

Studies of Inverse Emulsion Copolymerization of (2-Methacryloyloxyethyl) Trimethyl Ammonium Chloride and Acrylamide

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ABSTRACT: Inverse emulsion copolymerization of (2-methacryloyloxyethyl) trimethyl ammonium chloride with acrylamide initiated with potassium persulfate has been studied dilatometrically. 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 of conversion versus time curves. Monomer reactivity ratios have been derived as $r_{AM} = 0.38$ and $r_{DMC} = 1.69$ at pH 6.8. The effects of initiator concentration, concentration, and composition of the monomer, emulsifier concentration, etc., on the polymerization rate and intrinsic viscosity of polymer have been examined. The rate of polymerization (R_p) can be represented by $R_p \propto I^{0.52}[M]^{1.50}[E]^{0.38}$. The overall activation energy for the rate of polymerization is 66.0 kJ mol⁻¹ (40–65°C). Based on these experimental results, some aspects of the polymerization mechanism are discussed. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1005–1010, 1998

Key words: inverse emulsion polymerization; acrylamide; (2-methacryloyloxyethyl) trimethyl ammonium chloride; water-soluble cationic polymers

INTRODUCTION

During the last 20 years, there has been an increasing interest in water-soluble cationic polymers. They are commonly used in the paper industry where they are needed for the adhesion between fillers and the wood fibers and as flocculation aids in wastewater treatment. They are also used in mining and in tertiary oil recovery. These polymers are generally produced by copolymerization of cationic monomers with acrylamide to obtain high-molecular-weight polyelectrolytes.

Since the basic article of Vanderhoff et al.¹ in 1962, several studies have been devoted to the inverse emulsion polymerization in order to eluci-

date the kinetics and mechanism of this process. Although water-soluble copolymers have been recognized as very useful in terms of technological applications and scientific investigations, up to now, very few studies have been reported in the case of inverse emulsion copolymerization. Moreover, the preparation and characterization of copolymers are of increasing interest for the control of their structural and properties is becoming increasingly important. In this study, the copolymerization of (2-methacryloyloxyethyl) trimethyl ammonium chloride (DMC) with acrylamide in inverse emulsion was initiated with potassium persulfate to investigate the polymerization mechanism.

EXPERIMENTAL

Materials

Acrylamide (AM) from Huibei Daxue Chemicals, Inc. (Huibei, China), was recrystallized from ace-

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tone. Technical grade DMC (Xing Yu Chemicals Co. Ltd., Wuxi, China) was used without further purification. Kerosene was purchased from market and washed with concentrated H_2SO_4 and NaOH solutions. SPAN80 and OP10 from Shanghai Chemical Reagent Co. (China) were used as supplied. Other reagents were GR. grade and used as received.

Preparation and Polymerization of Inverse Emulsion

Inverse emulsion was prepared by adding monomer aqueous solution to the kerosene-emulsifier mixture under stirring (2000 rpm). Purified nitrogen was bubbled at room temperature through the emulsions for about 30 min.

Before polymerization, the inverse emulsion was degassed twice with water bump to remove oxygen. After that, it was fed directly into the dilatometer and held in a bath whose temperature was accurately controlled with a regulator. The polymer conversion was recorded as function of time, and the polymerization rate was gotten by further differentiation.

Particles Size Observation

The monomer emulsions and the polymer latex were observed, and their particle sizes were estimated with an Leica Galen-III biological microscope. Dilution was carried out with kerosene containing the low hydrophile-lypophile balance (HLB) emulsifier (SPAN80) at the same concentration used in preparing the inverse emulsions.

