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Synthesis of Acrylic Emulsion Containing High Hydroxyl Content

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ABSTRACT

Using butyl acrylate (BA), methyl methacrylate (MMA), acrylic acid (AA), and hydroxylethyl methacrylate as comonomers, along with ammonium persulfate as initiator, emulsions with high hydroxyl content (10–35%) and carboxyl groups were synthesized from semi-continuous seed emulsion polymerization methods. Emulsifier types and levels, reaction temperature, level of hydroxyl monomer, and level of monomer carboxyl on stability of the emulsion polymerizations were investigated. Viscosity of the emulsion was discussed. It was found that when the sodium lauryl sulfate (SLS) and *p*-octyl polyethylene glycol phenyl ether (OP) mixed emulsifiers were used, at a level of 3%, and a ratio of SLS/OP of 4/6, along with a reaction temperature at 65–75°C, the polymerization process had lower coagulum. As the levels of hydroxyl monomer and carboxyl monomer increased, the coagulum increased, and the viscosity of the resulting emulsion.

Key Words: Synthesis; Acrylate emulsion; Hydroxyl monomer.

INTRODUCTION

Nowadays acrylic emulsions are widely used in the coatings, adhesives, sealant, plastics, and rubber industries.^[1] Many studies have been carried out on the preparation, stability,

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mechanism, and kinetics, influence on the emulsions.^[2-8] But, these studies mainly concentrated on emulsions without functional groups. Much less work has been done on emulsions with functional groups, such as hydroxyl, carboxyl, amino, and so on. Emulsions with the latter functional groups are prepared from monomers having these functional groups.

Sauzedde et al.^[9] prepared emulsions from styrene (ST) and two different amino-monomer, with the emulsion particle size and surface amino density determined. Iris^[10] prepared monodisperse latex particles with surface amino groups by a two-step emulsion polymerization. The influence of the different conditions used to synthesize the latexes on the colloidal stability of the particles was evaluated. Hidalgo^[11] prepared latex with ST/butyl acrylate (BA)/amide functional monomer through emulsion polymerization, varying the hydrophilicity of the functional monomer employed. The second-stage polymerization kinetics, the size and morphology of latex particles, and the location of the functional groups in the final latexes were studied. It had been shown that, increasing the hydrophobicity leads to better homogeneity in the copolymer formed during the second-stage polymerization, while the more hydrophilic functional monomer partly homopolymerizes in a separate phase. Hsu et al.^[12] synthesized the composite latex particles of poly(methyl methacrylate)-poly(methacrylic acid) through soapless emulsion polymerization. The reaction kinetics, morphology, and size of latex particles, composition, glass transition temperature, and molecular weight of polymer products were studied under different experimental conditions.

The monomers with functional groups are more hydrophilic, so the reaction location and mechanism are different from these hydrophobic monomers, which the conventional micellar nucleation mechanism is based on. Because of this, preparing of emulsions is difficult compared to that without functional groups. But, emulsions with functional groups give many benefit to the property of the emulsion product, such as improving good adhesion onto substrates ($-\text{COOH}$), providing reaction groups ($-\text{NH}_2$, $-\text{OH}$) and so on, so they have become more and more important in industrial applications. Emulsions with hydroxyl and carboxyl groups may be used in waterborne two-package polyurethane coatings,^[13,14] as the replacement of traditional solvent-based two-package polyurethane coatings. In this way, volatile organic compounds (VOC) are greatly reduced. Thus, the study of these emulsions with functional groups is very useful in theory and in practice.

The aim of this paper is to investigate the polymerization process of emulsions with both high hydroxyl and carboxyl groups together, and also the influences of emulsifier type and level, reaction temperature, ratio of anionic/nonionic surfactant in the mixed emulsifiers, levels of hydroxyl monomer and levels of carboxyl monomer on the emulsions coagulum, viscosity, particle size, and conversion.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) and BA were distilled under reduced pressure before use. All the other materials were used as received, including acrylic acid (AA) and hydroxyethyl methacrylate (HEMA) monomers. Ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$, APS) and sodium hydrogen carbonate (NaHCO_3) were used as initiator and buffer, respectively. Ammonia was used as the neutralization agent. The surfactants used were



sodium lauryl sulfate (SLS), sodium dodecyl benzyl sulfonate (SDBS), nonylphenol polyethylene oxide ether (NP) and *p*-octyl polyethylene glycol phenyl ether (OP). Deionized water was used in all the experiments.

