

Preparation of Aqueous Dispersible Polyurethane: Effect of Acetone on the Particle Size and Storage Stability of Polyurethane Emulsion

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ABSTRACT: An aqueous dispersible polyurethane was prepared by the reaction of hydroxyl-terminated poly(ethylene adipate), dimethylol propionic acid, 4,4'-diphenylmethane diisocyanate, and ethylene glycol. Formation of the dispersion was achieved by phase inversion of an acetone solution of the polyurethane with water, utilizing carboxylate anion groups as the internal emulsifying sites. The amount of acetone added has a large effect on the particle

diameter (0.08 to 8.61 μm) and particle size distribution of the polyurethane emulsion. The storage stability was evaluated in terms of particle size distribution breadth. The aqueous emulsion obtained with no use of acetone was sufficiently stable in storage for at least 6 months. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3455–3461, 2004

Key words: polyurethanes; particle size distribution

INTRODUCTION

Polluting organic solvents [volatile organic compounds (VOCs)] that evaporate during the formulations of coatings, inks, and paints cause a wide variety of air quality problems. Consequently, government regulator such as the Environmental Protection Agency (EPA) in the United States and local Air Quality Regulators have stepped up their efforts to limit the amount of VOCs released to the atmosphere.¹ These regulations and consumer demands are forcing industries to develop environmentally friendly products. Among several options to develop technology, water is the best choice to use as a medium in formulating coating systems. To reduce or eliminate organic solvents from the formulations, solvents should be partially or completely replaced with an environmentally benign solvent (e.g., water), in the coating formulations to achieve little or no VOC content.²

Polyurethanes (PUs) are widely used in the coating industry because of their excellent performance. The organic solvent-based [e.g., *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMAc)] PUs will be restricted in their traditional applications sooner or

later because of the demands of economics, safety, and environmental regulations. In contrast, aqueous PU dispersions would be candidates with promise to replace them.

Generally, aqueous PU dispersions can be prepared by incorporating hydrophilic groups into the polymer backbone or by adding a surfactant. The former material has become known as a PU ionomer in which the ionic groups act as internal emulsifiers. These ionomers usually contain pendant acid groups or tertiary amine groups.^{3–6} Water-dispersible anionomer PU is obtained by neutralization of the acid groups. Various processes have been developed for the preparation of aqueous PU dispersions.^{4–6} Among these processes, the acetone process represents one of the most popular processes.⁷ In that process acetone is inserted with respect to the PU formation, is freely miscible with water, and the low boiling point solvent can be removed with ease.⁸ The addition of water to an acetone solution of PU ionomer followed by removal of the acetone results in an aqueous PU emulsion.

In practice, PU emulsion is stored for a while prior to use; therefore, storage stability is an important characteristic of an emulsion. In dilute emulsion systems, creaming velocity (ν_{Stokes}) is described using the Stokes terminal velocity equation^{9,10}

$$\nu_{\text{Stokes}} = \frac{d_p^2 |\rho - \rho_o| g}{18\mu_c} \quad (1)$$

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TABLE I
Formulation Details for PU Dispersions^a

Formulation	PUD1	PUD2	PUD3	PUD4
[NCO]/[OH] _{EGAA} /	1/0.49/	1/0.49/	1/0.47/	1/0.48/
[OH] _{DMPA} /[OH] _{EG}	0.17/0.34	0.17/0.34	0.20/0.33	0.18/0.34
DMPA (w/w% solid PU)	3	3	3	3
Neutralization (%)	120	120	120	120
Soft segment ^b (%)	60.88	61.11	59.06	60.21
Acetone (w/w% dispersion)	0	12	24	30

^a All urethane prepolymer were prepared at a 1.5 : 1, NCO/([OH]_{DMPA} + [OH]_{EGAA}) molar ratio. The final dispersion after removal of acetone had a polymer solid content of 30% (w/w).

^b Soft Segment Content = $\frac{[\text{EGAA}] (\text{g})}{[\text{MDI} + \text{EGAA} + \text{DMPA} + \text{EG} + \text{TEA}] (\text{g})} \times 100$.

where d_p is the diameter of emulsion particle, ρ and ρ_o are the density of the water and the emulsion, μ_c is the viscosity of water, and g is the gravity acceleration velocity. Obviously, in the dilute emulsion system, diameter of the emulsion particle has a significant effect on the creaming velocity. That is, the smaller the particle, the slower the creaming velocity.

