Water-Soluble Copolymers. II. Inverse Emulsion Terpolymerization of Acrylamide, Sodium Acrylate, and Acryloyloxyethyl Trimethylammonium Chloride

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ABSTRACT: Inverse emulsion terpolymerization of acrylamide, sodium acrylate, and acryloyloxyethyl trimethylammonium chloride was investigated. Aqueous monomer solutions were emulsified in diesel oil with a blend of two surfactants (SPAN80 and TWEEN80) using 2,2'-azobis(2-amidinopropen)-dihydrochloride as the initiator. The effects of temperature, initiator concentration, monomer concentration and composition, and emulsifier content on the polymerization conversion and the polymer intrinsic viscosity were examined. Polymer intrinsic viscosity increased with a decreasing concentration of initiator and an increasing concentration of monomer. The sizes of the latex particles of the terpolymer emulsions were observed with a scanning electron microscope, and the structure of the terpolymer was identified by FTIR spectroscopy. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 1381–1385, 2006

Key words: inverse emulsion polymerization; terpolymer; sodium acrylate

INTRODUCTION

Water-soluble homopolymers and copolymers with acrylamide have become increasingly important in industrial applications over the past several decades. These polymers are used for flocculants in wastewater treatment, as retention aids in papermaking, and as solid–liquid separation reagents in mineral dressing.[1–3] High-molecular-weight ampholytic polymer has been widely used in the same applications because it is highly effective and low in cost. Amphoteric polyacrylamide is representative of a special sort of water-soluble polymers that contain both positively and negatively charged groups along the macromolecular backbone. A combination of cationic and anionic groups was found to more effectively neutralize the charge in the sludge.[4]

Inverse emulsion polymerization has proved to be a very suitable technique for the production of water-soluble polymers of high molecular weight. Inverse emulsion polymerization of water-soluble polymers in organic media has been studied by many reasearchers.[5,6] However, only a few works have studied inverse emulsion polymerization of amphoteric polyelectrolyte in organic media. In this article, we report on the amphoteric terpolymerization of acrylamide, sodium acrylate, and acryloyloxyethyl trimethylammonium chloride based on inverse emulsion. The effects of the initiator concentration, monomer composition and concentration, and emulsifier content on polymerization are discussed, as well as the structures of terpolymers and latex particle distribution.

EXPERIMENTAL

Materials

Acrylamide (AM), obtained from Jiaozuo Duo Shengduo Chemical Co. Ltd. (Jiaozuo, China), was recrystallized from acetone. Technical-grade acryloyloxyethyl trimethylammonium chloride (DAC) and 2,2'-azobis(2-amidinopropen)-dihydrochloride (AIBA) from Green Chemical Co. Ltd. (Guangzhou, China) was used without further purification. Acrylic acid (AA), which had been purified from active carbon, was provided by Tianjin No. 2 Reagent Manufacturer (Tianjin, China). Diesel oil was purchased from the market and was washed with concentrated H_2SO_4 and NaOH solutions. SPAN80 and TWEEN80, obtained from Shanghai Chemical Reagent Co. (Shanghai, China), were used as supplied. Other reagents were GR grade and were used as received.

Inverse emulsion polymerization

A designated amount of acrylic acid was dissolved in deionized water. To this solution was added an

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equimolar concentration of sodium hydroxide, and the pH was adjusted to 7.5.

Acrylamide and acryloyloxyethyl trimethylammonium chloride were dissolved in an aqueous solution of sodium acrylate (NaAA) to the appropriate concentrations. The required amount of SPAN80 and TWEEN80 dissolved in diesel oil was put into the reactor, and the water phase was added to it to attain an oil:water ratio (v/v) of 0.4–0.6. The required amount of initiator was added, and the emulsion was deaerated by bubbling oxygen-free N_2 gas for 15 min, while the mixture was stirred at 1000 rev/min. The temperature was maintained by passing water from the thermostatically controlled water bath through the jacket of the reaction vessel. The stirrer speed was then decreased to 400 rev/min, and a positive pressure of N_2 was maintained over the reaction mixture. After 8 h of polymerization, the emulsion was removed from the reactor. The conversion of monomers was determined by the bromination titration method.[7]

Viscosity measurement

The polymer emulsions were precipitated in excess acetone while stirring, followed by several washings and drying at 45°C. The intrinsic viscosity of the polymer was determined in aqueous $1M$ NaCl using an Ubbelohde viscometer at 30°C.

