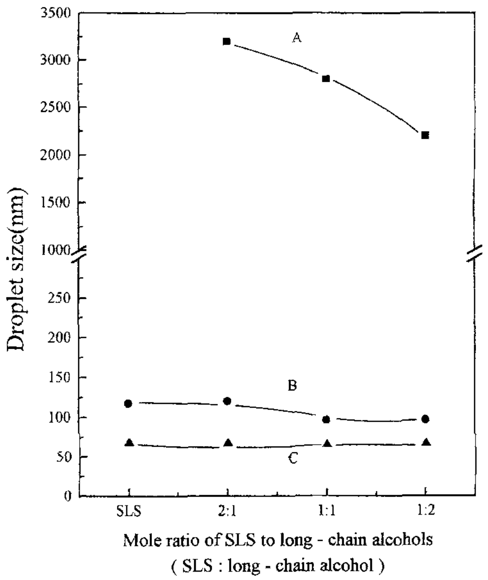


Fig. 2 Droplet size changes of urethane acrylate emulsions with molar ratio of SLS to long-chain alcohol (-■- UA, -●- UA1, -▲- UA2). * Droplet size of UA emulsion is not represented, because this emulsion cannot be prepared using SLS alone

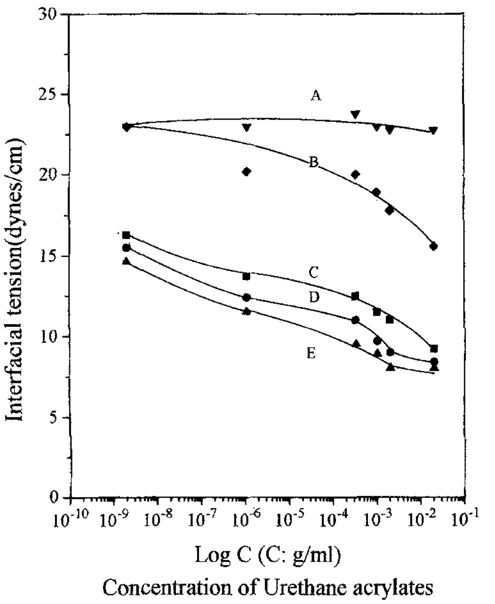


Fig. 3 Interfacial tension changes of water/benzene with the concentration of urethane acrylates in benzene (-▼- UA, -◆- UA1, -■- UA2, -●- UA3, -▲- UA4)

These results were attributed to the interfacial activity of urethane acrylate molecules containing polyoxyethylene groups introduced by the reaction of PEG with residual isocyanate groups. The polyoxyethylene groups in urethane acrylate molecule ends aid interfacial activity of surfactant molecules and are associated with surfactant molecules, so strong liquid film at the O/W interface was formed. Thus, finer droplet emulsions of PEG-modified urethane acrylates could be formed.

Figure 3 illustrates the interfacial tension changes with the concentration of urethane acrylates in benzene. The urethane acrylates (UA, UA1, UA2, UA3, UA4) were dissolved in benzene, and these solutions were brought into contact with water to form the interface. 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 urethane acrylate in benzene.

Curve A of Fig. 3 indicates the change of interfacial tension of water/benzene containing unmodified urethane acrylate (UA). The interfacial tension was unchanged with concentration of urethane acrylates. However, for PEG-modified urethane acrylate (UA1, UA2, UA3, UA4), the interfacial tensions (Curve B, C, D, E) decreased as the concentration of urethane acrylates in benzene increased. UA4, 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, so could play a role as a polymeric surfactant. Therefore, the reason that PEG-modified urethane acrylates showed finer droplet sizes than unmodified urethane acrylate was confirmed by these results.