Emulsions Preparation

Polymerizations were carried out in a 250 mL glass reactor fitted with a reflux condenser, stainless-steel stirrer, nitrogen gas inlet, thermometer, and funnels. The semi-continuous emulsion copolymerizations were carried out using the recipes given in Table 1 (otherwise indicated). Glass transition temperature of the emulsion were kept at 10°C (calculated, according to the Fox equation). The solids of the emulsion was designed as 40% weight and this initiator (APS) was kept at 5%, based on the total weight or amount of monomers used. Surfactant types and levels, and levels of hydroxyl monomer and carboxyl monomer were variable.

The initial charge in the reactor was water, buffer, and mixed surfactants. The feed was divided into two streams. The first was a solution of initiator, and the second was a mixture of monomers. When the first charge was heated to 75°C (otherwise indicated) and the reaction degassed with nitrogen gas for 20 min, the first stream was started by dropwise addition and 5% weight of the second stream was added at the same time. After about 30 min, the system had an even bluish color, the rest of the second stream was added dropwise in 2 h, and finishing about the same time as the first stream. The mixture was kept at this temperature for an additional 1 h, after that the temperature was reduced to 50°C, neutralized with $\text{NH}_3 \cdot \text{H}_2\text{O}$ to pH = 7–8, and filtered with a 100 mesh filter. The procedure produced emulsions with high hydroxyl content.

Characterization

Conversions were determined gravimetrically. The coagulum retained was collected together with that deposited on the reactor walls, agitator and thermometer. The dry weight of these coagulum related to the total monomer was defined as the coagulum percentage.

Table 1. Recipe used for the emulsion polymerization.

Reactants	Initial charge (g)	Stream 1 (g)	Stream 2	
			g	%
Deionized water	88	8		
Mixed surfactants	1.6			
NaHCO_3	0.2			
APS		0.4		
BA			33.2	41.50
MMA			25.8	32.25
HEMA			18.5	23.13
AA			2.5	3.12



The particle size of the latex was measured by light scattering methods.^[15] The absorption valued emulsions diluted to 1.6×10^{-4} mol/L and 3.2×10^{-4} mol/L were measured at wavelengths of 370, 430, 500, and 650 nm, using a U3400 spectrum (Hitachi, Japan) instrument, and subsequent calculation of the mean particle size achieved.

Viscosities were measured with a NDJ-8S digital viscometer (Shanghai Balance Factory, China), at 25°C, using a No. 2 rotor at a rotating velocity of 60 rpm.

RESULTS AND DISCUSSION

Emulsifier

Emulsifiers play a key role in emulsion polymerization. The anionic emulsifier can impart repulsive forces between similarly charged electric double layers to the latex particle, whereas the nonionic surfactant can provide the interactive particles with the steric stabilization and also improve the chemical and freeze-thaw stability of the latex products. It is common practice to use mixed surfactants in emulsion polymerization in industrial production with semi-continuous operation, and where the monomers are pre-emulsified. In this study, we tried to use this method to investigate the effect of the emulsifier on the polymerization process. In our experiment stable pre-emulsified mixtures of monomers could not be obtained, due to hydrophilicity of HEMA and AA, in spite of emulsifier types and level or ratios of mixed anionic/nonionic surfactants used. Thus, the pre-emulsified mixture of monomers with emulsifier was not prepared. Rather, the mixture of monomers was directly fed to the reactor. The choice of mixed emulsifier is shown in Fig. 1.

Figure 1 shows that the mixed SLS/OP emulsifier system provided minimum coagulum content at complete monomer conversion, whereas the coagulum content reached 59.66% for the SDBS/NP emulsifier system. It was very difficult to obtain stable emulsions for SDBS/NP mixed emulsifier system. The results also show that SLS, was superior to both SDBS/OP and to NP. This can be explained from the hydrophile-lipophile balance (HLB) value of the emulsifier. The HLB is a characteristic of an emulsifier which indicates the hydrophilicity and hydrophobicity balance. The higher the HLB, the more hydrophilic the emulsifier. The HLB of emulsifier SLS, SDBS, OP, and NP was 40, 30, 13.3, and 12.8, respectively. According to weight percent of each emulsifier, the HLB of the mixed emulsifier SLS/OP, SLS/NP, SDBS/OP, SDBS/NP was 24, 23.7, 17, and 16.7, respectively. In order to maintain polymerization stability of an emulsion with a hydrophilic monomer, a higher HLB emulsifier is needed. The HLB of the mixed SLS/OP emulsifiers was higher than that of other mixed emulsifiers, close to the HLB needed for the emulsion polymerization. Thus, the SLS/OP emulsifier system was suitable for these systems, with a large amount of hydrophilic monomers.