It has been reported that in the ionic content, the degree of neutralization,^{11–15} the type of ionic component,¹¹ the counterion used,^{11,15,16} the molecular weight of soft segment,^{14,17} and the amount of cosolvent,⁷ each has a considerable effect on the particle size of PU emulsion.

Here, we describe the synthesis of PU having built-in carboxylic (COOH) groups as an internal emulsifier and the preparation of aqueous PU emulsions using a two-step process. Because storage stability is an important characteristic of an emulsion, the effect of acetone content on the storage stability of the resulting emulsions was also investigated in terms of particle size, particle size distribution (PSD), and particle size distribution breadth (B).

EXPERIMENTAL

Materials

Hydroxyl-terminated poly(ethylene adipate) (EGAA, $M_n = 1000$, Asahi Denka Kogyo) was dried by azeotropic distillation with toluene. The distillation was continued until no further distillate was collected. The moisture content of EGAA was determined by Karl Fisher titration (<0.03 wt %). Ethylene glycol (EG, Nacalai Tesque), and triethylamine (TEA, Wako Pure Chem. Ind.) was dried according to standard methods just before use. *N*-Methyl-2-pyrrolidone (NMP, Wako Pure Chem. Ind.) and acetone (Wako Pure Chem. Ind.) were dried over 4 Å molecular sieves. Dimethylol propionic acid (DMPA, Tokyo Kasei Kogyo) and 4,4'-diphenylmethane diisocyanate (MDI, Nippon Polyurethane Ind.) were used as received.

Preparation of aqueous dispersion polyurethane

A series of water-borne PUs were prepared with varying amounts of acetone. Their formulations are presented in Table I and a typical synthetic procedure is shown in Figure 1. DMPA (ca. 3 wt % based on total solid PU) was dissolved in a minimum amount of NMP in a round-bottom flask equipped with a stirrer, a thermometer, and an inlet of dry nitrogen. Molten EGAA and solid MDI (1.5 equiv) were added to the flask on a heating oil bath. Prepolyaddition was carried out with mechanical stirring at 40°C under a nitrogen atmosphere until the consumption of isocyanate (NCO) groups reached a theoretical amount estimated by assuming an equimolar reaction of the NCO and OH groups. This temperature and atmosphere were maintained to avoid any competitive side reactions, such as the formation of allophanates.¹⁸ The unreacted NCO groups were determined by back-titration using di-*n*-butylamine. After the resulting viscous prepolymer was diluted with a given amount of acetone, EG (an equiv amount to the unreacted NCO groups) was added. The chain-extension reaction was continued at 50°C until the IR spectrum showed no stretching band due to the NCO groups at 2270 cm⁻¹. The COOH groups in the resulting chain-extended PUs were neutralized with TEA (1.2 equiv) in acetone at 50°C for 1 h, and then water was added dropwise with vigorous stirring (750 rpm) at 50°C. The stirring was continued for further 30 min. Removal of acetone by a rotary vacuum evaporator gave a milky white aqueous PU emulsion or suspension, which contained about 30 wt % PU.

Characterization

Gel permeation chromatography was performed on a Shimadzu LC-10A high-speed liquid chromatography system equipped with a differential refractometer, using tetrahydrofuran as an eluent with a flow rate of 1.0 mL min⁻¹ at room temperature; maximum porosities of two polystyrene-gel columns connected in series, 7

