Vinyl Polymerization by a Copper(II) Complex

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ABSTRACT: The kinetics of the polymerization of acrylamide and methacrylamide initiated by bis[2-((2-hydroxyethyl)amino)ethoxo]copper(II) in aqueous solution at pH=1.8 was studied at 45°C. The rate of polymerization was followed gravimetrically, and the chain lengths of the polymers were determined viscometrically. There was no polymerization at pH > 5. The rate of polymerization was found to be proportional to the [Monomer]^{1.0} and the [Initiator]^{0.5}. In the case of methacrylamide polymerization, the order with respect to initiator was found to be 0.4. The apparent activation energies for the polymerization reactions have been calculated to be -53.3 kJ mol⁻¹ and -38.1 kJ mol⁻¹ for acrylamide and methacrylamide respectively. A kinetic reaction scheme is proposed on the basis of the experimental data.

KEY WORDS Kinetics / Polymerization / Acrylamide / Methacrylamide / Bis[2-((2-hydroxyethyl)amino)ethoxo]Copper(II) / pH Dependence / Reaction Scheme / Chain Length /

The effect of metal complexes on polymerization reactions are very diverse depending on the type of metal ion, the associated ligand, the nature of the monomer and probably the medium in which the reaction is carried out. The polymerization of vinyl monomers initiated by copper(II) complexes has been reported.¹⁻⁹ Barton, *et al.*,¹⁰ reported that the aminoalcohol derivatives were the most effective bidentate ligand used for the polymerization of vinyl chloride in presence of a transition metal salt and a halogen containing compound. Recently, Barton and Vlckova¹¹ reported the polymerization of methyl methacrylate initiated by copper(II)—2-aminoethanol. In this paper, we present a systematic kinetic study of the polymerization of acrylamide and methacrylamide initiated by bis[2-((2-hydroxyethyl)amino)ethoxo]copper(II) in aqueous solution at 30—50°C.

EXPERIMENTAL

Preparation of the Complex

Bis [2-((2-hydroxyethyl)amino)ethoxo] copper(II) was prepared according to the method of Atre-

menko¹² and its purity was checked by spectrophotometry.¹³

Reagents

Perchloric acid (E. Merck, G. R., ca. 60-% HClO₄) was used to maintain the pH level. Acrylamide and methacrylamide were purified as reported previously.¹⁴

Kinetic Measurements

The polymerization experiments were carried out in a Pyrex test tube (20 cm × 4 cm) of 80-ml capacity fitted with an inlet and an outlet. A thermostatted monomer solution containing the calculated quantity of HClO₄ to maintain the pH of the reaction mixture at 1.8, was deaerated by bubbling oxygen-free nitrogen through the inlet tube for 30 min. The complex solution was then added through the outlet tube which was then closed with a stopper. There was no induction period and the steady state was attained in about 15 min. The rate of polymerization was studied gravimetrically by precipitation and weighing the polymer, which was isolated by pouring the reaction mixture into an excess of methanol. pH measurements were taken by an Elico pH meter

model L-10, provided with glass and calomel electrodes.

Chain Length Measurements

The polyacrylamide samples were dissolved in water, and precipitated by methanol. It was further purified by precipitation twice. After drying in vacuum, the viscosity of a series of aqueous solutions was measured in an Ubbelohde viscometer at $30^\circ \pm 0.05^\circ$ and the viscometric average molecular weight calculated¹⁵ from the equation

$$[\eta] = KM^\alpha$$

taking $K = 6.31 \times 10^{-5}$, where concentration is in g/100 ml and $\alpha = 0.8$.

RESULTS

The free radical nature of the reaction was inferred from the absence of any induction period in the deaerated system and the presence of a long induction period in the undeaerated system.

The effect of monomer concentration was studied over a 5-fold concentration range. The plot of R_p vs. $[M]$ was a straight line passing through the origin, indicating that the order with respect to monomer was unity, in the case of both acrylamide and methacrylamide (Figure 1).

Figure 1. Dependence of the rate of polymerization at 45°C on monomer concentration: (A), acrylamide; (B), methacrylamide; $[\text{Complex}] = 1.367 \times 10^{-3} \text{ M}$; $[\text{H}^+] = 2.8 \times 10^{-2} \text{ M}$.

The rate of polymerization was studied over a wide range of concentration of the complex, viz., 0.1367 to $2.734 \text{ mmol dm}^{-3}$ for acrylamide and methacrylamide. The rate of polymerization was found to increase with an increase in the initiator concentration. The order with respect to ini-

Figure 2. Dependence of the rate of polymerization at 45°C on initiator concentration: (A), acrylamide; (B), methacrylamide; $[\text{Acrylamide}] = 0.2132 \text{ M}$; $[\text{Methacrylamide}] = 0.3215 \text{ M}$; $[\text{H}^+] = 2.8 \times 10^{-2} \text{ M}$.

Figure 3. Arrhenius plot of $\log R_p$ vs. $1/T$: (A), acrylamide; (B), methacrylamide; $[\text{Acrylamide}] = 0.2132 \text{ M}$; $[\text{Methacrylamide}] = 0.3215 \text{ M}$; $[\text{Complex}] = 1.367 \times 10^{-3} \text{ M}$; $[\text{H}^+] = 2.8 \times 10^{-2} \text{ M}$.

tiator was 0.5 for acrylamide and 0.4 for methacrylamide (Figure 2).