Level of Emulsifier

Based on the above experiment, the SLS/OP system was used as a mixed emulsifier, the effect of levels of the emulsifier on the polymerization process was tested. The result is listed in Fig. 2.



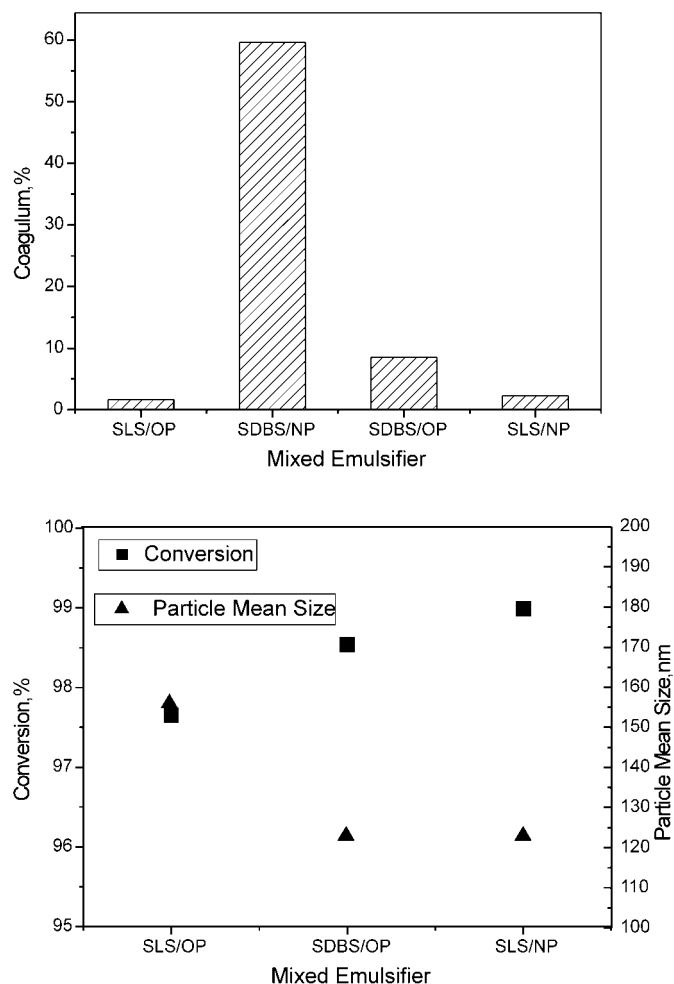


Figure 1. Effect of mixed emulsifier on the stability of polymerization (anionic/nonionic = 4/6).

Figure 2 shows that as the level of mixed emulsifier is increased from 1.5% to 4% (based on total weight amounts of monomers), the coagulum and particle size decreased and the conversion rate increased. From the micellar nucleation mechanism, more micellars were formed as the level of emulsifier increased, i.e., more active centers were produced and monomers polymerization reactions finished more completely. The possibility of agglutination between particles was reduced greatly, as well as the particle size of the emulsion also reduced. A large amount of emulsifier may damage the water-resistance of a latex product, but small amount of emulsifier, such as Fig. 2, when the emulsifiers level was 1.5%, may produce more coagulum because surface of the particle might not be covered with emulsifier molecule completely. From these experiments, the best level of emulsifier for this system was 3%, based on monomer total weight.