FTIR measurement

The precipitated products obtained during the viscosity measurement were dissolved into water and were further purified by reprecipitation in acetone, followed by vacuum drying for 2 days at room temperature. The FTIR spectrum of the terpolymer was recorded on a Nicolet MAGNA-IR 760 Fourier transform infrared spectrometer. The film was prepared using KBr disc.

SEM measurement

The polymer emulsion was diluted about 20-fold by diesel oil, and approximately 0.1 mL of the solution was placed on a washed-up cover glass and dried naturally. The morphology and particle diameter of the polymer emulsion were investigated with a LEO1530VP scanning electron microscope (SEM). The particle size distribution was determined from the micrographs obtained.

RESULTS AND DISCUSSION

Effect of polymerization temperature

Figure 1 shows polymerization conversion and intrinsic viscosity versus polymerization temperature. In
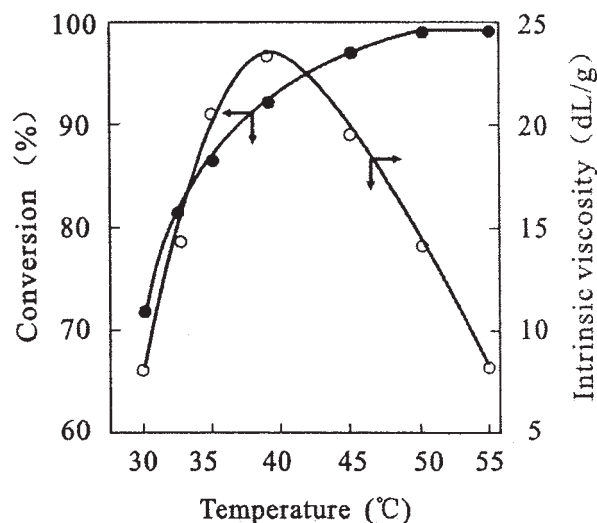
Figure 1 Effect of temperature on polymerization [conditions: DAC/NaAA/AM, 8:70:22 (mol %); monomer, 40 wt %; AIBA, 0.364 mmol/L; emulsifier, 3.74 wt %; HLB, 6.0; V_0/V_w, 0.45; pH, 7.5].

this polymerization, conversion increased with increasing temperature, in the same way as in solution polymerization. With increasing temperature, radical-producing velocity increased, and then the radical concentration in water phase increased, resulting in an increased rate of polymerization.

Figure 1 also shows that intrinsic viscosity reached a maximum at 37°C–42°C. This is because radical-producing velocity was slower at temperatures below 40°C, so the polymerizing rate decreased; but at higher temperatures, the temperature dependence of the termination and chain transfer reactions was greater than the chain propagation reaction, which decreased the intrinsic viscosity.[8]

Effect of initiator concentration

Figure 2 shows polymer conversion against initiator concentration and polymer intrinsic viscosity against initiator concentration in the aqueous phase. The dependence of the conversion on initiator concentration is represented by an S-shaped curve. The linear portion of the curve extends to very high conversion levels (around 50%–60%), showing no constant rate (conversion: 10%–40%), typical of conventional emulsion polymerization.[9] The gel effect is evident in the curve.

