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Radiation copolymerization of acrylamide and cationic monomer in an inverse emulsion

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The inverse emulsion copolymerization of (2-methacryloyloxyethyl)trimethylammonium chloride with acrylamide using gamma rays has been studied. Aqueous monomer solutions were emulsified in kerosene with a blend of two surfactants (Span80 and OP10). The gel effect is evident from the increase of the molecular weight with conversion and also from the percentage conversion *versus* irradiation time curves. The effects of dose rate, concentration and composition of the monomer, emulsifier content, temperature, etc. on the polymerization conversion and the intrinsic viscosity of the polymer have been examined. The polymer molecular weight increases with decreasing dose rate and increasing monomer concentration. These results are discussed in connection with the mechanism of inverse emulsion polymerization. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: inverse emulsion polymerization; radiation-induced polymerization; acrylamide)

INTRODUCTION

The production of water-soluble polymers exceeds 5 000 000 tonnes per annum. Polyacrylamide, poly(acrylic acid) and their copolymers are the most important among them. It is well known that the polymer of (2-methacryloyloxyethyl)trimethylammonium chloride (DMC) and its copolymer with acrylamide (AM) are used as effective cationic flocculants for the treatment of wastewater containing organic suspensions.

Although water-soluble copolymers have been recognized as being very useful in terms of technological applications and scientific investigations, up to now very few studies have been reported for the case of inverse emulsion copolymerization. Generally, radiation polymerization is one of the most convenient methods because of its non-temperature-dependent initiation and extremely large *G*-value. Also, the radiation process can easily lead to a higher molecular weight copolymer. The radiation-induced copolymerization of DMC with AM in aqueous solution has been studied previously (by Okada *et al.*[1], Ishigaki *et al.*[2], and Fukuzaki *et al.*[3]). In order to obtain a water-soluble copolymer, solution copolymerization should be carried out using a relatively low monomer concentration. However, polymerization at a lower monomer concentration requires much energy and complicated processes to obtain a powdery product; for example, by drying with heating or precipitation with excess organic solvent. In the present work, we first investigate radiation-induced copolymerization in an inverse emulsion. The effects of composition of the monomer, dose rate, temperature, monomer concentration, etc. on the polymerization are studied.

EXPERIMENTAL

Materials

Acrylamide, obtained from Huibei Daxue Chemicals, Inc., was recrystallized from acetone. Technical grade (2-methacryloyloxyethyl)trimethylammonium chloride from Xing Yu Chemicals Co. Ltd. was used without further purification. Kerosene was purchased from the market and was washed with concentrated H_2SO_4 and NaOH solutions. SPAN80 and OP10, obtained from the Shanghai Chemical Reagent Co. were used as supplied. Other reagents were GR grade and were used as received.

Polymerization of the inverse emulsion

Polymerization was carried out in a sealed glass ampoule after the emulsion was bubbled with nitrogen. The ampoule was then subjected to γ-ray irradiation using a ^{60}Co source. The dose rate was controlled by changing the distance between the ampoule and the ^{60}Co source and was determined using a Fricke dosimeter. After irradiation, the polymerization product was removed from the glass ampoule at room temperature.

Viscosity measurement

The polymerized emulsions were precipitated in a large quantity of ethanol, and then washed with acetone. The polymer was then dried to constant weight at room temperature under vacuum. The intrinsic viscosity of the polymer was determined in aqueous 1 N $NaNO_3$ using an Ubbelode capillary viscometer at 30°C.

RESULTS AND DISCUSSIONS

Effect of irradiation dose

Figure 1 shows the polymer conversion against irradiation dose and the polymer intrinsic viscosity against irradiation dose, respectively. The irradiation dose dependence of the conversion is represented by S-shaped curves. The linear portions of the curves extend to very high conversion levels (around 45–60%) showing no constant-rate region typical of conventional emulsion polymerization[4]. The influence of the gel effect is evident in the curves. Under normal conditions the polymerization rate would

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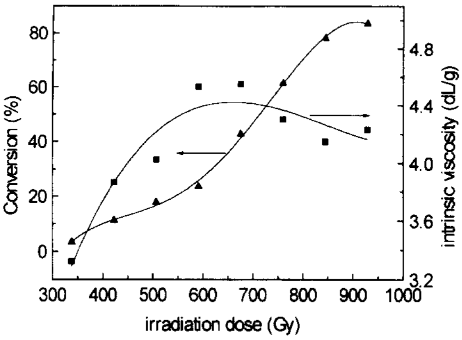