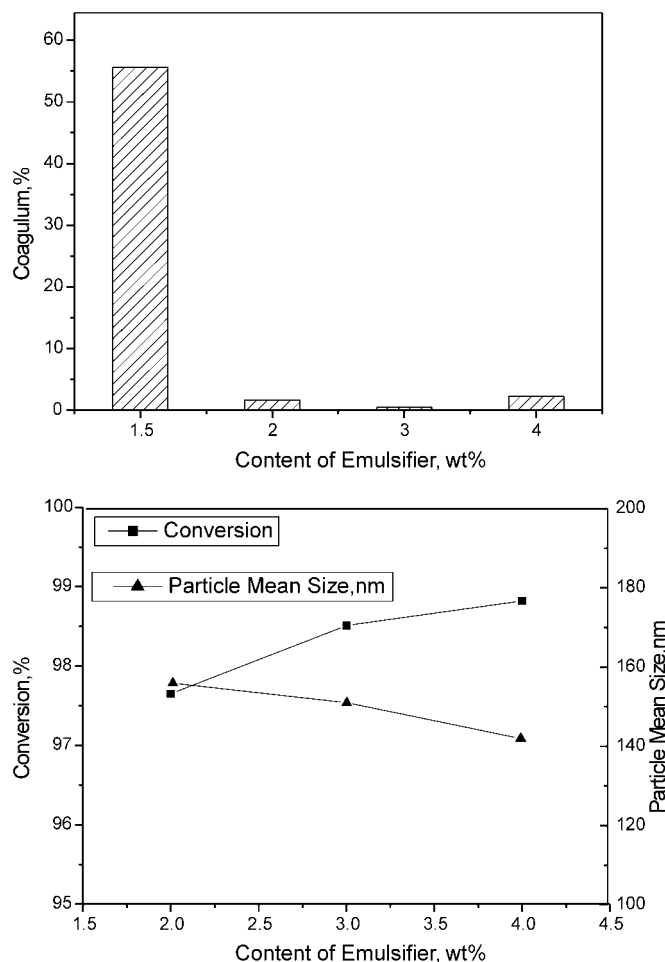


Figure 2. Effect of levels of emulsifiers on the stability of polymerization (emulsifier: SLS/OP, anionic/nonionic = 4/6).

Ratio of Anionic/Nonionic Emulsifier

When SLS/OP was used as mixed emulsifiers, and the level was kept at 2%, the weight ratio of SLS to OP had some important effect on the polymerization process and property. Figure 3 shows these effects. From Fig. 3, we noticed that when the weight ratio of SLS/OP varied from 2/8 to 6/4, the coagulum produced decreased gradually to minimum, and then when the ratio was 8/2, the coagulum increased again. Variation of these ratio on the effect of particle size was complicated, while the viscosity of the resulting emulsion increased more gradually. As the ratio of SLS/OP increased, the HLB of the system also increased, coming more closed to the HLB needed in the emulsion polymerization process. Thus, the increased SLS/OP ratio had a better emulsifying result



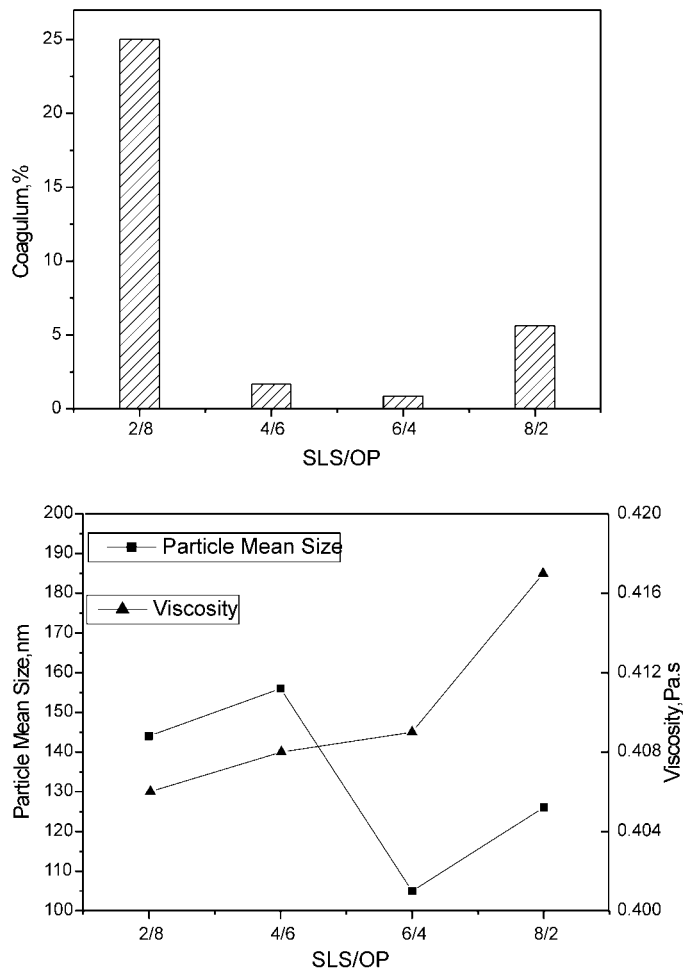


Figure 3. Effect of ratio of anionic/nonionic emulsifier on the stability of polymerization (emulsifier: SLS/OP, anionic/nonionic = 4/6).

for emulsion particles, while producing. As the ratio of SLS/OP increased further, the level of the nonionic emulsifier (OP) was too low, which failed to provide steric space to avoid agglutination between particles. In the latter case, much coagulum was also produced.