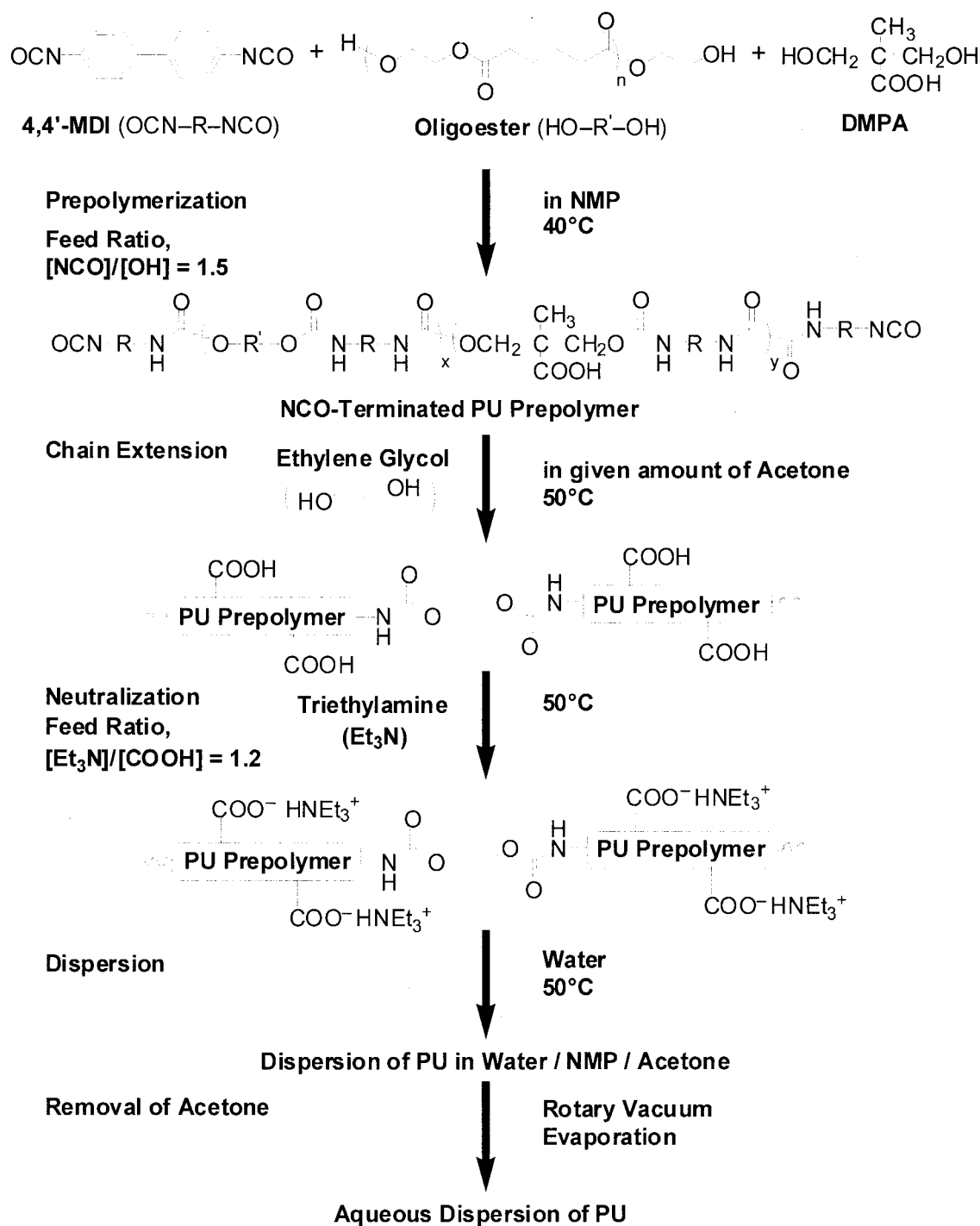


Figure 1 Preparation of aqueous PU dispersion.

$\times 10^4$ and 5×10^3 . The molecular weight calibration curve was obtained using polystyrene standards. Infrared spectra were recorded on a JASCO model FT/IR-3 or A-202 infrared spectrometer. The particle size and particle size distribution (PSD) of PU emulsions were measured using a laser diffraction particle size analyzer (Shimadzu Model SALD 2001) at ambient temperature. Because the PU emulsions exhibited a skewed distribution function; the lognormal distribu-

tion was used for describing the particle size of PU emulsion. On the basis of the lognormal distribution, the geometric mean diameter (d_g) and geometric standard deviation (σ_g) were calculated according to eqs. (2) and (3), respectively.¹⁹

$$d_g = \exp \left(\frac{\sum (n_i \ln d_i)}{N} \right) \quad (2)$$

TABLE II
Properties of PU Dispersions with Increasing Amount of Acetone

Property	PUD1 0 wt % acetone ^a	PUD2 12 wt % acetone	PUD3 24 wt % acetone	PUD4 30 wt % acetone
Particle Size ^b (μm)	0.08	0.10	2.11	8.61
σ_g^c	1.27	1.30	1.34	1.25
$M_w (\times 10^{-4})$	2.13	1.94	1.76	1.68
M_w/M_n	3.62	2.98	2.22	2.90

^a Weight percent of the acetone content based on the total weight of the PU dispersion.

^b Geometric mean diameter of the PU emulsion particle left for 1 day after the removal of acetone.

^c Geometric standard deviation, which was calculated according to eq: (3).

$$\sigma_g = \exp \left(\frac{\sum n_i (\ln d_i - \ln d_g)^2}{N - 1} \right)^{1/2} \quad (3)$$

where n_i is the number of particles in group i , having a midpoint of size d_i , and where $N = \sum n_i$, that is, the total number of particles.