Copolymer Characterization

^1H -NMR spectra were run on a 400 MHz EM360L nuclear magnetic resonance (NMR) spectrometer. The spectra of the polymer were obtained using 5–10 wt % aqueous (D_2O) polymer solutions with DSS as the reference. The procedure for quantitative determining copolymer compositions from ^1H -NMR spectra has been discussed in detail elsewhere.²

Viscosity Measurement

The polymerized emulsions were precipitated in a large quantity of ethanol and then washed with acetone. The copolymer was then dried under vacuum. The intrinsic viscosity of polymer was determined in 1N NaNO_3 aqueous with Ubbelode capillary viscometer at 30°C.

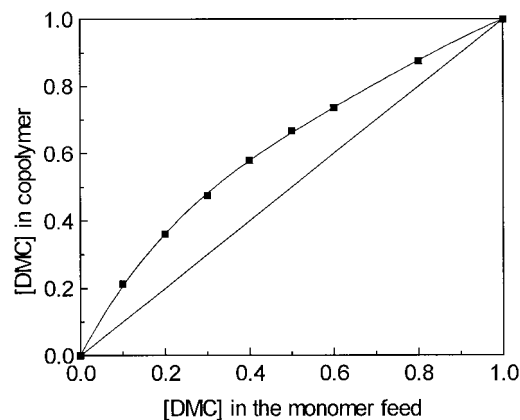


Figure 1 Relationship between compositions of monomer and copolymer: KPS, $6.342 \times 10^{-3} \text{ mol l s}^{-1}$; monomer concentration, 1 mol l; pH, 6.8; T , 333 K; polymer conversion, 6–11%.

RESULTS AND DISCUSSIONS

Particle Size Analysis

The monomer emulsions and the polymer latex were diluted and observed by an Leica Galen-III Biological microscope. No apparent change in particle size was observed after polymerization. The particle diameters of the monomer droplet and the polymer latex were roughly estimated as around 1–3 μm , without significant change with the emulsion ingredient and the polymerization condition, as observed by the biological microscope. This similarity between the initial emulsion droplet size and latex particle size corroborate the hypothesis made by several authors that the polymerization loci are mainly in the aqueous monomer droplets.

Compositional Analysis and Reactivity Ratio Studies

The copolymers of DMC with AM were synthesized by varying the feed ratios of AM : DMC. Copolymer compositions were determined from ^1H -NMR. Integration of ^1H hydrogen peaks gave the mol % of AM and DMC in the copolymers. The copolymer composition as a function of feed composition for the DMC series is shown in Figure 1.

The Fineman–Ross method gave reactivity ratios for AM and DMC of $r_1 = 0.38$ and $r_2 = 1.69$, respectively. There is a great difference between the reactivity ratios in the inverse emulsion and solution³ ($r_1 = 0.20$ and $r_2 = 1.75$). Because the addition of a cationic monomer to a cationic end group of the growing polymer radicals is strongly

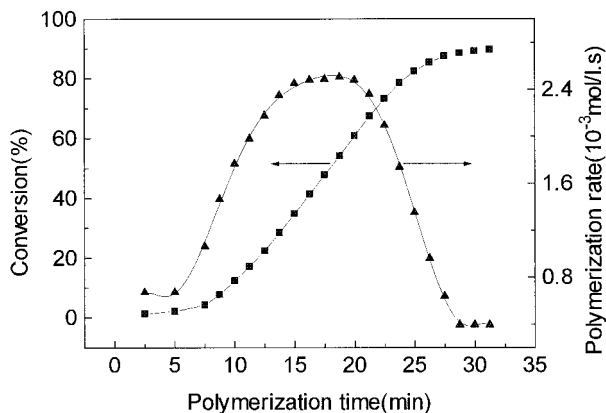


Figure 2 Conversion versus time curve and polymerization rate versus time curve: KPS, $6.342 \times 10^{-3} \text{ mol l s}^{-1}$; AM, 6.7 wt %; DMC, 2.2 wt %; kerosene, 26 wt %; Span80, 3 wt %; OP10, 1 wt %; H_2O , 61.1 wt %; T , 333 K.

influenced by electrostatic interactions, it is believed that this step in inverse emulsion is slower than in solution. This may be explained by the presence of a small amount of oil in water phase, which may change the dielectric constant or the quarternization equilibrium. In addition, DMC may be more liphophilic than AM, which causes the AM concentration in aqueous phase increases relatively. This also causes r_{AM} increases and r_{DMC} decreases relatively.

