Ampholytic Terpolymers of Acrylamide with Sodium Acrylate and (2-Methacryloyloxyethyl)trimethylammonium Chloride. Synthesis with ^{60}Co γ-Ray and Polymerization Kinetics

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ABSTRACT: A new terpolymer of acrylamide with sodium acrylate and (2-methacryloyloxyethyl)trimethylammonium chloride initiated with ^{60}Co γ-ray was prepared in inverse emulsion. Polymerization conversion was studied dilatometrically and molecular weight was determined viscometrically. The effects of dose rate, monomer concentration, emulsifier content, temperature, etc. on the polymerization rate or conversion and the molecular weight of polymer were examined. The rate of polymerization (Rp) can be represented by $Rp \propto D^{1.03}[M]^{0.69}[E]^{-0.02}$. The overall activation energy for the rate of polymerization is $12.90\,\text{kJ}\,\text{mol}^{-1}$ (33—56°C). Based on these experimental results, aspects of the polymerization mechanisms are discussed.
KEY WORDS Ampholytic Terpolymer / Radiation Polymerization / Inverse Emulsion / Water-Soluble Polymers / Acrylamide /

Inverse emulsion polymerization of water-soluble monomers, like conventional emulsion polymerization, is a unique method to increase the polymerization rate and molecular weight simultaneously. Since Vanderhoff's first report on inverse polymerization in 1962,[1] research in this area is becoming more and more active. Studies on fundamental theories are receiving increased attention.

Acrylamide based polyelectrolytes are of interest for a wide variety of industrial applications. Ampholytic copolymers represent a special class of polyelectrolytes which contain positive and negative charges along the macromolecular backbone. During the last 20 years, there has been increasing interest in water-soluble ampholytic copolymers because of potential applications, including enhanced oil recovery, drag reduction, absorbency, flocculants in water treatment. Several studies have been conducted on synthesis of aliphatic and aromatic sulphobetaine polyampholytes by incorporating positive and negative charges within the monomeric unit.[2-5] Some papers recently report the synthesis of ampholytic polymers including non-charged monomers for optimum viscosity behavior.[6]

In this article, the synthesis and polymerization kinetics of terpolymers of cationic {[(2-methacryloyloxyethyl)-trimethyl ammonium chloride] (DMC)}, anionic[sodium acrylate (NaAA)] and non-charged [acrylamide (AM)] monomers are studied in inverse emulsions with ^{60}Co γ-rays. Polymerization conversion was recorded by dilatometer and the molecular weight of polymer (M_w) was determined by viscometer. The influence of dose rate, monomer concentration, emulsifier content, temperature, etc. on the Rp and M_w were investigated.

EXPERIMENTAL

Materials

AM from Huibei Daxue Chemicals, Inc. (Huibei, China) was recrystallized from acetone. Technical grade DMC (Xing Yu Chemicals Co., Ltd., Wuxi, China) was used without further purification. Acrylic acid purchased from Shanghai Chemical Reagents Co. (China) was neutralized with NaOH. Market grade kerosene was washed first with concentrated H_2SO_4 and then with NaOH solution. SPAN80 and OP10 were used as purchased from Shanghai Chemical Reagents Co. (China). Other reagents were GR grade and used as received.

Preparation of Inverse Emulsion and Polymerization

Inverse emulsion was prepared by adding aqueous monomer solution to a kerosene-emulsifier mixture under stirring (2000 rpm). Purified nitrogen was bubbled through the emulsion at room temperature for about 15 min to remove oxygen.

The emulsion was directly fed into a dilatometer and held in a bath at temperature accurately controlled by a regulator, or fed into a sealed glass ampoule. The polymerization conversion was recorded as function of time, and the polymerization rate was gound by further differentiation.

