THE KINETICS OF RADICAL COPOOLYMERIZATION OF ACRYLONITRILE AND METHYLACRYLATE WITH HEXADECYLTRIMETHYLLAMMONIUM BROMIDE AS A PHASE-TRANSFER CATALYST

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Abstract – The phase-transfer radical copolymerization of acrylonitrile and methacrylate with hexadecyltrimethyl ammonium bromide was investigated in (NH₄)₂S₂O₈ aqueous-organic two-phase system at 55°C and under nitrogen atmosphere. The rate of copolymerization was expressed in terms of quaternary ammonium ion and peroxodisulfate ion in the aqueous phase rather than the fed concentrations of HTAB and (NH₄)₂S₂O₈. The observed initial rate of copolymerization was used to analyze the copolymerization mechanism with a cyclic phase-transfer initiation step.

Key words: Phase-Transfer Catalyst, Copolymerization, Acrylonitrile, Methacrylate

INTRODUCTION

The use of phase-transfer catalysts (PTC) to accelerate the rate of two-phase reactions by bringing together chemical reactions which generally do not have a common solvent has become common practice in recent years [Starks and Liotta, 1978]. A wide variety of reactions such as anion displacement reactions, alkylation, acrylation, oxidation, reduction, elimination, and hydrolysis could be successfully accelerated by using phase-transfer catalysts.

As for the applications of polymerization reactions, they have been employed in condensation polymerization [Yamazaki and Imai, 1983], and anionic polymerization [Yamada et al., 1976; Reetz and Ostarek, 1988]. Recently, several authors [Rasmussen and Smith, 1981; Jayakrishnan and Shah, 1983, 1984; Shimada et al., 1991; Bulacovski and Mihailauscu, 1991; Park et al., 1993a, b, 1995a, b, 1996a, b] reported the use of PTC for free-radical polymerization of hydrophobic vinyl monomers in aqueous-organic two-phase. In most cases of polymerization reaction, peroxydisulfate was used as a water soluble initiator with a PTC such as crown ether or quaternary ammonium salts. They demonstrated the superior efficiency of PTC for polymerization of vinyl monomers as compared to initiators such as AIBN or peroxide.

In view of the fact that the circumstances of reaction condition in a heterogeneous reaction such as phase-transfer catalyzed reaction are different from those in a homogeneous reaction, it was considered worthwhile to investigate the kinetics of phase-transfer catalyzed reaction together with the mechanism of mass transfer with chemical reaction, that is, the diffusion effect of solutes across the interface of the heterogeneous phases.

The present paper is concerned with kinetic studies on radical copolymerization of acrylonitrile (AN) and methacrylate (MA) with ammonium peroxydisulfate as initiator and hexadecyltrimethylammonium bromide (HTAB or QBr) as a PTC in toluene/water two-phase system.

THEORY

Fig. 1 presents the reactions characterizing the copolymerization of AN(M₁) and MA(M₂) initiated by (NH₄)₂S₂O₈/HTAB in toluene/water two-phase systems. It is assumed that dissociation of QBr and (NH₄)₂S₂O₈ formation of Q₂S₂O₈ in aqueous phase, dissociation of Q₂S₂O₈ transferred into organic phase from aqueous phase and initiation of monomers in organic phase occur along the reactions such as Eqs. (1)-(5).

The equilibrium constants in reaction (1)-(3) and distribution constants of QBr and Q₂S₂O₈ are defined as follows, respectively,

\[ K_1 = \frac{[O']_w[Br']_w}{[Q'O']_w} \]  \hspace{1cm} (6)
\[ K_2 = \frac{[NH_4']_w[S_2O_8^{2-}]_w}{([NH_4])_w[S_2O_8^{2-}]_w} \]  \hspace{1cm} (7)
\[ K_3 = \frac{[Q'Br]_w}{[QBr]_w} \]  \hspace{1cm} (8)
\[ \alpha_1 = \frac{[Q'O']_w}{[O']_w} \]  \hspace{1cm} (9)
\[ \alpha_2 = \frac{[Q'Br]_w}{[QBr]_w} \]  \hspace{1cm} (10)