Variation of Polymerization Rate and Copolymer Intrinsic Viscosity with Conversion

Figure 2 shows typical conversion–time curve is generally S-shaped. In general, the curve could be reproduced with a measurement error below 3%. An induction period caused by residual O_2 in the system is normally observed, typically 3–30 min, depending mainly on the initiator concentration. The influence of the gel effect is evident in the conversion versus time curve. The linear portions of the curves extend to very high conversion levels (~ 45 –60%) showing no constant rate region that is typical for conventional emulsion polymerization.⁴ Under normal conditions, the R_p would have decreased with increasing conversion due to decreasing $[M]$ at about 10% conversion. However, in the present case, this decrease is fortuitously compensated by the gel effect up to a very high conversion level. The maximum reaction rate given by the slope of the linear part of the conversion–time curve was taken for determination of the kinetic relations.

The variation of $[\eta]$ with conversion as shown

in Figure 3 is similar to that reported by Hunkeler et al.⁵ for the inverse emulsion polymerization of acrylamide initiated with azo-bis-isobutyronitrile (AIBN). The increase of molecular weight with conversion is also indicative of the existence of the gel effect. The tapering of the molecular weight at higher conversion may arise from two opposing effects; namely, the increase of molecular weight due to the gel effect is opposed by the molecular weight decrease brought about by the depletion of $[M]$. Hunkeler et al. attributed the molecular weight tapering to the latter, reaching the limiting value dictated by monomer transfer.

Polymerization Kinetics

Effect of the DMC Content in the Initial Comonomer Feed

The effects of copolymer composition on polymerization rate and the intrinsic viscosity of the copolymers were shown in Figure 4. The polymerization rate was fairly insensitive to the initial comonomer feed. The decrease in the intrinsic viscosity is due to decreases in molecular weight, as well as increasing intermolecular interactions, which constrict the polymer coils. One might expect such effects to be especially strong as microheterogeneous associations lead to local decreases in dielectric constant of the domains.

Effect of Initiator Concentration

The effect of initiator concentration on polymerization kinetics was shown in Figure 5, as follows:

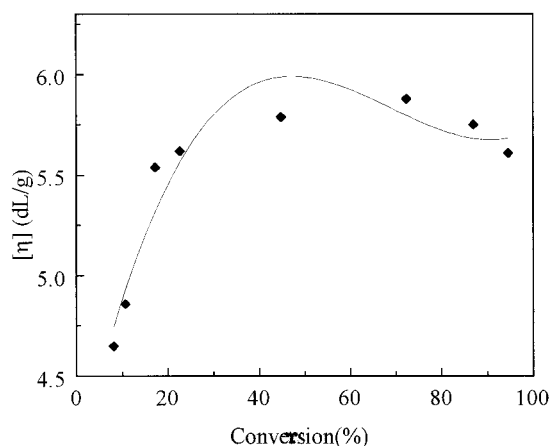


Figure 3 Dependence of intrinsic viscosity on conversion: KPS, $6.342 \times 10^{-3} \text{ mol l s}^{-1}$; AM, 6.7 wt %; DMC, 2.2 wt %; kerosene, 26 wt %; Span80, 3 wt %; OP10, 1 wt %; H_2O , 61.1 wt %; T , 333 K.