Viscosity Measurement

After irradiation, the polymerization product was removed from the dilatometer or the glass ampoule at room temperature. The polymerized emulsion was precipitated and washed with acetone and dried in oven. The molecular weight of the polymer was determined in $1\,N$ $NaNO_3$ aqueous solution with Ubbelode capillary viscometer at 30°C. The average molecular weight was calculated with the Mark–Houwink relation: $[\eta] = 3.37 \times 10^{-4} M_w^{0.66}$.[7]

RESULTS AND DISCUSSION

Variation of Polymerization Rate with Conversion

Figure 1 shows generally S-shaped typical conversion–time curves. The curve could be reproduced with measurement error below 3%. An induction period caused by residual O_2 in the system is normally observed at
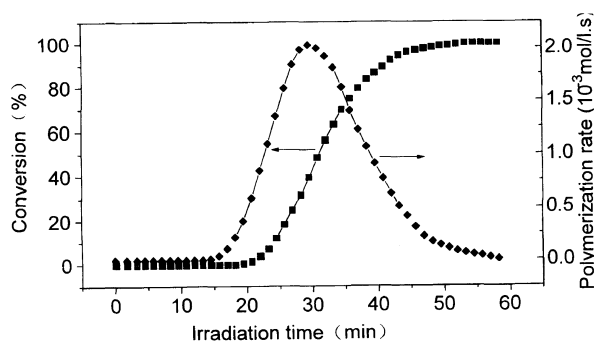
Figure 1. Conversion *versus* irradiation time curve and polymerization rate *versus* irradiation time curve. Dose rate, 11.66 Gy min^{-1}; AM, 12 wt%; DMC, 2 wt%; NaAA, 2.6 wt%; Kerosene, 21 wt%; SPAN80, 3 wt%; OP10, 1 wt%; T, 311 K.
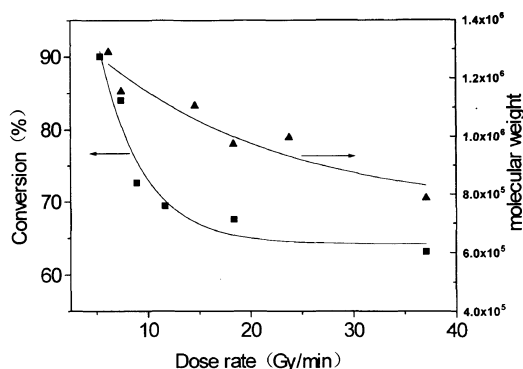

Figure 2. Effects of irradiation dose rate on polymerization. Absorbed dose, 600 Gy; AM, 12 wt%; DMC, 2 wt%; NaAA, 2.6 wt%; Kerosene, 21 wt%; SPAN80, 3 wt%; OP10, 1 wt%; T, ambient temperature.
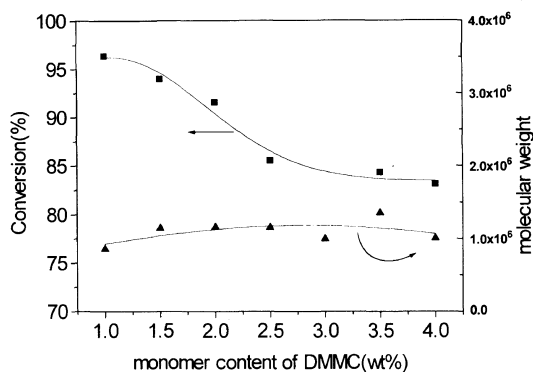

Figure 3. Effects of comonomer composition on polymerization. Dose rate, 11.66 Gy min^{-1}; total dose, 700 Gy, total monomer content, 16.6 wt%; AM, 12 wt%; Kerosene, 21 wt%; SPAN80, 3 wt%; OP10, 1.0 wt%; T, ambient temperature.

3—30 min depending mainly on the dose rate. The influence of the gel effect is evident in the conversion *versus* time curves. The linear portions of the curves extend to very high conversion levels (~45—60%) showing no constant-rate-region typical for conventional emulsion polymerization.[8] Under normal conditions, Rp would have decreased with increasing conversion due to decreasing [M] at about 10% conversion. However, in the present case, this decrease fortuitously compensated for by the gel effect up to a very high conversion level. The initial rate of polymerization for a given run cannot be reproduced with satisfactory accuracy because of the induction period. The maximum reaction rate given by the slope of the linear part of the conversion–time curve was thus taken for determination of kinetic relations.

