

SYNTHESIS OF SOAP-FREE ACRYLIC HYDROSOLS

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Abstract Poly(methyl methacrylate/ethyl acrylate/acrylic acid) hydrosols were prepared by employing soap-free polymerization, and (acrylic acid/butyl acrylate) oligomer was used as the polymeric surfactant. The effect of reaction condition on the morphology and particle size of the hydrosols was investigated. The minimum amount of acrylic acid in the hydrosols is 2%. The maximum weight average molecular weight (M_w) of polymer that assures soap-free emulsion conversion into hydrosol is about 1.2×10^5 – 1.3×10^5 . The particle transforming process was investigated, and an obvious change of particle diameter and morphology was observed.

Keywords Hydrosol, Acrylic resin, Water-borne resin, Soap-free polymerization

INTRODUCTION

Acrylic hydrosols (particle diameter = 10–100 nm), which may be called acrylic colloid dispersions or micro emulsions, have many advantages such as high molding rate, good mechanical strength, glossiness and excellent water-resistance, and also having the advantages of solvent-borne acrylic resins and emulsions.

In previous work^[1], hydrosols were made by using suspension-polymerization or emulsion-polymerization. However, they usually need a complex production process and consume a lot of solvent or emulsifiers which have a bad effect on practical application, and the weight average molecular weight (M_w) was only 3×10^4 – 4×10^4 .

In recent years, soap-free polymerization was used to prepare water-borne coatings, which can be used as no-pollution coatings with excellent water-resistance and high molding rate, so most disadvantages of traditional emulsions can be overcome. The stability mechanism of soap-free polymerization can be classified into three different categories: by initiator fraction^[2, 3], by ionized monomers^[4], and by reactive emulsifiers^[5]. Some kinds of soap-free emulsions have been developed as coatings and paints^[6], and the polymerization process, especially the mechanism of stabilization^[7] and kinetics^[8, 9] were studied widely. But how to obtain hydrosols with smaller particle size (particle diameter between 10–100 nm) by soap-free polymerization was not reported.

We studied the synthesis of hydrosols by using soap-free polymerization in the presence of acrylic acid-butyl acrylate (AA/BA) oligomer, and obtained a colloidal dispersion with a particle diameter between 70–90 nm. The reaction conditions, morphology and particle size of hydrosols were investigated.

EXPERIMENTAL

Materials

The formulation for preparing the hydrosols is listed in Table 1. Technological grade methyl methacrylate (MMA), ethyl acrylate (EA), butyl acrylate (BA) and acrylic acid (AA) were purified by redistillation. Potassium persulfate (KPS), lauryl mercaptan (C_{12} -SH), 3-mercaptopropionic acid, diethyl glycol monoethyl ether (DGME), isopropyl alcohol (IPA) and ammonium hydroxide ($NH_3 \cdot H_2O$) were AR grade and used directly. Water is

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Received January 4, 2002; Revised February 29, 2002; Accepted March 4, 2002

deionized.

Table 1. The formulation for the synthesis of soap-free emulsion and hydrosol

Formulation	Weight (g)
A	
a) H ₂ O	80
b) AA	0–0.9
BA	0.9–0
c) KPS	0.05
H ₂ O	5
B	
a) MMA	10
EA	20
AA	0.3–1.5
C ₁₂ -SH	0–0.45
b) KPS	0.09–0.18
H ₂ O	5
C	
DGME	4
IPA	6
H ₂ O	10
D	
NH ₃ • H ₂ O	2.1
H ₂ O	10

PREPARATION OF HYDROSOLS

AA, BA, KPS were added to a four-necked reaction vessel equipped with a mechanical stirrer and a reflex condenser. The mixture was reacted at 85°C for 1 h to reach a 90% conversion. MMA, EA, AA, KPS and the chain transfer agent (C₁₂-SH or 3-mercaptopropionic acid) were added within 2 h at 85°C. After reaction for 2 h, the reaction temperature was lowered to 70°C, DGME and IPA were dissolved in water and were added to the reaction vessel within 30 min with constant stirring for 30 min. NH₃ • H₂O solution was then added in 30 min, and stirred for another 30 min. Upon cooling, an apparently clear water dispersion was obtained.