Reaction Temperature

Figure 4 shows the effect of reaction temperature on the stability of polymerization. It showed that as the reaction temperature rose, monomer conversion rose, along with an amount of coagulum. There was not much difference at 65°C and 75°C in particle



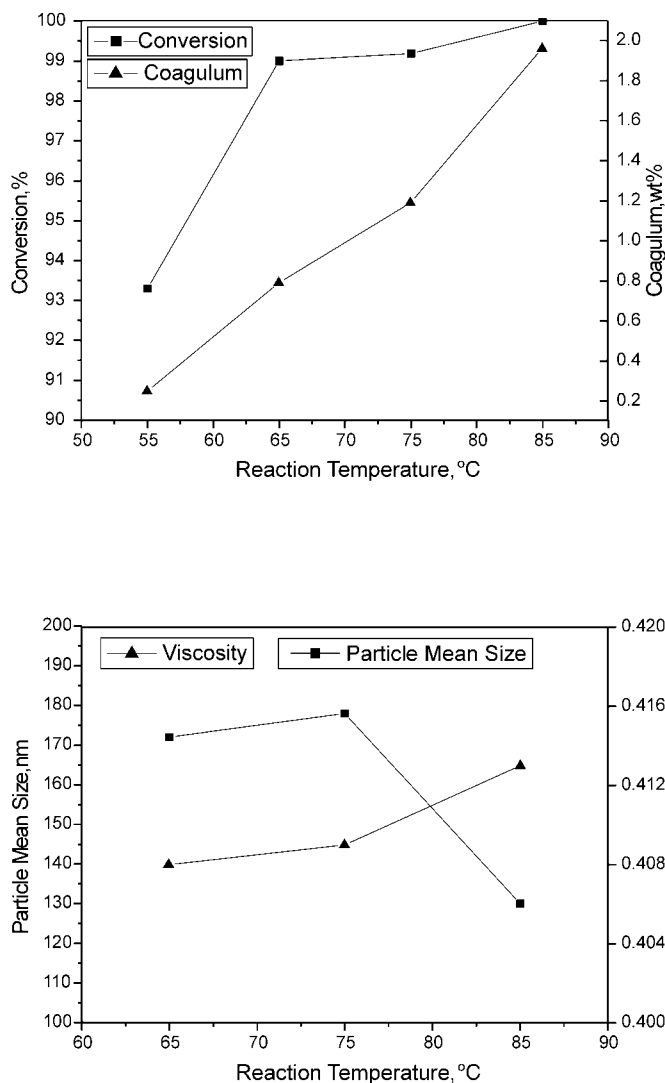


Figure 4. Effect of reaction temperature on the stability of polymerization (emulsifier: SLS/OP = 4/6).

size of the emulsions, but it became smaller at 85°C. Viscosity of the emulsion had little increase from 65°C to 85°C. This may be explained that as the reaction temperature rose, movement of the particle increased, probability of coagulation increased because of collision between particles, and stability of the emulsion decreased. At the same time, the hydration layer on the particle surface diminished, resulting in decreasing the emulsion stability. The loss of stability led to higher coagulum. The thinned hydration layer at the particle surface accounted for the smaller particle size.