Effects of Irradiation Dose Rate at Fixed Absorbed Dose

Figure 2 shows plots of polymerization conversion and polymer molecular weight against irradiation dose rate, in polymerization at a constant absorbed dose. Polymer molecular weight decreased with increasing dose rate, as in solution polymerization. Based on the basic law of radical reaction, the concentration of radical reactive center increases with the dose rate, polymer molecular weight decreases accordingly.

Effects of Comonomer Composition

The effects of comonomer composition on polymerization conversion and molecular weight of the copolymers are shown in Figure 3. Molecular weight of the copolymer was fairly insensitive to comonomer composition of DMC : NaAA in the feed. Polymerization conversion decreased with increasing composition of the ratio in the feed.

Terpolymer composition for DMC-NaAA-AM was calculated from elemental analysis for carbon, hydrogen and nitrogen. Terpolymer feed and compositional data are illustrated in Table I. Monomer reactivity ratio of DMC was much larger than that of NaAA.

Optional Polymerization Conditions

Based on experimental data, optional conditions for polymerization are : Absorbed dose = 450—550 Gy; Dose rate = 0.1—20 Gy min^{-1}; monomer composition (AM : DMC : NaAA) = 12 : 1.0 : 3.6—12 : 2.5 : 2.1.

Polymerization Kinetics

Effects of Absorbed Dose Rate. Figure 4 shows percentage conversion *versus* time curves at different absorbed dose rate. Figure 5 displays the correlation of the dose rate with Rp and M_w of the polymer as : $Rp \propto D^{1.03}$, $M_w \propto D^{-0.32}$. The monomers presumably

Table I. Composition studies of terpolymer elemental analysis

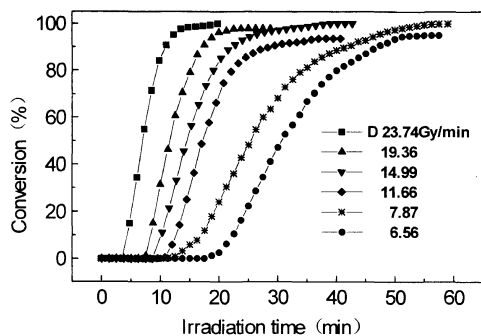| Sample number	Feed composition AM : DMC : NaAA wt%	Elemental analysis data C : H : N wt%	Terpolymer AM : DMC : NaAA wt%
Sample 1	69.36 : 23.12 : 7.51	48.06 : 7.03 : 13.89	63.41 : 30.32 : 6.27
Sample 2	72.29 : 12.05 : 15.66	47.20 : 6.68 : 13.98	67.14 : 21.44 : 11.42
Sample 3	71.01 : 5.92 : 23.07	50.02 : 6.95 : 15.55	72.81 : 14.53 : 12.66

Figure 4. Conversion *versus* irradiation time at different dose rates. AM, 12 wt%; DMC, 2 wt%; NaAA, 2.6 wt%; Kerosene, 21 wt%; SPAN80, 3 wt%; OP10, 1 wt%; T, 318.4 K.
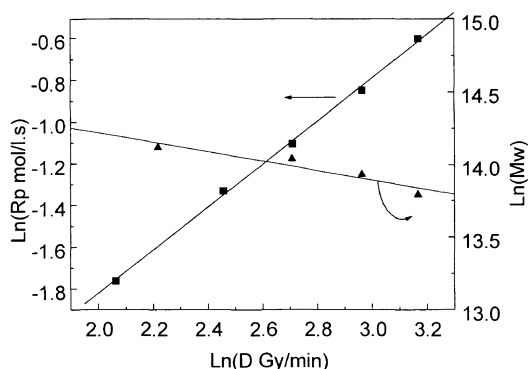

Figure 5. Effects of dose rate on polymerization. AM, 12 wt%; DMC, 2 wt%; NaAA, 2.6 wt%; Kerosene, 21 wt%; SPAN80, 3 wt%; OP10, 1 wt%; T, 318.4 K.

polymerize mainly *via* radical mechanism, and thus termination reaction of two propagating polymer radicals was depressed because of decrease in mobility at higher viscosity. Clearly, traditional one-half order dependence is not observed. In general, unimolecular termination involves reaction of polymeric radical with monomer or emulsifier, as confirmed by previous investigation of inverse-microsupensions[9] with water-soluble initiators, where transfer to stearic and oleic acid portions on emulsifier is rate-controlling. Molecular weight of the polymer decreases with increasing dose rate as shown in Figure 5.