Particle size distribution breadth (B) was calculated according to eq. (4).

$$B = \frac{(D_{90} - D_{10})}{D_{50}} \quad (4)$$

where D_{90} , D_{50} , and D_{10} are the particle diameters for the 90th, 50th, and 10th cumulative mass percentiles, respectively.

RESULTS AND DISCUSSION

Preparation of an aqueous emulsion of COOH-built-in PU

The PU prepolymer, having NCO groups at both extremities, was prepared by the polyaddition of hydroxyl-terminated EGAA with an excess amount of MDI in the presence of 3 wt % of DMPA. No CO_2 gas bubbles were observed in these reactions, suggesting that no significant amount of water reacts with NCO groups and no reaction takes place between NCO groups and sterically hindered COOH groups in DMPA. Moreover, esterification would not take place because it requires a higher temperature;^{11,20} therefore, the NCO groups of MDI react preferentially with the hydroxyl groups of EGAA and DMPA. The PU prepolymer was diluted with a given amount of acetone, and then chain-extended by the coupling between the unreacted NCO groups and EG. The PU post-polymer thus obtained had ternary diOH segments, such as EGAA, EG, and DMPA units. The DMPA unit has a potentially ionizable COOH group, which can act as an internal emulsifying site. A stoichiometric amount of TEA was added to neutralize the built-in COOH groups of DMPA. As the ionomers were formed, an increase of viscosity was attributed to the formation of microionic latices.^{4,15} Lorenz et al.²¹

have demonstrated that the COOH and COO^- in carboxylate anionomers are located substantially at the particle surfaces. Thus, the aqueous PU emulsion was prepared by phase inversion from an acetone solution to an aqueous emulsion by addition of water. The water would penetrate from the ionic groups into the bulk of the polymer, with the result that the polymer finally divides into spherical particles surrounded by water; the hydrophobic segments are contained in the interior of these particles, while the ionic groups are situated outside. The hydrophilic groups facilitate mutual repulsion between the particles and provide particle stability. From the experiments, it was observed that the initial addition of water produced local turbidity that quickly disappeared with vigorous stirring. More addition of water made the bulk turbid, which was an indication of the formation of a dispersed phase. As water was continually added to a certain content, the phase inversion process was achieved. Probably an electrical double layer forms at the water/polyurethane particle interface and a stable aqueous dispersion is formed.

Table II shows the properties of PU dispersions; the molecular weight distributions (M_w/M_n) are somewhat broad. These might be a result of interaction with column packing. Other workers^{22–24} also have reported similar results, and claimed that some COOH groups might participate in limited side reaction with NCO groups, resulting in some branches that caused a higher polydispersity.²³

Effect of acetone on the particle size

Dilution of the prepolymer with acetone was suitable for reducing viscosity and, especially, facilitating dispersion of PU in water. However, the amount of acetone added had a large effect on the particle size of the PU emulsion. A similar phenomenon has also been reported by other workers.^{7,24,25} Thus, different aqueous PU emulsions were prepared varying the acetone content from 0 to 30 wt % based on the total weight of the PU emulsion (30 wt % of PU in 70 wt % of water and NMP after removal of acetone). Table II shows the