Level of Hydroxyl Monomer

The level of hydroxyl monomer had significant influence on the polymerization process. Yu^[16] reported that when the level of hydroxyl monomer was below 10%, based on total weight of monomers, the more coagulum was produced. Figure 5 summarizes changes of conversion, coagulum, particle size and viscosity, when the level of hydroxyl monomer was above 10%. As shown, coagulum, particle size and viscosity increased as the level of hydroxyl monomer increased. It was not in agreement with the result stated above. This may be due to the hydrophilicity of HEMA and AA. Hydroxyethyl methacrylate and AA are water-soluble. Thus, a great amount of HEMA and AA were dissolved in water and polymerized in the water phase by free radical from APS, forming the particle. When the emulsifier level was low, the emulsifier molecules cannot cover the

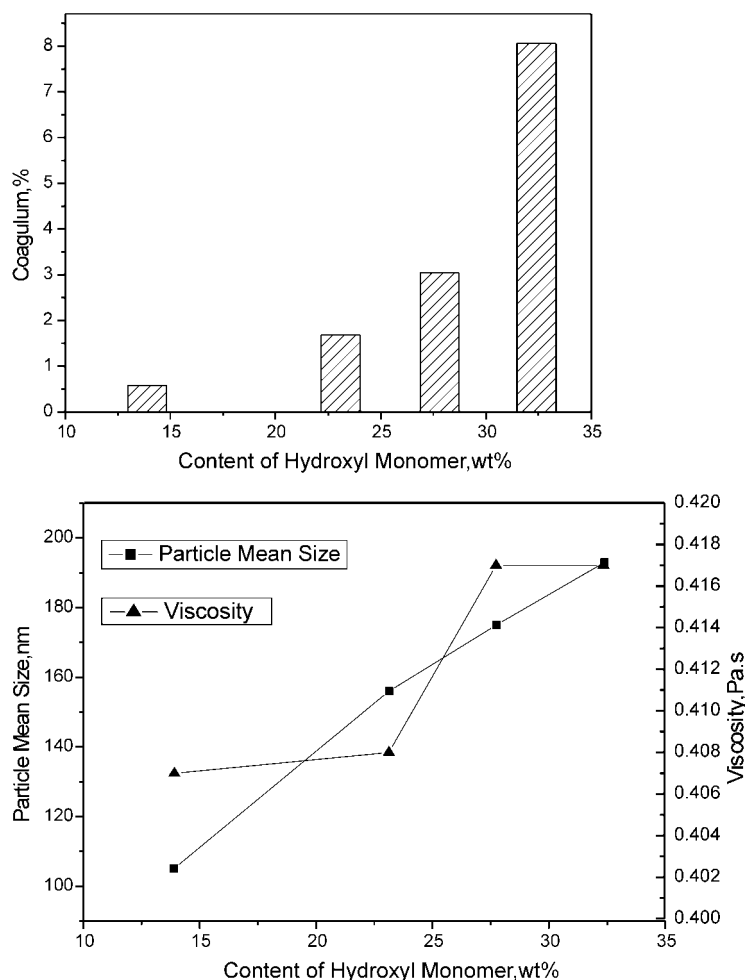


Figure 5. Effect of content of hydroxyl monomer on the stability of polymerization (emulsifier: SLS/OP = 4/6).

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surface of the particle, causing the particle to be inclined to coagulate with bigger coagulum formed and gradually settling. The more hydrophilic the monomer, the greater the tendency to settle. It also showed that, the particle mean diameter of the emulsion particle increased as the level of the hydroxyl monomer increased. The latter was due to the increasing hydrophilicity at the emulsion particle surface, thickening the hydration layer on the particle surface.

Levels of Carboxyl Monomer

The use of small amounts of monomer containing carboxyl in the emulsion may increase the stability of the emulsion and the adhesion onto the substrates. Figure 6