Measurements

The viscosity of hydrosols was measured with a rotating B viscometer (Jap., Tokyo Keiki) and a #4 Ford cup at 25°C. The particle size of hydrosols was determined by Malvern Laser diffraction mastersizer 2000 (UK). A JEM-100CX transmission electron microscope (TEM, Jap.) was used to observe the particle morphology with an accelerating voltage of 80 kV. The molecular weight of the oligomers and hydrosols was measured by using a Waters HPLC2410 instrument (USA), and calibrated with polystyrene standard sample. The light transmittance of the dispersion was measured by using a 721 viscible colorimeter Model 721 at 580 nm and the surface tension was measured by using a Kruss K10ST digital surface tension instrument (Ger).

RESULTS AND DISCUSSION

(AA/BA) Oligomer and Soap-Free Emulsion

In order to stabilize the soap-free emulsion, AA-BA oligomer was used as the polymeric surfactant because it is amphoteric. When the mass ratio (weight%) of AA and BA in the oligomer is higher than 20:80, the oligomer can be dissolved in water easily. When the ratio is between 30:70 and 70:30, stable soap-free emulsions can be obtained. We chose AA:BA = 60:40, and prepared poly (AA-BA) solutions of different concentrations and found that the maximum stable solution concentration is 5%. The stability of poly(AA-BA) solutions at different pH values (Table 2) was good except at very low pH value (*ca.* 1.0). With the increase of pH value, the viscosity of

the oligomer changed from 10.42 to 12.08 s. Since the concentration of oligomer solution was low and the viscosity of this solution will be very small, therefore, the relative viscosity was measured by counting the flowing time (s, #4 Ford cup). The M_n of the oligomer was 7.7×10^3 and its polydispersity index (M_w/M_n) was 3.86. The surface tension of the oligomer solution was decreased by the addition of (AA/BA) oligomer (Fig. 1). When the concentration reached over 2%, the surface tension remained constant.

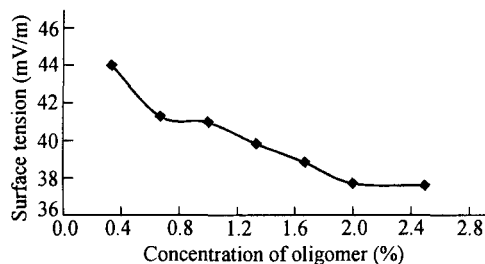


Fig. 1 Surface tension of (AA/BA) oligomer solution at different concentrations

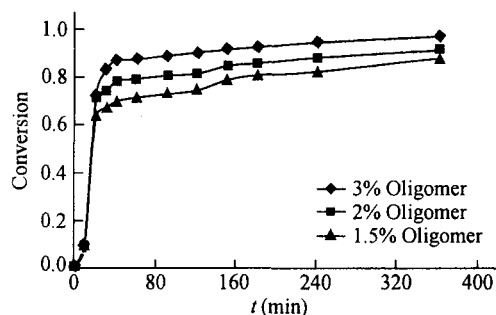


Fig. 2 Relationship between conversion and reaction time of soap-free emulsion in the presence of (AA/BA) oligomer

Table 2. Influence of pH value on the stability of (AA/BA) oligomer solution (AA/BA = 60:40, $M_n = 7.7 \times 10^3$)

pH	1	2	3	4	5	6	7	8	9
Stability	-	+	+	+	+	+	+	+	+

Note: - unstable; + stable

Table 3. Influence of content of (AA/BA) oligomer on the stability of soap-free emulsion (AA/BA = 60:40)

Content of (AA/BA) oligomer (%)	0	0.5	1.0	1.5	2.0	3.0
Stability of soap-free emulsion	-	-	Little amount of coagulate	+	+	+

Note: - unstable; + stable

The kinetics of soap-free polymerization was studied by using MMA/EA (molar ratio 1:2) as the model compounds in the presence of (AA-BA) oligomer (85°C), and a quick reaction rate can be observed in Fig. 2 (the monomer's conversion reached about 90% after 1 h). With the increase of the concentration of oligomer, the reaction rate and the final conversion became higher and higher. As shown in Table 3, the minimum concentration of (AA-BA) solution required to obtain a stable soap-free emulsion is 1.5%. The pH values, solid content and viscosity of soap-free emulsion were also measured and found to be 2.0%–3.0%, 25% and 2–3 centipoise (c.p.), respectively.