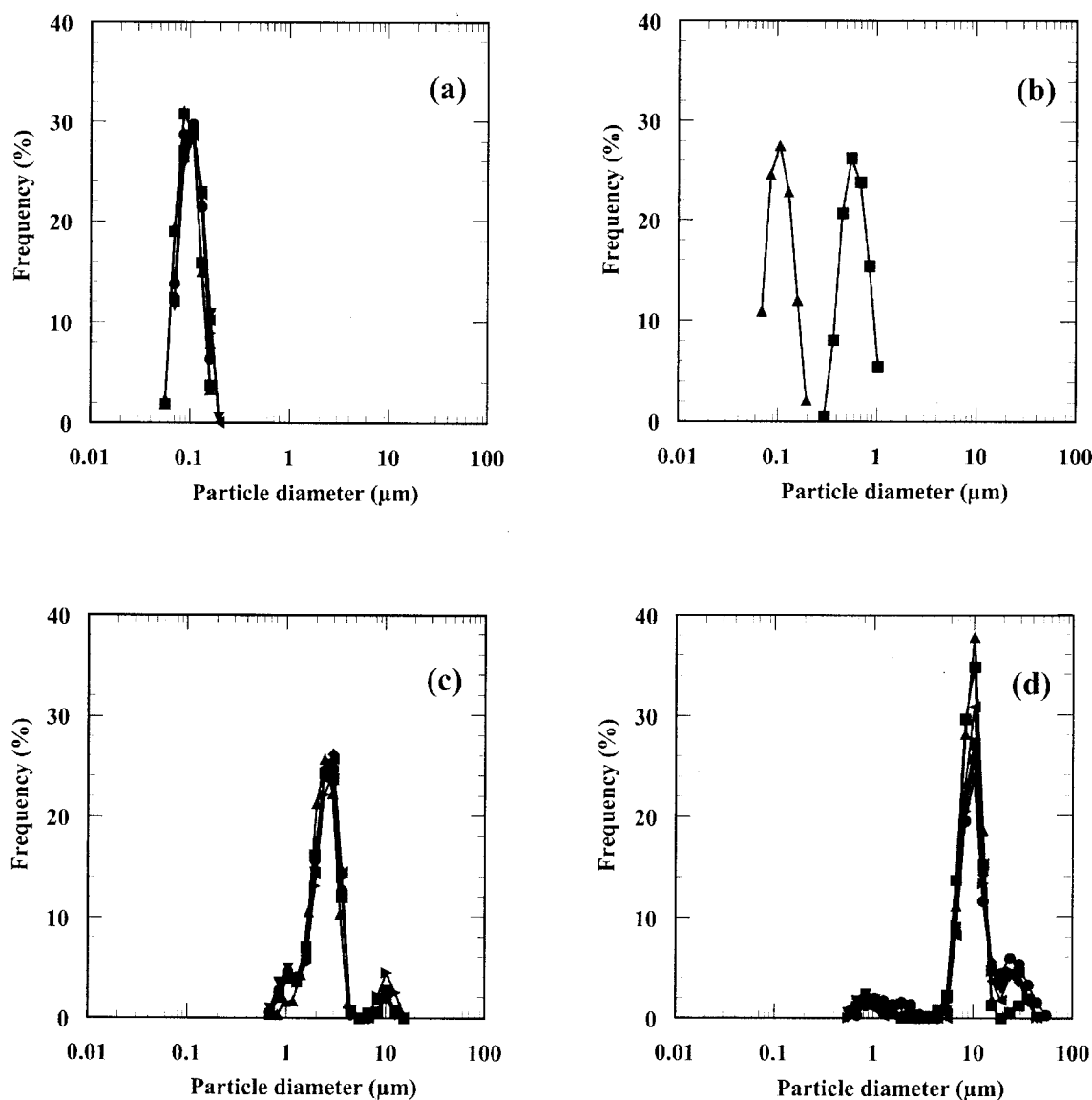


Figure 2 Time dependence of the PSD for the aqueous PU emulsions: (▲) after 1 day; (■) after 1 month, (●) after 2 months, (◆) after 3 months, (▼) after 4 months, (left-pointing filled triangle) after 5 months, (right-pointing filled triangles) after 6 months. (a) 0 wt % of acetone, (b) 12 wt % of acetone, (c) 24 wt % of acetone, and (d) 30 wt % of acetone.

weight-average molecular weight and particle size of the emulsions left for one day after the removal of acetone. A similar effect of the acetone content on the particle size was also visually observed as a transition from a bluish-white emulsion at 0 wt % of acetone to a milky white dispersion at high content of acetone. Apparently, the particle size increased with increasing the acetone content. One possible explanation for this phenomenon lies in the retained acetone among the chains, even after the process of evaporation. Such acetone is probably adsorbed by the hydrophobic part of PU chain resulting in the swelling of particles.⁷

The effect of acetone can be explained in terms of the solubility parameter. According to the Hildebrand theory, the solvate power of a polymer-solvent me-

dium can be estimated from $(\delta_1 - \delta_2)^2$, where δ_1 and δ_2 are the solubility parameters for the solvent and polymer, respectively. The solubility of a polymer in a solvent is favored when $(\delta_1 - \delta_2)^2$ is minimized, that is, when the solubility parameters of the two components are most closely matched. In this case, the lower the difference between the solubility parameters of the hydrophobic part and the acetone, the higher the affinity between these two components. Literature data indicate that the solubility parameter for acetone²⁶ is 20.3 MPa^{1/2} and that for polyurethane^{27,28} ranges from 19.4 to 21.5 MPa^{1/2}. Thus, the affinity between the hydrophobic chain and acetone is high, so that the polyurethane chain configuration easily spread out in the presence of acetone in the reaction process. Scaling

arguments can be used to interpret the dependence of the polymer size on the concentration of acetone.²⁹ If $c \gg c^*$, the chain is ideal, and $R_g \propto c^{-1/8}$ (where c^* is the overlap concentration, c is the number of segment per unit volume, and R_g is the radius of gyration of the polymer); therefore, a higher amount of acetone causes more swelling of the PU polymer.