Effects of Monomer Concentration. The dependence of polymerization rate on monomer concentration is shown in Figures 6 and 7. The order: $Rp \propto [M]^{0.69}$, $M_w \propto [M]^{0.63}$, was less than for conventional radical polymerization and inverse emulsion polymerization of one and half. This is likely due to shielding of ionic charges along the polymer chain resulting in disruption of positive-negative charge attractions.

Effects of Emulsifier Content. Figure 8 shows conversion–time curves at various emulsifier content. The effects of this content on polymerization kinetics are indicated in Figure 9 as: $Rp \propto [E]^{-0.02}$, $M_w \propto [E]^{-0.85}$. Increase in the bulk level of emulsifier causes interfacial and organic-phase concentrations to rise. There is initially lower surface tension, to produce smaller particles and slightly faster rate. But, these effects are small compared to the decrease in rate caused by consumption of primary radicals and oligoradicals due to additional soluble emulsifier. The decrease of M_w with
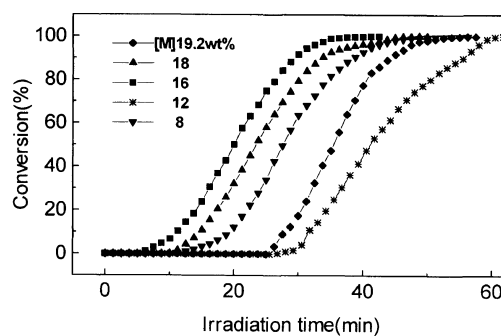
Figure 6. Conversion *versus* irradiation time curves at different monomer contents. Dose rate 11.66 Gy min^{-1}; monomer composition (AM : DMC : NaAA) 12 : 2.0 : 2.6 (wt%); Kerosene, 21 wt%; SPAN80, 3 wt%; OP10, 1 wt%; T, 306 K.
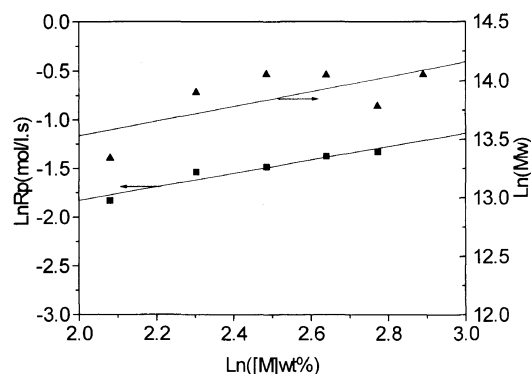

Figure 7. Effects of monomer content on polymerization. Dose rate, 11.66 Gy min^{-1}; monomer composition (AM : DMC : NaAA) 12 : 2.0 : 2.6 (wt%); Kerosene, 21 wt%; SPAN80, 3 wt%; OP10, 1 wt%; T, 306 K.
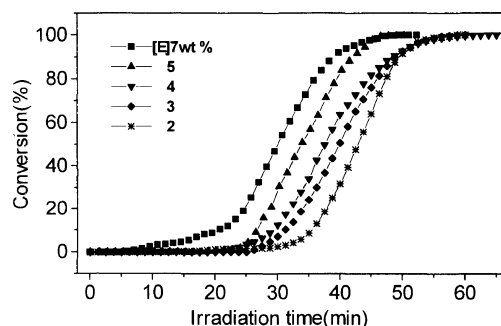