The rate of polymerization was found to decrease with an increase in temperature. A plot of the logarithmic rate of polymerization against the reciprocal of the absolute temperature (Figure 3) in the range 30–50°C gave $-53.3 \text{ kJ mol}^{-1}$ for the overall activation energy in the case of acrylamide and $-38.1 \text{ kJ mol}^{-1}$ in the case of methacrylamide.

It was observed that polymerization took place at $\text{pH} < 5$; however, above $\text{pH} = 5$, there was no polymerization at all. The rate of polymerization was proportional to $[\text{H}^+]^{0.6}$ in the case of acrylamide and $[\text{H}^+]^{0.67}$ in the case of methacrylamide (Figure 4).

Figure 4. Effect of H^+ concentration on the rate of polymerization at 45°C: (A), acrylamide; (B), methacrylamide; [Acrylamide] = 0.2132 M; [Methacrylamide] = 0.3215 M; [Complex] = 1.367×10^{-3} M.

DISCUSSION

Effect of Monomer Concentration

The first order dependence of the rate of polymerization on monomer concentration precludes the possibility of the monomer participation in the initiation of polymerization.

Effect of Initiator Concentration

The initiator exponent for methacrylamide polymerization is less than 0.5 which is due also to

the termination by primary radicals; and this mode, if used exclusive, would lead to an expression for the rate of polymerization independent of the initiator concentration. Similar observations were made by Venkatarao and Santappa¹⁶ in the uranyl ion sensitized polymerization of methacrylamide.

Effect of Temperature

The diffusion of primary radicals in solution is more difficult than in the gas phase and this phenomenon is referred to as the Frank—Rabinowitch effect or Cage effect.¹⁷ As the temperature is increased, the cage effect becomes less pronounced and the primary radicals can increasingly take part in termination reactions thus reducing the overall rate of the reaction with increase of temperature.

In the equation¹⁹

$$\ln R_p = \ln A_p (A_d/A_t)^{1/2} + \ln f [\text{I}]^{1/2} [\text{M}] - \frac{E_R}{RT}$$

it must be remembered that the frequency factor is not necessarily independent of temperature. The term includes kT/h and also the partition functions for the reactants and activated complex. In this particular system, the termination increases with temperature and hence the entropy term must play a major role in the kinetics. With an increase in termination, a large decrease in entropy appears to result as the polyacrylamide and polymethacrylamide radicals combine either mutually or with the primary radical to give polymer molecules of increasing order.

The theory of high frequency factors has been considered by Steel and Laidler¹⁸ in some detail; they relate these to the high entropies of activated complexes. These high entropies may arise from the looseness of certain vibrations in the activated state. This can be visualized as the different types of rocking, bending, and torsional motions in the simple case of two methyl radicals formed by the dissociation of an ethane molecule. Since the carbon—carbon bond is greatly extended, there is little restoring force of the displacements of the methyl radicals and the motions such as the rocking motion may occur with a very low frequency. This effect may also be described in another way: the radicals rotate freely in the activated state.

Kinetic Scheme

The following kinetic scheme appears to explain most of the experimental results.

At pH 1.8, the complex decomposes to give a hydrated species and the radical $(C_2H_4OH)_2\dot{N}H$ which adds to the monomer and initiates the polymerization.

Radical Production

where DEA is diethanolamine[bis(2-hydroxyethyl)-amine]. Polymerization by the diethanolamine radical has been postulated by us in the sodium bisdiethanolamine cobaltate initiated polymerization of acrylamide and methacrylamide.¹⁴

Initiation

M = monomer.

Propagation

Termination

Assuming stationary state kinetics for $(C_2H_4OH)_2\dot{N}H$ and $M_n^\bullet$ and termination by mutual combination, the rate expression is derived as

$$R_p = k_p (k_r/k_{t1})^{1/2} [H^+]^{1/2} [I]^{1/2} [M] \quad (5)$$

This rate expression fits the experimental data. The same rate expression is obtained by assuming termination by disproportionation (eq 4e).

Chain Lengths

On the basis of mutual termination, the ex-

pression for kinetic chain length is,

$$\nu = k_p \frac{[M]}{(k_{t1} \cdot k_r)^{1/2} [H^+]^{1/2} [I]^{1/2}} \quad (6)$$

It was observed that the chain lengths were proportional to $[I]^{-1/2}$ and $[M]$ as required by eq 6. Chain length measurements at different temperatures reveal the novel and interesting feature that the chain length increases with temperature (Figure 5). This proves that with an increase in temperature, the reaction is accompanied by a large decrease in entropy through the combination of polyacrylamide and polymethacrylamide radicals to give polymer molecules with greater order.

Figure 5. Variation of chain length of polyacrylamide with monomer concentration, initiator concentration, and temperature: ○, plot of $\log n$ vs. $1 + \log M$; △, plot of $\log n$ vs. $4 + \log I$; □, plot of $\log n$ vs. $\log t$.

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