Figure 1 The effect of irradiation dose on polymerization. (Dose rate, 8.44 Gy min^{-1}; composition: AM, 8.88 wt.%; DMC, 11.12 wt.%; kerosene, 21.8 wt.%; Span80, 2.4 wt.%; OP10, 0.8 wt.%; H_2O, 55.0 wt%; pH 6.8; *T*, 291 K)

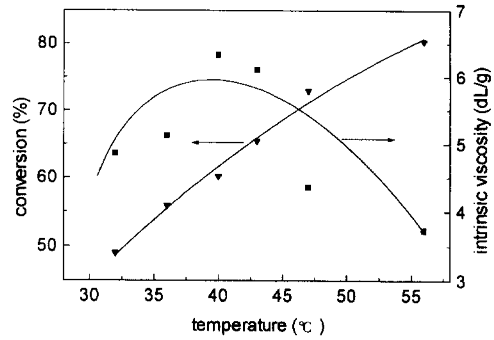

Figure 3 The effect of temperature on polymerization. (Dose rate, 10.0 Gy min^{-1}; total dose, 700 Gy; composition: AM, 15.10 wt.%; DMC, 4.90 wt.%; kerosene, 21.8 wt.%; Span80, 2.4 wt.%; OP10, 0.8 wt.%; H_2O, 55.0 wt.%; pH 6.8)

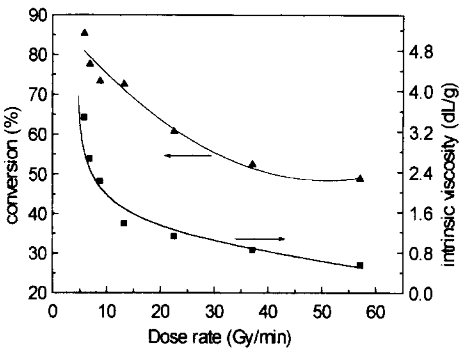

Figure 2 The effect of irradiation dose rate on polymerization. (Total dose, 700 Gy; composition: AM, 8.88 wt.%; DMC, 11.12 wt.%; kerosene, 21.8 wt.%; Span80, 2.4 wt.%; OP10, 0.8 wt.%; H_2O, 55.0 wt.%; pH 6.8; *T*, 288 K)

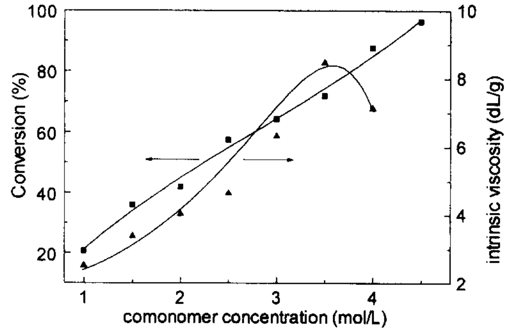

Figure 4 The effect of monomer concentration on polymerization. (Dose rate, 13.16 Gy min^{-1}; total dose, 950 Gy; composition: AM/DMC 7:3 (mol); kerosene, 21.8 wt.%; Span80, 2.4 wt.%; OP10, 0.8 wt.%; pH 6.8; *T*, 293 K)

have decreased with increasing conversion due to decreasing [M] at about 10% conversion[5]. However, in the present case this decrease is fortuitously compensated by the gel effect up to a very high conversion level.

The polymer intrinsic viscosity increases with irradiation dose in the early stages of the reaction and then reaches a steady value. The result is similar to that reported by Hunkeler *et al.*[6] for the inverse emulsion polymerization of acrylamide initiated with AIBN. The increase in intrinsic viscosity with conversion is also indicative of the existence of the gel effect. The tailing-off of the molecular weight at higher conversion may arise from two opposite effects, namely the increase in molecular weight due to the gel effect is opposed by a molecular weight decrease brought about by the depletion of the [M]. Hunkeler *et al.* attributed the molecular weight tailing-off to the latter.

Effect of irradiation dose rate

Figure 2 shows the polymerization conversion and polymer intrinsic viscosity *versus* the irradiation dose rate, respectively, for polymerization at a constant irradiation dose. The polymer intrinsic viscosity decreases with increasing dose rate. This is similar to the result found for solution polymerization. Based on the basic law of radical reactions, the concentration of the radical reactive centre increases with the dose rate, so the polymer intrinsic viscosity decreases accordingly.

Effect of polymerization temperature

The effects of temperature on the polymerization conversion and the polymer intrinsic viscosity were studied. In the polymerization, the conversion increases with increasing temperature as shown in *Figure 3*. This is in line with solution polymerization. With increasing temperature, the radical concentration increases, resulting in an increase in the polymerization rate.