Polymer intrinsic viscosity increased with increasing initiator concentration and then reached a steady value (about 0.3 mmol/L). The increase in intrinsic viscosity with conversion also was indicative of the gel effect, which was strengthened with high conversion in inverse emulsion.
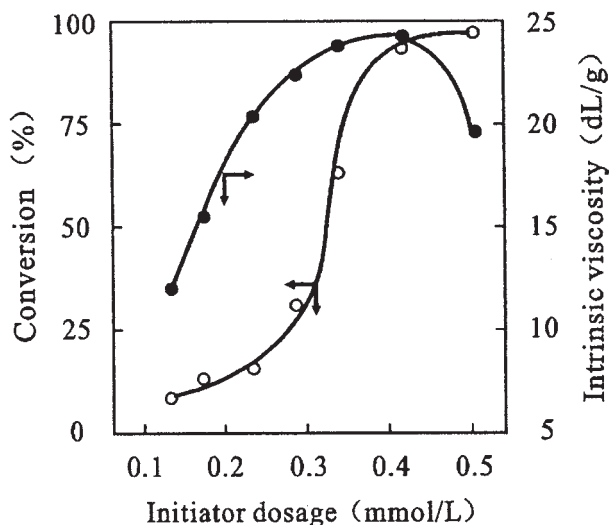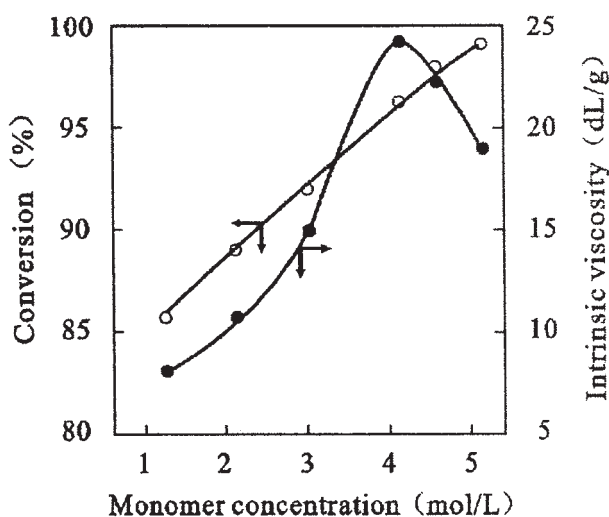
Figure 2 Effect of initiator dosage on polymerization [conditions: DAC/NaAA/AM, 8:70:22 (mol %); monomer, 40 wt %; emulsifier, 3.74 wt %; HLB, 6.0; V_0/V_w, 0.45; pH, 7.5; T, 40°C].
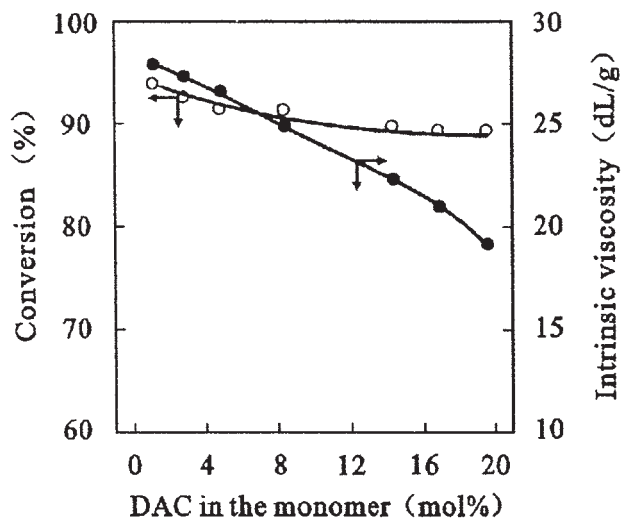

Figure 4 Effect of DAC composition on polymerization [conditions: monomer, 40 wt %; NaAA, 70 mol %; AIBA, 0.364 mmol/L; emulsifier, 3.74 wt %; HLB, 6.0; V_0/V_w, 0.45; pH, 7.5; T, 43°C)

The intrinsic viscosity leveled off at higher conversion, mainly because when the initiator concentration was too large, the radical concentration increased, and then the radical termination rate increased much faster than the chain propagation rate, resulting in decreased molecular weight.