Hydrosols

MMA and EA were chosen as the hydrophobic monomer (molar ratio = 1:2) and AA as the hydrophilic monomer, the influence of AA content, molecular weight (M_w), initiator on the synthesis of soap-free emulsion, preparation of hydrosols and conversion behavior from soap-free emulsion to hydrosols were studied.

From Fig. 3, it can be seen that with the increase of AA content, the light transmittance of the latex increases. When the content of AA reaches a certain value (3%), the opaque emulsion turned into an apparently clear dispersion (light transmittance over 60%), but their particle diameter dropped to 89 nm when the concentration was 2%. To assure formation of a clear dispersion, the final pH value must be adjusted to a rather high value (8.0–8.5). Under such circumstances, all carboxyl groups in the polymer chains were neutralized.

The effects of molecular weight on the transmittance, viscosity and particle diameter of hydrosols were also studied and the results were tabulated in Table 4, Figs. 4 and 5. Lauryl mercaptan and 3-mercaptopropionic acid

were used as the chain transfer agent. If 3-mercaptopropionic acid was used, the stability of the emulsion was bad with the appearance of many gels. Lauryl mercaptan was an appropriate chain transfer agent for this latex, and when the amount of lauryl mercaptan reached 0.3%, the emulsion can be converted into hydrosols. The maximum M_w to yield particles with diameter $< 100\text{ nm}$, was about $1.2 \times 10^5\text{--}1.3 \times 10^5$. From Table 4, it can be seen that the particle diameters of hydrosols are uniform or the latexes are monodispersed.

Table 4. Influence of molecular weight of copolymer on the properties of hydrosols
(Oligomer: 2%, AA: 5%)

Amount of chain transfer (%)	0	0.15	0.3	0.5	1.0	1.5
Light transmittance (%)	5	8	89	90	90	91
pH	8.71	8.72	8.72	8.76	8.75	8.87
$M_w (\times 10^{-4})$	13.28	12.62	10.47	9.39	8.97	5.01
MWD	2.76	3.86	2.83	3.23	2.79	2.97
Viscosity (cp)	9.9	10.1	7.6	7.0	8.0	11.7
Uniformity of particle diameter	0.266	0.233	0.213	0.215	0.225	0.232

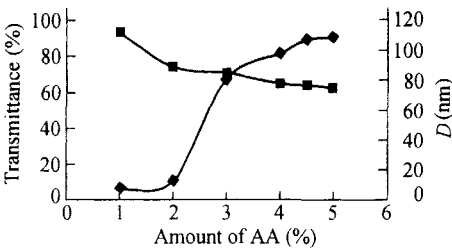


Fig. 3 Effect of the amount of AA on transmittance and particle diameter (D) of hydrosol
Oligomer: 2%
◆ Transmittance (%); ■ D (nm)

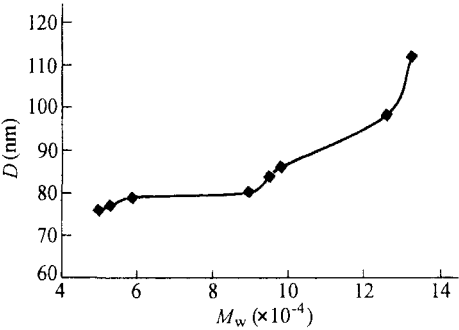


Fig. 4 Relationship between particle diameter (D) and M_w
Oligomer: 2%, AA: 5%, pH: 8–9

Initiator plays an important role in controlling the molecular weight of latex particles, and the fragment of the decomposed initiator can act as the stabilizer of polymer particles in soap-free emulsion^[3]. So we studied the effect of initiator on the stability of latexes. Our experiments demonstrate that if the amount of initiator is $< 0.3\%$, the latex is unstable. The minimum amount of initiator required to obtain a stable and an almost transparent hydrosol is 0.45% (Fig. 6).