Figure 3 also shows that the intrinsic viscosity reaches a maximum value at 35–45°C. According to the basic theory of radiation polymerization, the relationship between the average degree of polymerization (P_n) and temperature was expressed as follows[7]

$$\ln[P_n(T_2)/P_n(T_1)] = [(E_p - E_t/2) - E_i/2] \times (1/T_1 - 1/T_2)/R \quad T_2 > T_1$$

This is a simple kinetics model where E_p, E_t, and E_i are the activation energies for the propagation, termination and initiation reactions, respectively. The activation energy of initiation is about zero because of radiation initiation, so ($E_p - E_t/2$) is greater than zero and the polymerization degree increases with increase of temperature. However, at higher temperature, the chain transfer rate constant k_{tr} increases much faster than the chain propagation rate constant k_p, which lowers the intrinsic viscosity.

Effect of monomer concentration in the aqueous phase

Figure 4 shows polymerization conversion against monomer concentration. In the polymerization, the conversion increases with increasing monomer concentration as shown in *Figure 4*. This is also in line with the results for solution polymerization.

Figure 4 also shows the relationship between the intrinsic viscosity of the copolymer and the monomer concentration.

The polymers produced at monomer concentrations of 4.0 and 4.5 mol l^{-1} are water-insoluble (cross-linked). It can be seen that the intrinsic viscosity of the copolymer increases as the monomer concentration increases. However the increase in the monomer concentration causes an increase in the polymerization heat and gelation, which does not make the polymerization heat scatter and disappear easily. This causes a rise in the system temperature, which makes the polymerization rate increase sharply, and the higher the monomer concentration, the more conspicuous the action. However, at higher temperatures, the temperature dependences of the termination and chain transfer reactions are larger than that of the propagation reaction, which lowers the intrinsic viscosity of the copolymer. In our experiment, the critical value of the monomer concentration is about 4.0 mol l^{-1}.

Effect of emulsifier content

Figure 5 displays the effect of the emulsifier content on the polymerization. In this series, the overall concentration of (monomer + water) was kept constant. The conversion increases with increasing emulsifier content. Increasing the bulk level of emulsifier will lower the surface tension, which leads to smaller particles and a slightly faster rate.

The decrease in the intrinsic viscosity with increasing emulsifier content was due to the chain transfer reaction to the emulsifier. This is verified experimentally over a broad range of emulsifier contents.

Effect of oil/water phase ratio

The changes in the polymerization conversion and polymer intrinsic viscosity with aqueous weight fraction (φw) at constant emulsifier content are shown in *Figure 6*. The polymerization conversion and polymer intrinsic viscosity both increase with increase in φw. A probably interpretation is that when the φw is changed, a decrease in the aqueous weight fraction accompanied by a decrease in the monomer concentration in the system is unfavourable to *R*p and [η], so the polymerization conversion and the polymer intrinsic viscosity decrease with the decrease in the φw.

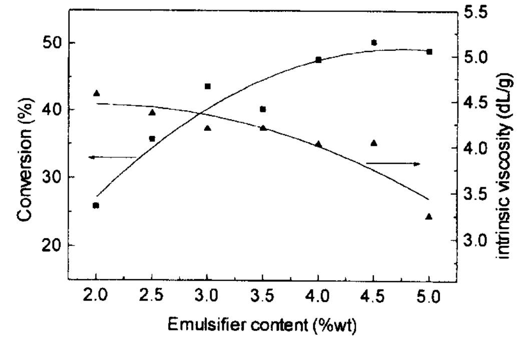

Figure 5 The effect of emulsifier content on polymerization. (Dose rate, 10.0 Gy min^{-1}; total dose, 700 Gy; composition: AM, 8.88 wt.%; DMC, 11.12 wt.%; H_2O, 55.0 wt.%; pH 6.8; *T*, 287 K)

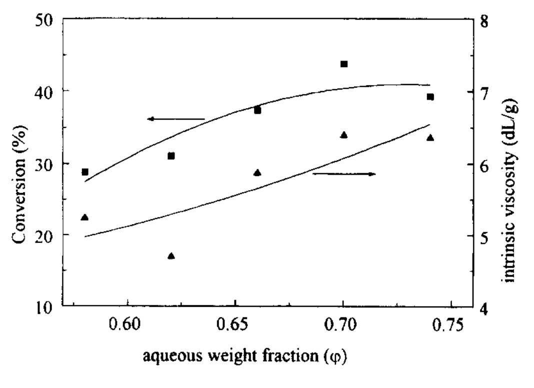

Figure 6 The effect of water/oil ratio on polymerization. (Dose rate, 8.72 Gy min^{-1}; total dose, 700 Gy; composition: AM/DMC 7:3 (mol); monomer, 20 wt%.; pH 6.8; *T*, 313 K)