Storage stability of the aqueous PU emulsions

Although the COOH built-in PUs were capable of forming aqueous emulsions just after the removal of acetone, some emulsions aggregated during storage at room temperature, resulting in a cream or precipitates. These phenomena seemed to associate closely with the amount of acetone used for preparing the emulsion. Thus, the storage stability of the PU emulsions prepared in 0 to 30 wt % of the acetone content was evaluated in terms of PSD change during storage. In the case of a labile emulsion, the PSD should broaden and shift toward a larger particle size due to aggregation of the original particles.³⁰ After one-day storage, the geometric particle diameter of the emulsion particle prepared with no use of acetone was $0.08 \mu\text{m}$, and the size rarely changed even over six-month storage. Moreover, the emulsion showed almost no change of unimodal PSD during the storage, as shown in Figure 2(a). This indicates the high storage stability of this emulsion. However, the system was rather difficult to mix and disperse with water because of its extremely high viscosity. To facilitate the mixing and dispersing process, acetone was added to the reaction system. The particle size of the emulsion particle prepared in 24 wt % of acetone was $2.11 \mu\text{m}$ after one-day storage. The size of this emulsion rarely changed up to four-month storage, and the PSD was only slightly broaden during the storage, as shown in Figure 2(c).

On the other hand, the particle size of the genetic emulsion particle prepared in 12 wt % of the acetone content was increased from 0.10 to $0.54 \mu\text{m}$ by about four times, after one-month storage, resulting in a cream. Figure 2(b) shows the change of PSD, indicating a remarkable shift to a larger size during the storage. This phenomenon will be studied further. In contrast, the emulsion obtained in 30 wt % of acetone showed no significant change in both mean particle size and PSD at least for a storage period of one month. However, the particle size was slightly increased from 8.48 to $8.99 \mu\text{m}$ by about 6% during an additional one-month of storage, and the PSD shifted to a larger size after two-month storage, as shown in Figure 2(d).

Regardless of the relatively small difference observed in particle size distribution, the particle size distribution breadth (B) was found to be a useful index for evaluating colloidal stability. Figure 3 shows the plots of B against storage time for the aqueous PU

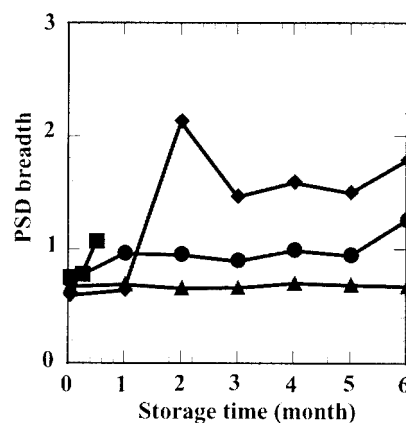


Figure 3 Particle size distribution breadth vs storage time plots for aqueous PU dispersions: (▲) 0 wt % of acetone, (■) 12 wt % of acetone, (●) 24 wt % of acetone, and (◆) 29 wt % of acetone.

dispersion series. The PU emulsion prepared in 12 wt % of acetone was barely permitted to analyze the particle size until two-weeks storage, because of its poor stability. The indices of B for PU emulsions prepared in 0 and 24 wt % of acetone were constant over storage at room temperature for six and five months, respectively, while that for the labile emulsion obtained in 30 wt % of acetone greatly increased after only one-month storage.

CONCLUSIONS

A COOH built-in PU has been prepared using 3 wt % of DMPA, which, as one of the diol components also acts as an internal emulsifying agent. The aqueous emulsion was prepared by neutralization of the COOH groups with TEA, followed by phase inversion of an acetone solution of the PU with water. The particle size of the PU emulsion increased with increasing the acetone content. The storage stability was evaluated in terms of particle distribution breadth (B). The PU emulsion prepared with no use of acetone showed the highest storage stability at room temperature over more than 6 months with almost no change of PSD.

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