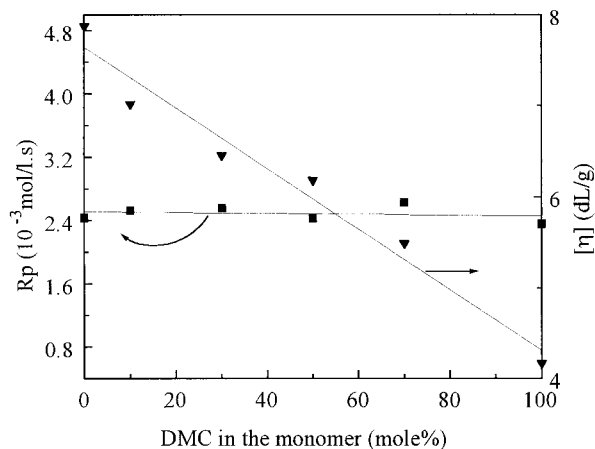


Figure 4 The effect of copolymer composition on polymerization: KPS, $6.342 \times 10^{-3} \text{ mol l s}^{-1}$; monomer concentration, 3 mol l; kerosene, 26 wt %; Span80, 3 wt %; OP10, 1 wt %; T , 333 K.

$R_p \propto I^{0.52}$, $[\eta] \propto I^{-0.04}$. The overall polymerization rate increases with the increase of initiator concentration. Clearly, the traditional one-half-order dependence is observed. Because the initiation takes place in aqueous phase just as in solution, so the dependence of polymerization rate on initiator concentration should be similar in the two systems. On the other hand, $[\eta]$ of the polymer formed is found to decrease very slightly with increasing initiator concentration, as shown in Figure 5.

Effect of Monomer Concentration in Aqueous Phase

The effect of monomer content on polymerization kinetics was shown in Figure 6, as follows: R_p

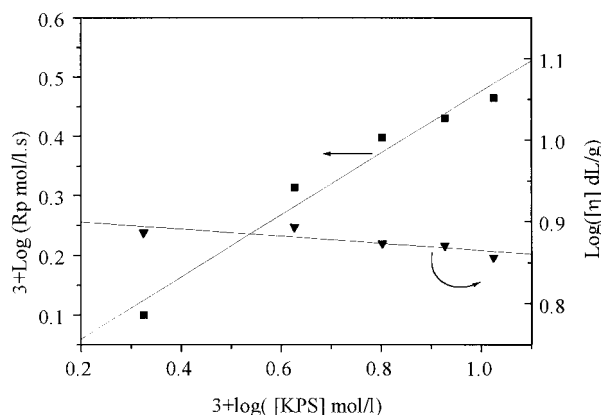


Figure 5 The effect of initiator concentration on polymerization: AM, 13.4 wt %; DMC, 4.4 wt %; kerosene, 26 wt %; Span80, 3 wt %; OP10, 1 wt %; H_2O , 52.2 wt %; T , 333 K.

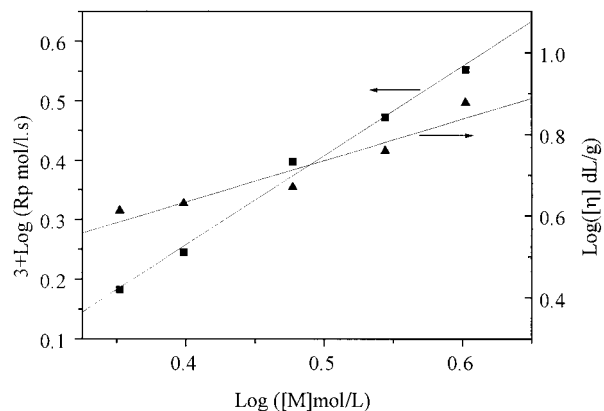


Figure 6 The effect of monomer concentration on polymerization: KPS, $6.342 \times 10^{-3} \text{ mol l s}^{-1}$; kerosene, 26 wt %; Span80, 3 wt %; OP10, 1 wt %; T , 333 K.