In order to investigate the effect of chain length of polyoxyethylene group on droplet size and stability of emulsion, UA3, UA5 and UA6 were synthesized using PEG 600, 200 and 1500 respectively (Table 1). The UA5 and UA6 emulsions prepared by the above-mentioned emulsification method were very unstable. The UA6 prepared using PEG 200 have relatively short chain lengths of polyoxyethylene groups, which could not overcome attraction between hydrophobic chains of urethane acrylate molecules. Thus, the location of polyoxyethylene group at the O/W interface was more difficult than UA3, so these groups could not assist the interfacial activity of surfactant molecules. The emulsion of UA6 prepared using PEG 1500 also was unstable, even though UA6 had longer chains of polyoxyethylene groups than UA3. This result was due to the melting point of PEG 1500 (45 °C). The UA6 was solidified in the process of emulsification, which made difficult the location of polyoxyethylene groups at the O/W interface. However, when the emulsification of UA6 was carried out at 50 °C, phase separation occurred at an early stage of emulsification, which was attributed to the decrease of hydrophilicity of polyoxyethylene groups with the increase of emulsification temperature [17–19].

Figure 4 shows the interfacial tension changes with the concentration of urethane acrylates (UA3, UA5, UA6) in

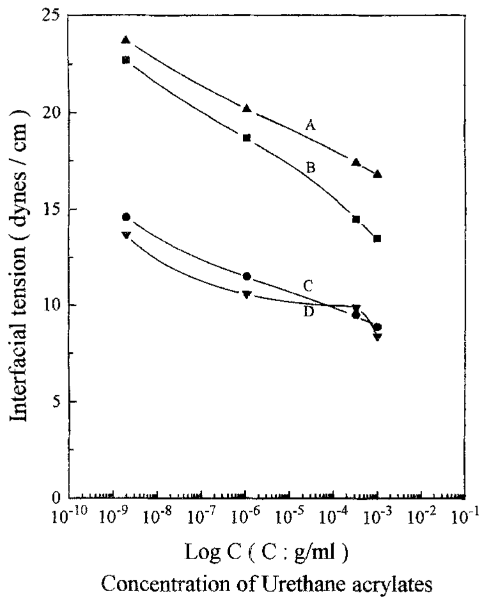


Fig. 4 Interfacial tension changes of water/benzene with the concentration of urethane acrylates in benzene (-▲- UA6(50 °C), -■- UA5, -●- UA3, -▼- UA6)

benzene. The interfacial tension of water/benzene containing UA5 (Curve A) was higher than that of water/benzene containing UA3 (Curve C). The interfacial tension of water/benzene containing UA6 (Curve D) was similar to UA3. However, the interfacial tension of UA6 at 50 °C (Curve B) was higher than that of UA3 at room temperature. As UA6 exists as a solid state at room temperature, this resin should be melted to be emulsified. Therefore, it was reasonable to compare interfacial activity of UA3 at room temperature with that of UA6 at 50 °C.

Emulsion polymerization with water-soluble initiator

According to our previous experiments, unmodified urethane acrylate could be emulsified using a mixture of SLS and co-surfactant (cetyl alcohol, stearyl alcohol or hexadecane). However, large amounts of surfactant were used and these emulsions were broken in the process of emulsion polymerization with a water soluble initiator, $K_2S_2O_8$ [6].

However, in the case of PEG-modified urethane acrylates, the droplet size of its emulsion did not change significantly with HLB and molar ratio of SLS to long chain alcohol. Moreover, PEG-modified urethane acrylates could be emulsified using SLS or TWEEN 60 alone and these emulsions showed very fine droplet size and excellent centrifugal stability compared to unmodified urethane acrylate emulsions.

Actually, the ultimate goal of our study is the preparation of core-shell latex comprised of polyurethane/PMMA. However, the surfactant used in emulsification exerts a negative effect on the property and morphology of core-shell composite particles, so we tried to reduce the amount of surfactant and simplify the surfactant system by modification of urethane acrylate. In the case of mixed surfactant system comprised of SLS and long-chain alcohol, these long-chain alcohols remain on the surface of particle after polymerization. Therefore, in order to prepare stable and fine droplet emulsion using SLS alone, we modified urethane acrylate by introducing hydrophilic groups into molecule ends. Fortunately, droplet size of PEG-modified urethane acrylate emulsion prepared using SLS only was similar to that of the emulsion prepared using mixture of SLS and long-chain alcohol. Therefore, in order to investigate whether PEG-modified urethane acrylate prepared using single surfactant can be polymerized without breakdown of emulsion or not, we carried out emulsion polymerization of PEG-modified urethane acrylate using a single surfactant system, that is, SLS or TWEEN 60.