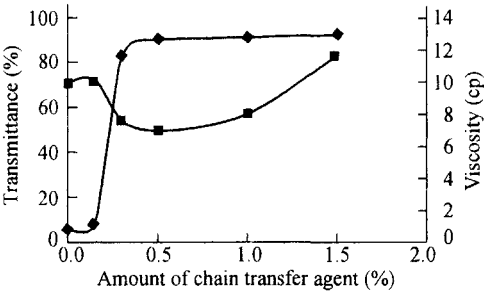


Fig. 5 Effect of amount of chain transfer agent (lauryl mercaptan) on transmittance or viscosity of hydrosols
Oligomer: 2%, AA: 5%, pH: 8–9
◆ Transmittance (%); ■ Viscosity (cp)

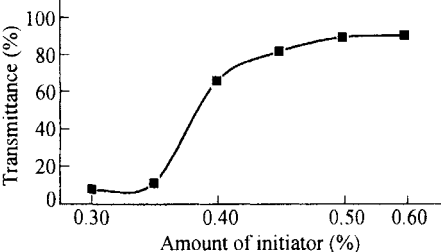


Fig. 6 Relationship between amount of initiator (KPS) and transmittance of hydrosols
Oligomer: 2%, AA: 5%, pH: 8–9

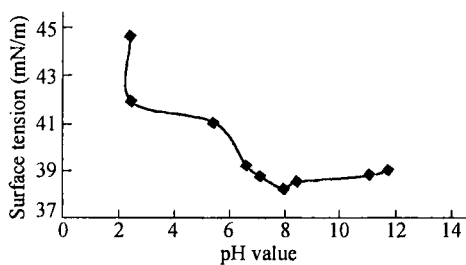


Fig. 7 Change of surface tension during the neutralization process
Oligomer: 2%, AA: 5%

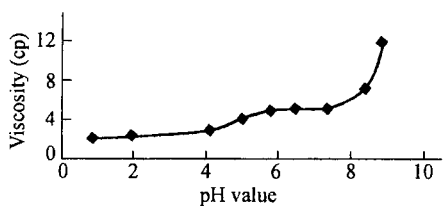


Fig. 8 Viscosity dependence on pH value during the neutralization process
Oligomer: 2%, AA: 5%

In order to obtain hydrosols, alkali must be used to neutralize the soap-free emulsion. From the change of surface tension and viscosity with increasing pH value during the neutralization process (Figs. 7 and 8), it can be observed that there is an obvious turning point at about pH 8.0, which can be considered as the critical point from the soap-free latex to hydrosol.

Particle Morphology

Ammonium hydroxide solution (28 wt%) was used to neutralize the soap-free emulsion in order to obtain the hydrosols. There was an obvious change of particle diameter as shown in Fig. 9. TEM was used to observe the morphology during the neutralization process (Fig. 10). For soap-free emulsion (Fig. 10a), the latex particles are agglomerated spheres with an average diameter of 190 nm. After the addition of mixed solvents, the particles become separated with an average diameter of 180 nm (Fig. 10b). With the addition of ammonium hydroxide, the particles are disrupted into irregular shapes and tend to cling together with an average diameter of 230 nm (Fig.10c). After the soap-free emulsion is completely converted into hydrosols, the average diameter of the particles decreases to approximate 70–90 nm (Fig. 10d).