$\propto [M]^{1.50}$, $[\eta] \propto [M]^{1.02}$. The dependence of polymerization rate on monomer concentration is similar to the result found in solution polymerization. The kinetics thus conforms to the view that the polymerization occurs in the monomer solution droplets. The polymerization therefore may be justifiably termed microsuspension polymerization. The higher monomer order is due to the fact that the gel effect becomes more and more evident with the increase of monomer concentration. In addition, the donor–acceptor interaction takes place between the monomer and potassium persulfate in polar media.⁶ The monomer is chiefly initiated with radicals formed during the decomposition of the acrylamide–peroxide complex. Figure 6 also showed the relationship between the intrinsic viscosity of copolymer at almost 100% polymer conversion and the monomer concentration. It can be seen that $[\eta]$ of the copolymer increases as the monomer concentration increases.

Effect of Emulsifier Concentration

Figure 7 displays the effect of emulsifier concentration on polymerization. The overall polymerization rate increased with the increase of emulsifier content, as follows: $R_p \propto [E]^{0.38}$; $[\eta] \propto [E]^{-0.14}$. This result deviates from the classical Smith–Ewart Equation, as follows: $R_p \propto [E]^{0.6}$; $M_n \propto [E]^{0.6}$. The emulsifier's sole function was stabilization. In such cases, increasing the level of emulsifier would lower the surface tension and produce a large number of smaller particles. Since the total interfacial area would be larger, the capture efficiency of primary radicals would rise, and the rate would increase. The decrease of $[\eta]$ with increasing $[E]$ was due to the chain transfer to

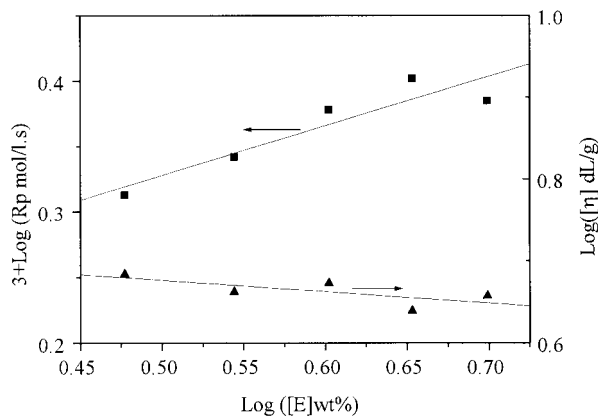


Figure 7 The effect of emulsifier content on polymerization: KPS, $6.342 \times 10^{-3} \text{ mol l s}^{-1}$; AM, 13.4 wt %; DMC, 4.4 wt %; H_2O , 52.2 wt %; T , 333 K.

emulsifier. This is verified experimentally over a broad range of emulsifier concentration.

Effects of Polymerization Temperature

The effects of temperature on the polymerization rate and polymer intrinsic viscosity were shown in Figure 8. According to Arrhenius Equation, the total activation energy of R_p and that of $[\eta]$ are 66.0 and -24.8 kJ mol , respectively. Although the relationship between $[\eta]$ of the copolymer and the polymerization temperature ($1/T$) is somewhat scattered, as seen in Figure 8; $[\eta]$ tends to decrease with increasing temperature. Also, the effect of temperature on the emulsion polymerization is in line with what one would expect for solution polymerization.

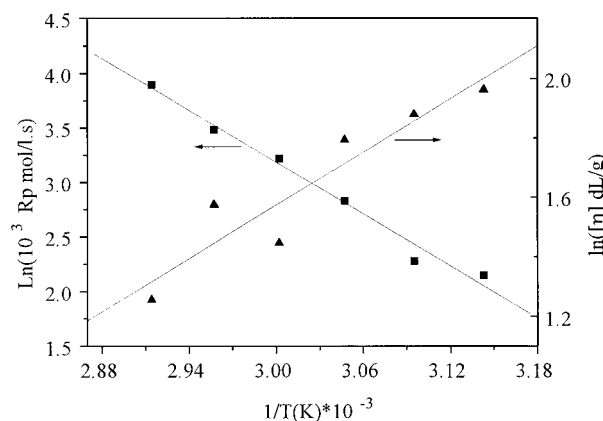


Figure 8 The effect of temperature on polymerization: KPS, $6.342 \times 10^{-3} \text{ mol l s}^{-1}$; AM, 13.4 wt %; DMC, 4.4 wt %; kerosene, 26 wt %; Span80, 3 wt %; OP10, 1 wt %; H_2O , 52.2 wt %.