Therefore, the polymerization of PEG-modified urethane acrylate emulsions was attempted using $K_2S_2O_8$. The recipes for emulsion polymerization and conversion changes with polymerization time were illustrated at Table 3 and Fig. 5.

The polymerizations of PEG-modified urethane acrylate emulsions prepared using SLS were carried out without any coagulation. At the same polymerization time, UA2 (Curve A in Fig. 6) showed the highest conversion and the highly PEG substituted UA4 (Curve C) emulsion showed the lowest conversion.

As the reaction molar ratio of PEG to 2-HEMA increased, the number of molecules containing polyoxyethylene groups increased. However, the number of molecules having vinyl groups at both ends decreased, so the conversion of polymerization decreased.

In the case of polymerization of UA2, UA3 and UA4 emulsions prepared using TWEEN 60 (Recipe B of Table 3), these emulsions were broken in the process of

Table 3 The emulsion polymerization recipe of PEG-modified urethane acrylates

	A	B	C	D
Urethane acrylate (g)	10	10	10	10
DDI water (g)	50	50	50	50
SLS (g)	0.15	–	0.15	–
TWEEN 60 (g)	–	0.45	–	0.45
AIBN (g)	–	–	0.15	0.15
$K_2S_2O_8$ (g)	0.15	0.15	–	–

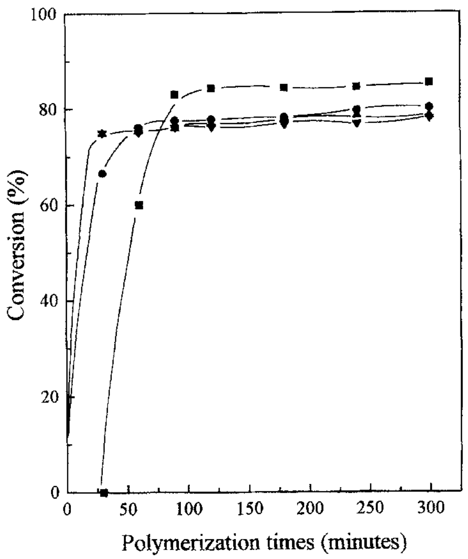


Fig. 5 Conversion changes of PEG-modified urethane acrylate emulsions with polymerization times (-■- UA1, -●- UA2, -▲- UA3, -▼- UA4)

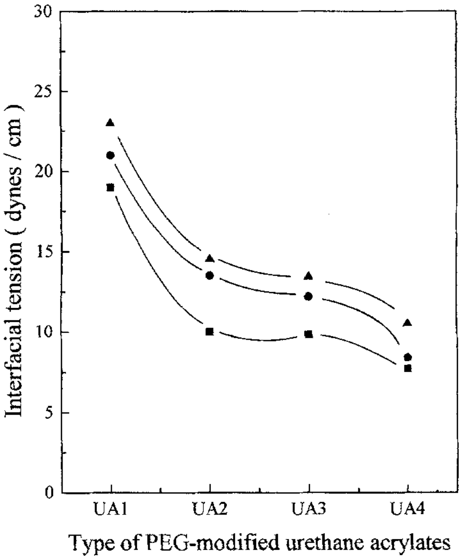


Fig. 6 Interfacial tension changes of water/benzene with the concentration of urethane acrylates in benzene at different temperature (-▲- 50 °C, -●- 40 °C, -■- 20°C)

emulsion polymerization. These results were attributed to the decrease of interfacial activity of TWEEN 60 and PEG-modified urethane acrylates, and the penetration of initiator radicals from the aqueous phase. Both PEG-modified urethane acrylate and TWEEN 60 contain polyoxyethylene groups in the molecular end. The hydrations of polyoxyethylene groups with water decreased with the increase of temperature so that the hydrophilicity of these groups decreased and the interfacial activity of these molecules decreased. Therefore, the emulsions of PEG-modified urethane acrylates formed using TWEEN 60 became unstable as the temperature increased, so these emulsions unstabilized by the raising of temperature were broken by penetration of initiator radicals formed in aqueous phase.