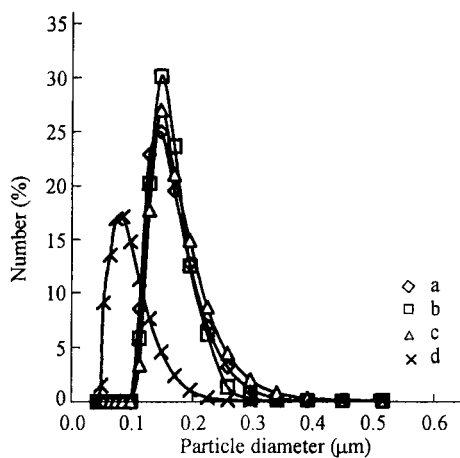
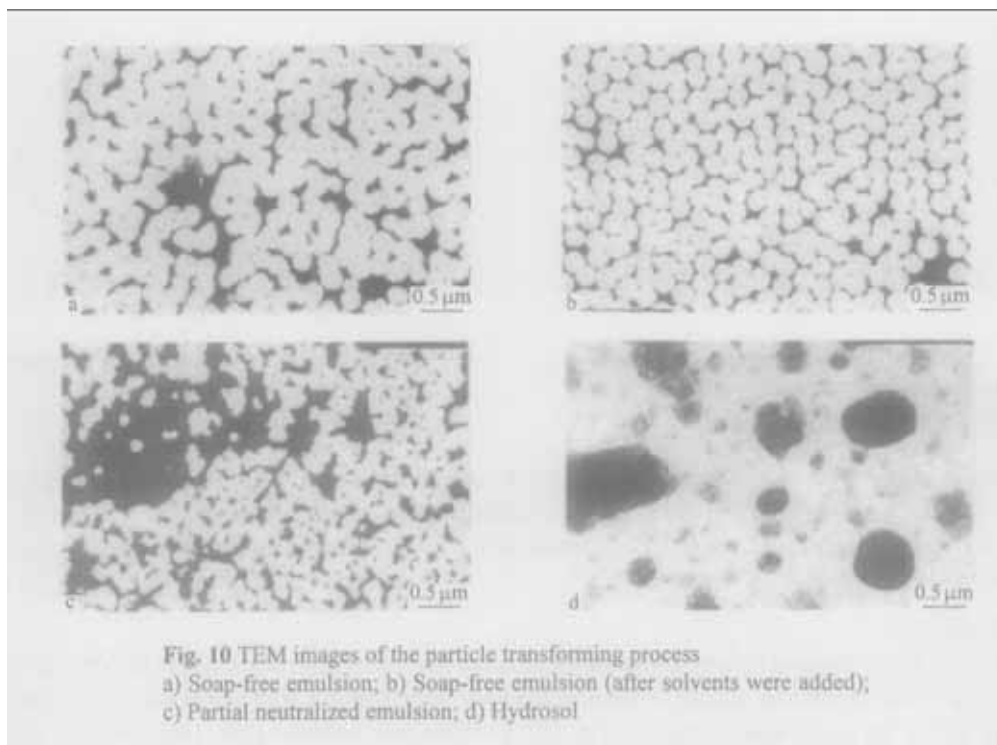


Fig. 9 Change of particle diameter during the neutralization process
(Number: relative amount of particles)
a) Soap-free emulsion (uniformity: 0.188); b) Soap-free emulsion (after solvents were added, uniformity: 0.151); c) Partially neutralized emulsion (uniformity: 0.197); d) Hydrosol (uniformity: 0.265)



Because each particle is composed of many polymer chains in the soap-free polymerization, many coagulated particles are produced. When solvent is added to the solution, the interaction among the neighboring particles is reduced, and the particles can easily be separated. After the addition of alkali, the carboxyl groups in the polymer chains become ionized, and the particle chains repel each other and become separated, showing an enlarged particle size. These separated chains coil again to assume a thermodynamic stable state. During this new particle formation, fewer chains twist together in the particles and form new particles with an average particle diameter about 70–90 nm. Since the number of polymer chains to form a new particle is random, the uniformity of hydrosols is slightly inferior to the soap-free emulsion.

CONCLUSION

Soap-free hydrosols can be synthesized by using soap-free polymerization with (AA/BA) oligomer as the polymeric surfactant. Lauryl mercaptan is an appropriate chain transfer agent and its minimum amount to obtain hydrosols is 0.3%. The M_w of hydrosols is 1.2×10^5 – 1.3×10^5 . During the conversion from soap-free emulsion to hydrosols, the particles of latex show different forms with the addition of alkali; the final particle size is about 70–90 nm.

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