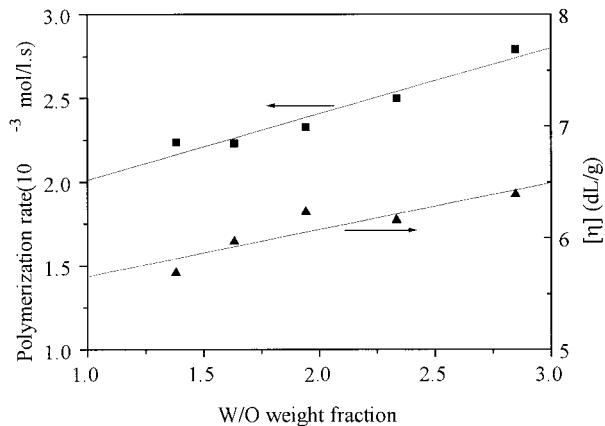


Figure 9 The effect of W/O ratio on polymerization: KPS, $6.342 \times 10^{-3} \text{ mol l s}^{-1}$; monomer concentration, 3 mol l; emulsifier content, 4 wt %; T , 333 K.

Effect of W/O Weight Ratio

The changes of polymerization rate and polymer intrinsic viscosity with aqueous weight fraction at constant emulsifier concentration are shown in Figure 9. Both the polymer intrinsic viscosity and the polymerization rate increase with the increase of aqueous weight fraction ϕ_w . A probable interpretation is that a decrease of aqueous weight fraction accompanied by decrease of monomer content in system is unfavorable to R_p and $[\eta]$, so the polymerization rate decreases with the decrease of ϕ_w almost proportionally.

Nucleation Mechanism Studies

It is expected that the polymerization proceeds by a monomer-droplet-nucleation mechanism, namely, in the compartmentalized monomer droplets independently. Firstly, the experiments were carried out using potassium persulfate as the initiator. In this case, the initiator, located in the disperse phase, will most probably initiate *in situ* the monomer without having to migrate through the interface. Thus, the polymerization is initiated in the monomer droplets. Secondly, the particle size is almost unchanged after polymerization. If the polymer particles nucleate from micelle as in classical emulsion, the final particles should be much smaller than the monomer droplet. Thirdly, the polymerization rate and polymer intrinsic viscosity both increase with the water-oil fraction. This also supports that polymerization mostly occurs in the aqueous monomer droplets. In addition, there is no evident constant rate region. It is also not consistent with the micellar nucleation mechanism. Lastly, the kinetic expression is given as $R_p \propto I^{0.52}[M]^{1.50}[E]^{0.38} \cdot [\eta]$

$\propto I^{-0.04}[M]^{1.02}[E]^{-0.14}$. There is a great difference between this result and the classical Smith–Ewart Equation.⁴ In summary, the particles nucleate in the monomer droplet instead of nucleating from micelle.

CONCLUSION

The specific features of the inverse emulsion copolymerization of acrylamide with DMC using a blend of emulsifiers and water-soluble initiator have been studied. No apparent change between the initial emulsion droplet size and polymer latex particle size was observed. In general, the conversion–time curves are S-shaped due to the gel effect. The increase in molecular weight with conversion is also indicative of the existence of the gel effect. Furthermore, it is clearly evidenced that polymerization occurs mostly in the aqueous monomer droplets, regardless of the various con-

ditions. In order to synthesize model hydrosoluble copolymers, additional work is needed to study several other kinetic features, such as the polymerization rate or the degree of polymerization as a function of the ionic monomer content, pH, and type of process.

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