It has been known that the hydrophilicity and interfacial activity of SLS is virtually independent of temperature [17]. Therefore, in emulsions of PEG-modified urethane acrylates prepared using SLS, the stability of these emulsions was maintained, so these emulsions could be polymerized without any coagulation even though penetration of initiator radicals occurred. Table 3 showed that the droplet sizes of UA2, UA3 and UA4 emulsions were nearly unchanged before and after polymerization.

In order to confirm the change of interfacial activity of PEG-modified urethane acrylates containing polyoxyethylene groups with temperature, the adsorption change of PEG-modified urethane acrylates at the interface of water/benzene with temperature was investigated, and this result was illustrated in Fig. 6. As expected, the interfacial tension increased as temperature increased. This result indicated that the hydrophilicity of polyoxyethylene group decreased as temperature increased, so that the number of molecules located at interface was reduced and the interfacial tension was increased. Therefore, the reason for the PEG-modified urethane acrylate becoming very unstable as temperature increased was confirmed by the above investigation.

Polymerization of PEG-modified urethane acrylate emulsions with oil-soluble initiator

For the emulsions prepared using TWEEN 60, penetrations of initiator radicals and raising the temperature to

Table 4 The droplet size of PEG-modified urethane acrylate emulsions

	UA2		UA3		UA4	
	D_A (nm)	D_B (nm)	D_A (nm)	D_B (nm)	D_A (nm)	D_B (nm)
Recipe A	74.9	73.6	56	52	41.9	40.7
Recipe B	72.3	99.1	54	90.6	42.5	147.5

* D_A: The droplet size before emulsion polymerization.
D_B: The droplet size after emulsion polymerization.

generate radicals made these emulsions very unstable. Therefore, the polymerization of these emulsions with oil-soluble initiator (AIBN) was attempted, because radicals of oil-soluble initiator were formed at oil droplets and the polymerization by radicals took place mainly at oil droplets. According to our previous experiments [6, 20], the emulsion polymerization by oil-soluble initiator could be carried out by excluding penetrations of radicals from aqueous phase to oil droplets (microsuspension polymerization).

When the polymerization of the emulsions prepared by TWEEN 60 were carried out with oil soluble initiator AIBN, these emulsions were not broken in the process of polymerization. However, the droplet size of these emulsions were significantly changed before and after polymerization (Recipe B in the Table 4) compared with the polymerization of emulsions prepared by SLS with KPS (Recipe A in the Table 4), because the stability of emulsions prepared by TWEEN 60 were decreased by the raising temperature.

Therefore, it was thought that the polymerizations of the PEG-modified urethane acrylate emulsions prepared using TWEEN 60 could be carried out by diminishing penetration of radicals, so the polymerization mechanism of these emulsion was close to microsuspension polymerization, and the effect of temperature on the emulsion stability was greater than that of penetration of radicals.

Conclusion

The emulsions of PEG-modified urethane acrylates had much finer droplets than those of unmodified urethane acrylates of the same surfactant composition. Moreover, the droplet size of these emulsions decreased significantly with the increase of PEG reaction molar ratio. Therefore, it could be seen that the property of oil phase exerted more important effect on droplet size and centrifugal stability of emulsions than surfactant type and composition.

The interfacial activity of PEG-modified urethane acrylates containing polyoxyethylene groups as terminal groups could be confirmed by the degree of adsorption at the water/benzene interface with the concentration of urethane acrylate in benzene. In the case of emulsion polymerization, the conversion and stability were changed by the types of surfactant, initiator, and PEG-modified urethane acrylate.

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