Effect of monomer concentration and composition of both DAC and AM

The effects of monomer concentration in the aqueous phase and comonomer composition in the initial

monomer feed on polymerization conversion and polymer intrinsic viscosity were studied.

Figure 3 shows that polymerization conversion and polymer intrinsic viscosity increased with increasing total monomer concentration. This is in line with the results for solution polymerization. However, increased total monomer concentration caused an increase in polymerization exotherm and gelation, which made the polymerization rate increase sharply, and the higher the total monomer concentration was, the more conspicuous was the action. The tailing off of intrinsic viscosity at higher conversion could have
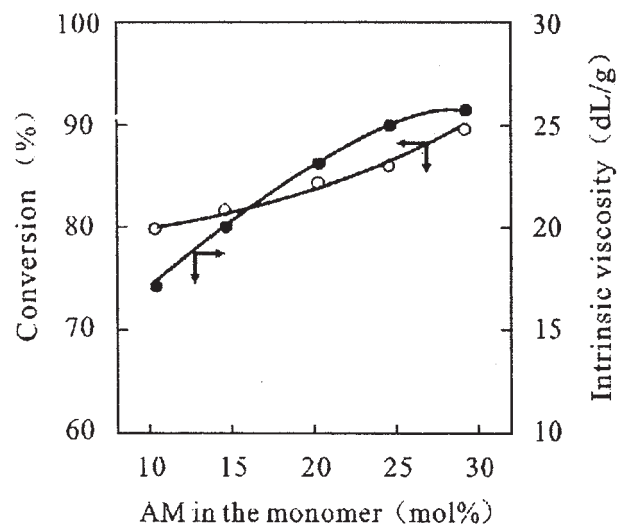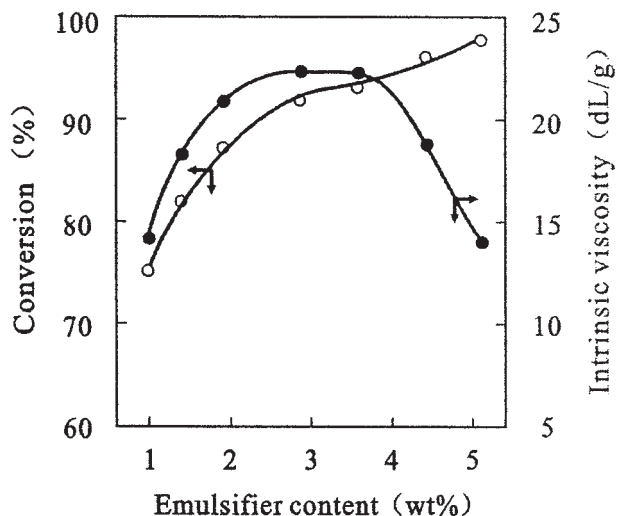

Figure 3 Effect of monomer concentration on polymerization [conditions: DAC/NaAA/AM, 8:70:22 (mol %); AIBA, 0.364 mmol/L; emulsifier, 3.74 wt %; HLB, 6.0; V_0/V_w, 0.45; pH, 7.5; T, 40°C].

Figure 5 Effect of AM composition on polymerization [conditions: monomer, 40 wt %; NaAA, 70 mol %; AIBA, 0.364 mmol/L; emulsifier, 3.74 wt %; HLB, 6.0; V_0/V_w, 0.45; pH, 7.5; T, 42°C)
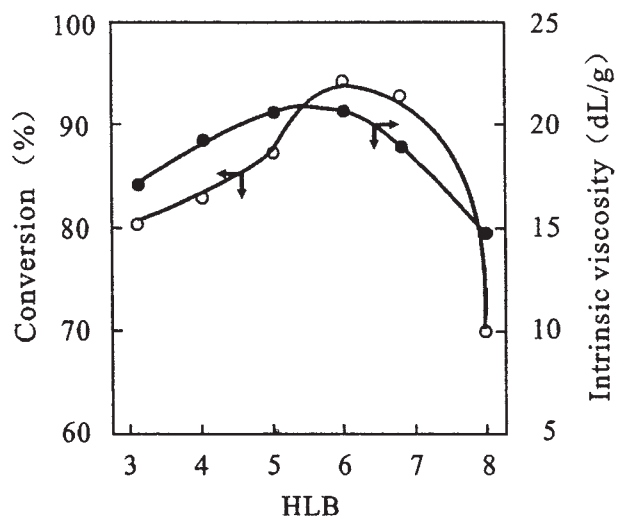
Figure 6 Effect of emulsifier content on polymerization [conditions: DAC/NaAA/AM, 8:70:22 (mol %); monomer, 40 wt %; AIBA, 0.364 mmol/L; HLB, 6.0; V_0/V_w, 0.45; pH, 7.5; T, 40°C].