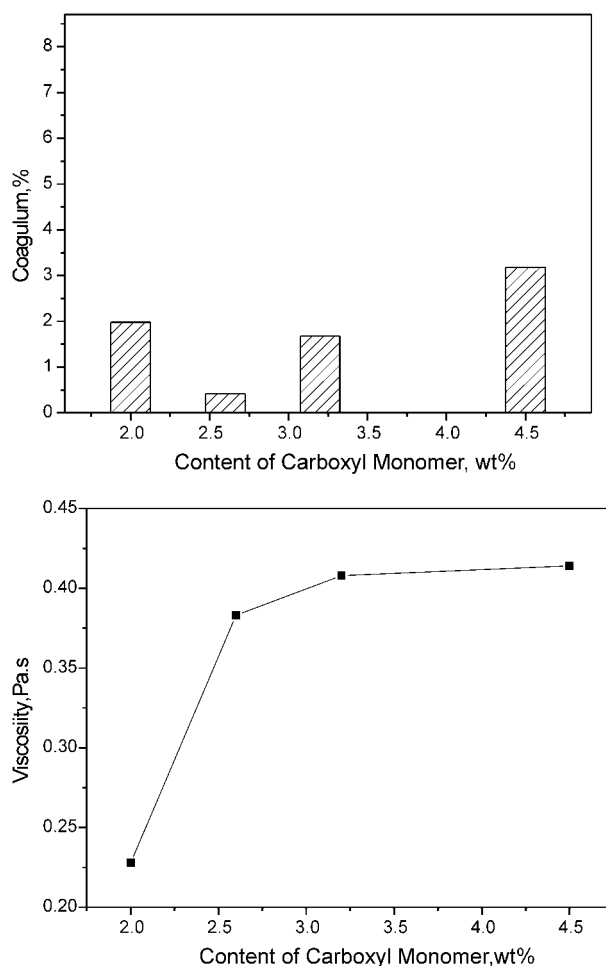


Figure 6. Effect of content of carboxyl monomer on the stability of polymerization (emulsifier: SLS/OP = 4/6).



indicates that, when the level of carboxyl monomer varied from 2% to 2.6%, the stability of emulsion increased, resulting in lower coagulum. When the level of carboxyl monomer increased further, more of the carboxyl monomer dissolved in the water phase, increasing the possibility of radical homopolymerization of the carboxyl monomer in the water phase, increasing coagulum content. The optimal level of carboxyl monomer existing for this emulsion polymerization system was 2.6%, based on total weight of monomers. More or less carboxyl monomer may cause more coagulum.

Figure 6 also indicates that the level of carboxyl monomer greatly influenced the viscosity of the resulting emulsion. When the level of carboxyl monomer was low, increasing the level of carboxyl monomer clearly increased the viscosity. Whereas, when the level of carboxyl monomer reached 3.2% and more, the viscosity of the emulsion increased gently as it increased, i.e., the level of carboxyl monomer had little influence on the viscosity of the emulsion. This may be explained as follows: after neutralization the carboxyl group was inclined to relax and stretch, with free volume of emulsion molecular chain diminished and movement of emulsion molecules hindered. As the level of carboxyl monomer increased, so the viscosity of the emulsion increased. Where the level of carboxyl monomer was low, this situation was more evident or more clear, after it reached to some extent this situation was less evident and less clear than before.

Viscosity of the Emulsion Containing High Hydroxyl Content

Comparing the emulsions without or with small amounts of hydroxyl content, the emulsion with high hydroxyl monomer had higher apparent viscosity and relatively poor fluidity. This was due to high polarity of the hydroxyl and carboxyl monomers. In the emulsion system, hydrogen bonds between hydroxyl group of monomers and water molecule may form, as well as between hydroxyl groups of the monomers and monomers. This was more evident after neutralization. Reference^[1] reported that the use of a small amount of electrolyte may diminish the apparent viscosity and improve the fluidity of emulsions. In essence, adding small amounts of electrolyte make the hydration layer of the emulsion particle thinner, and an increase of the continuous water phase of emulsion, with the action force between hydration particles declined. From another experiment, adding only 0.1 g potassium chloride in the initial charge in the emulsion polymerization, diminished the apparent viscosity from 0.408 to 0.263 Pa s and improved the fluidity of the emulsion. But, a higher level of electrolyte may damage the stability of the emulsion.

CONCLUSION

The emulsion with high hydroxyl content is very useful in the coating industry. This type of emulsion is relatively difficult to synthesize compared with emulsion without hydroxyl monomer, due to the hydrophilicity of the hydroxyl monomer. This monomer may polymerize in different locations with a different reaction mechanism. In the paper, two anionic and two nonionic surfactants were investigated in order to select the best emulsifier for the emulsion polymerization process. The influences of the level of emulsifier, the ratio of anionic and nonionic surfactant, reaction temperature, level of hydroxyl monomer, and level of carboxyl monomer on the polymerization process, particle



size, and viscosity were also studied. Experiments showed that, when the SLS/OP mixed emulsifiers were used and its level was 3% with a SLS/OP ratio of 4/6, and the reaction temperature at 65–75°C, the polymerization process had lower coagulum. As the levels of hydroxyl monomer and carboxyl monomer increased, the coagulum increased, and the viscosity of the resulting emulsion also increased.

The emulsion with high hydroxyl monomer had higher apparent viscosity and relatively poor fluidity. Adding small amounts of electrolyte diminished the apparent viscosity, and improved the fluidity of the emulsion.

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