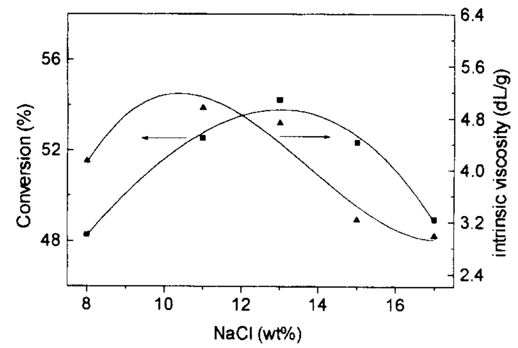

Figure 7 The effect of NaCl content on polymerization. (Dose rate, 10.0 Gy min^{-1}; total dose, 700 Gy; composition: AM, 8.88 wt.%; DMC, 11.12 wt.%; kerosene, 21.8 wt.%; Span80, 2.4 wt.%; OP10, 0.8 wt.%; pH 6.8; *T*, 283 K)

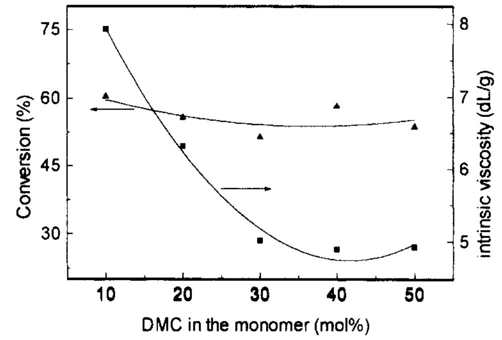

Figure 8 The effect of comonomer composition on polymerization. (Dose rate, 8.72 Gy min^{-1}; total dose, 700 Gy; composition: monomer, 20 wt.%; kerosene, 21.8 wt.%; Span80, 2.4 wt.%; OP10, 0.8 wt.%; pH 6.8; *T*, 287 K)

Effect of added electrolyte

Figure 7 shows the polymerization conversion and polymer intrinsic viscosity *versus* sodium chloride content in the aqueous phase. When [NaCl] in the aqueous phase is low, the salt effect results in more monomer dissolving in the aqueous phase, so the polymerization conversion and the intrinsic viscosity of the copolymer increase with increase of [NaCl]. When [NaCl] continues to increase, the salting-out effect causes less monomer to dissolve in the aqueous phase, so the polymerization conversion and the intrinsic viscosity of the copolymer will decrease with increase in [NaCl].

Effect of the DMC content in the initial comonomer feed

The effect of the comonomer composition on the conversion and intrinsic viscosity of the copolymer was studied. The polymerization conversion was fairly insensitive to the comonomer composition, as shown in *Figure 8*. However, it can be seen that the polymer intrinsic viscosity decreases sharply with increase of the mole percentage of DMC in the comonomer when it is below 30% and then decreases much more slowly when it is greater than 30%.

The best polymerization conditions

The best conditions for the polymerization are summarized in *Table 1*.

Table 1 Best polymerization conditions

Parameter	Value
Irradiation dose (Gy)	700–1100
Irradiation dose rate (gy min^{-1})	0.5–15
Temperature (°C)	25–40
DMC in the monomer (mol%)	5–25
NaCl content (wt.%)	8–13
Monomer concentration (mol l^{-1})	2.7–3.8
Emulsifier content (wt.%)	2.5–4.0
Oil/water ratio (v/v)	0.4–0.6

CONCLUSION

Specific features of the inverse emulsion copolymerization of acrylamide with DMC using a blend of two surfactants (Span80 and OP10) with gamma rays have been studied. In general, the conversion–time curves are S-shaped due to the gel effect. An increase in molecular weight with conversion is also indicative of the existence of the gel effect. In order to synthesize hydro-soluble copolymers with a higher conversion, higher molecular weight and better solubility, the effects of dose rate, monomer concentration, composition of the initial monomer, emulsifier content, polymerization temperature, added electrolytes, and oil/water phase ratio on the polymerization conversion and intrinsic viscosity of the polymer have been examined. The polymer molecular weight increases with decreasing dose rate, increasing aqueous weight fraction and increasing monomer concentration.

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