from two opposite effects: the increase in molecular weight based on the gel effect or the decrease in molecular weight brought about by the temperature exotherm. The tailing off of intrinsic viscosity actually was a result of the latter.

Figure 4 shows polymerization conversion and polymer intrinsic viscosity versus DAC composition in the initial monomer feed. However, it can be seen that polymer intrinsic viscosity apparently decreased with an increase in the molar percentage of DAC in the monomer.

The effect of the AM composition in the initial monomer feed on conversion and intrinsic viscosity is

Figure 7 Effect of value of emulsifier HLB on polymerization [conditions: DAC/NaAA/AM, 8:70:22 (mol %); monomer, 40 wt %; AIBA, 0.364 wt %; V_0/V_w, 0.45; pH, 7.5; T, 40°C].
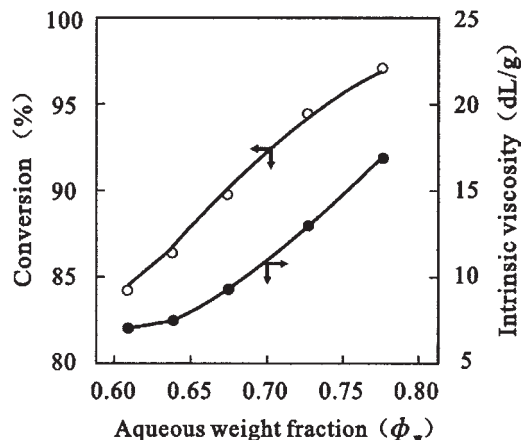
Figure 8 Effect of oil/water ratio on polymerization [conditions: DAC/NaAA/AM, 8:70:22 (mol %); monomer, 40 wt %; AIBA, 0.364 mmol/L; emulsifier, 3.74 wt %; HLB, 6.0; pH, 7.5; T, 44°C].

shown in Figure 5. Polymerization conversion and polymer intrinsic viscosity both increased with an increasing molar percentage of AM in the monomer. This was because emulsification of AM monomer was aided, which increased the stability of the inverse emulsion polymerization.

Effects of emulsifier content and HLB

Keeping the overall concentration (monomer plus water) constant, the polymerization conversion increased with increasing emulsifier content in the oil phase (see Fig. 6). Increasing the bulk level of emulsifier would cause both the interfacial and organic phase concentrations to increase. The first effect decreased the surface tension, which produced smaller particles and a slightly faster rate.

Figure 6 also shows that the intrinsic viscosity reaches a maximum value at 3–4 wt % of emulsifier content. For the matter of emulsion polymerization, the larger the emulsifier content, the more the particle number, and the longer the radical life, which increased the polymer molecular weight. However, the chain transfer reaction to the emulsifier was superior

TABLE I
Stable DAC-NaAA-AM Terpolymerization Conditions

Parameter	Value
Temperature (°C)	37–42
Initiator concentration (mmol/L)	0.35–0.45
Monomer concentration (mol/L)	3.5–4.5
DAC in monomer (mol %)	4–16
AM in monomer (mo %)	14–26
Emulsifier content (wt %)	3–4
Emulsifier HLB	5.5–6.0
Oil water ratio (v/v)	0.4–0.6

to the chain propagation reaction from the gel effect, whereas the emulsifier content was higher, resulting in a decrease in the intrinsic viscosity with increasing emulsifier content.