Figure 8. Conversion *versus* irradiation time curves at different emulsifier content. Dose rate, 11.66 Gy min^{-1}; AM, 12 wt%; DMC, 2 wt%; NaAA, 2.6 wt%; emulsifier composition (Span80 : Op10) 3 : 1; Kerosene, 21 wt%; T, 328 K.
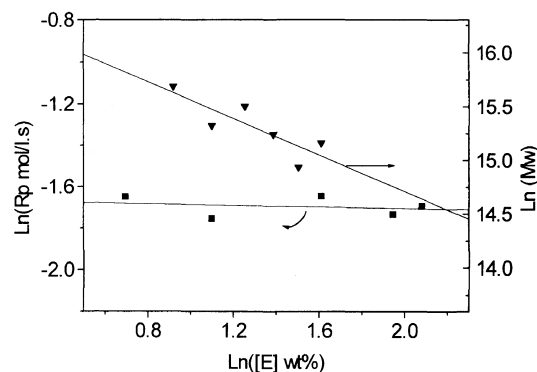

Figure 9. Effects of emulsifier content on polymerization. AM, 12 wt%; DMC, 2 wt%; NaAA, 2.6 wt%; Dose rate, 11.66 Gy min^{-1}; emulsifier composition (Span80 : Op10) 3 : 1; Kerosene, 21 wt%; T, 328 K.
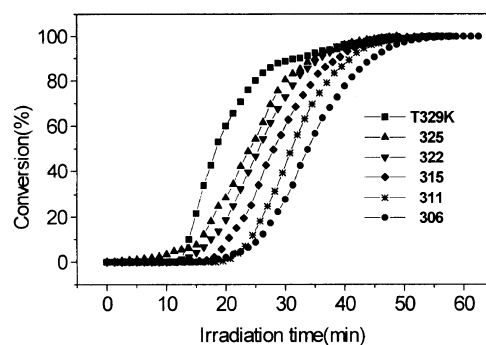
Figure 10. Conversion *versus* time at different temperature. AM, 12 wt%; DMC, 2 wt%; NaAA, 2.6 wt%; Dose rate, 11.66 Gy min⁻¹; Kerosene, 21 wt%; SPAN80, 3 wt%; OP10, 1 wt%.
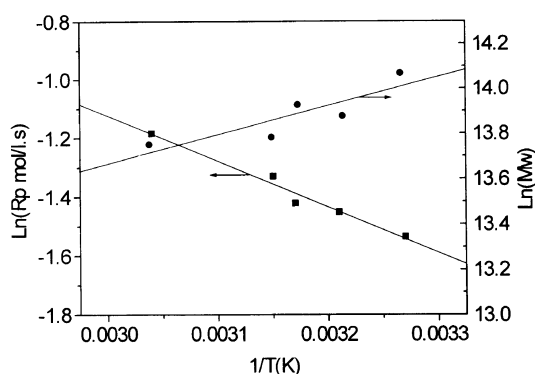

Figure 11. Effects of temperature on polymerization. AM, 12 wt%; DMC, 2 wt%; NaAA, 2.6 wt%; Dose rate, 11.66 Gy min⁻¹; Kerosene, 21 wt%; SPAN80, 3 wt%; OP10, 1 wt%.

increasing [E] is due to chain transfer to emulsifier.

Effects of Polymerization Temperature. Figures 10 and 11 show the effects of polymerization temperature on polymerization. According to the Arrhenius Equation, apparent activation energy of Rp and M_w are 12.90 and $-10.70\,\text{kJ}\,\text{mol}^{-1}$, respectively. These values are much less than that initiated by free radical initiator at high temperature. With increase in temperature, Rp increases

and M_w decreases, in agreement with solution polymerization kinetics.

CONCLUSION

Specific features of the inverse emulsion copolymerization of AM with DMC and NaAA using a blend of emulsifiers were studied. Conversion–time curves are generally S-shaped. There is no evident constant-rate-region typical of conventional emulsion polymerization. The rate of polymerization (Rp) can be represented by $Rp \propto D^{1.03}[M]^{0.69}[E]^{-0.02}$. The overall activation energy for the rate of polymerization is $12.90\,\text{kJ}\,\text{mol}^{-1}$ (33—56°C). The polymerization rate increases with dose rate, monomer concentration and raise in temperature, and is insensitive to emulsifier content. The molecular weight of the polymer increase with monomer concentration, and decrease in dose rate, emulsifier content and temperature. To synthesize a model hydro-soluble ampholytic polymer, additional work is needed to study several kinetic features such as the polymerization rate and degree of polymerization as function of electrolyte, pH, oil/water phase ratio and type of process.

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