Figure 7 displays the effect of the emulsifier HLB value on polymerization. The overall concentration of the oil and water phases was kept constant. The polymerization conversion and polymer intrinsic viscosity were both at maximum values at an HLB of 5.5–6.5, which was also the most stable region of the inverse emulsion polymerization.

Effect of oil/water phase ratio

Figure 8 shows the relationship among polymerization conversion, intrinsic viscosity of the terpolymer, and the aqueous mass fraction (ϕ_m). The probable explanation is that for the total system, an increase in the aqueous mass fraction accompanied by an increase in the monomer concentration was favorable to R_p and $[\eta]$, so polymerization conversion and polymer intrinsic viscosity both increased with an increase in ϕ_m.

Stable terpolymerization conditions

Table I summarizes the conditions for stable synthesis for inverse emulsion terpolymerization, based on the above experimental studies.
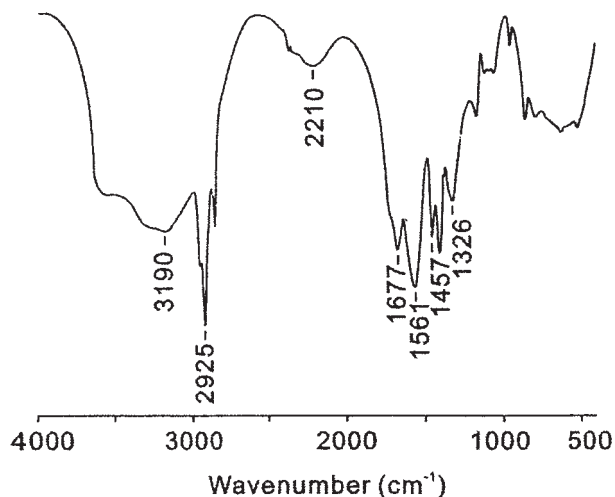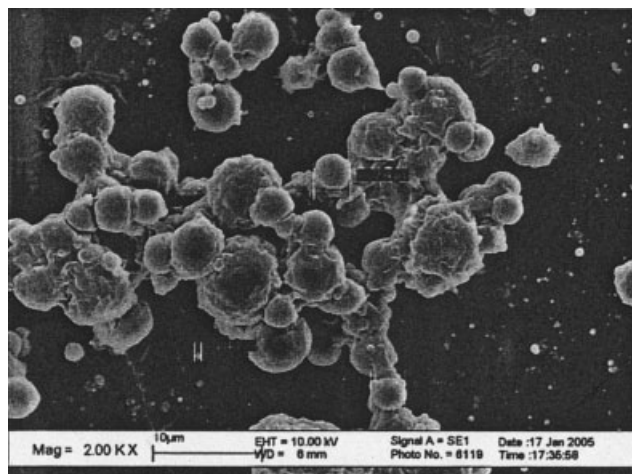

Figure 10 SEM photograph of DAC/NaAA/AM terpolymer emulsion.

FTIR spectrum and SEM observation

The FTIR spectrum of DAC-NaAA-AM terpolymer sample (Fig. 9) shows a broad absorbance at 3190 cm^{-1} and a sharp absorbance at 1677 cm^{-1}, attributed to amide group (—$CONH_2$) absorption, in the —AM— units. Similarly, the sharp absorbances at 1326 and 1561 (—CO_2Na) and at 1457 [—$N\oplus(CH_3)_3$] cm^{-1} are characteristic peaks of the —NaAA— and —DAC— units, respectively.

Figure 10 shows the SEM of the morphology of the DAC-NaAA-AM terpolymer emulsion particles. The particle size and distribution ranged from 0.6 to 8 μm, and the particles were globular in shape.

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Figure 9 FTIR spectrum of DAC/NaAA/AM terpolymer.