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Formation rate ($r_i$) of a $SO_4^{2-}$ in Eq. (4) may be represented as [Park et al., 1996a]

$$r_i = -\frac{d[SO_4^{2-}]}{dt} = 2k_1k_2[Q]_{w}^{\frac{1}{2}}[S_2O_5^{-}]_{w}$$

(11)

The growth of polymer molecules by successive addition of monomers according to reaction (5) to the radicals, $M_1^+$ and $M_2^+$, and to their successors may be represented by

$$M_1^+ + M_1 \rightarrow_{k_{11}} M_1 M_1^+$$

$$M_1^+ + M_1 \rightarrow_{k_{21}} M_1 M_2^+$$

$$M_2^+ + M_1 \rightarrow_{k_{21}} M_2 M_1$$

$$M_2^+ + M_2 \rightarrow_{k_{22}} M_2 M_2$$

(12)

The reaction rates in Eq. (12) are written for each propagation step under the assumption that the radical reactivity is independent of the chain length [Flory, 1953].

The rate of propagation steps in reaction (12) are

$$r_{p_1} = -\frac{d[M_1]}{dt} = k_{11}[M_1^+][M_1] + k_{21}[M_2^+][M_1]$$

(13)

$$r_{p_2} = -\frac{d[M_2]}{dt} = k_{22}[M_2^+][M_2] + k_{12}[M_1^+][M_2]$$

(14)

In general, termination of polymer is dependent on the forms of radicals. Because AN is terminated by coupling and MA by disproportionation [Seymour and Carrber, 1981], the rate of chain termination for AN and MA may be written, respectively,

$$r_{t_1} = k_{11}[M_1]^{2}$$

(15)

$$r_{t_2} = 2k_{22}[M_2]^{2}$$

(16)

Using Eq. (11), (15) and (16) at steady state, the initial rate of polymerization of Eq. (13) and (14) may be written

$$r_m = \frac{\left(\begin{matrix} k_{11} \\ k_{21} \end{matrix}\right)^{\frac{1}{2}} + \frac{2f_kk_3}{\alpha_2} \left(\begin{matrix} k_{12} \\ k_{22} \end{matrix}\right)^{\frac{1}{2}}}{[Q]_{w}^{\frac{1}{2}}[S_2O_5^{-}]_{w}^{\frac{1}{2}}[M_1]_{o}^{\frac{1}{2}}[M_2]_{o}^{\frac{1}{2}}}$$

(17)

$$r_m = \frac{\left(\frac{2f_k}{k_{22}} \right)^{\frac{1}{2}} + \frac{2f_kk_3}{\alpha_2} \left(\frac{k_{12}}{k_{22}} \right)^{\frac{1}{2}}}{[Q]_{w}^{\frac{1}{2}}[S_2O_5^{-}]_{w}^{\frac{1}{2}}[M_1]_{o}^{\frac{1}{2}}[M_2]_{o}^{\frac{1}{2}}}$$

(18)

where, $[M_1]_{o}$ and $[M_2]_{o}$ are the initial concentration of monomer, $M_1$ and $M_2$, respectively.

Adding Eq. (17) to (18), and taking concentration of $Q^*$ as total concentration by mass balance of species, $Q$, the total initial rate of polymerization may be written,

$$r_m = \gamma(b_1f_1 + b_2)$$

(19)

where,

$$f_1 = \frac{[M_1]_{o}}{[M_2]_{o}}$$

(20)

$$b_1 = \left[\frac{k_{11}}{k_{12}}\right]^{\frac{1}{2}} + \left[\frac{2f_kk_3}{\alpha_2} \left(\frac{k_{12}}{k_{22}} \right)^{\frac{1}{2}}\right]^{\frac{1}{2}}[M_1]_{o}^{\frac{1}{2}}[M_2]_{o}^{\frac{1}{2}}$$

(21)

$$b_2 = \left[\frac{k_{11}}{2k_{12}}\right]^{\frac{1}{2}} + \left[\frac{2f_k}{k_{22}} \left(\frac{k_{22}}{k_{12}} \right)^{\frac{1}{2}}\right]^{\frac{1}{2}}[M_1]_{o}^{\frac{1}{2}}[M_2]_{o}^{\frac{1}{2}}$$

(22)

$$\gamma = \frac{[Q]_{w}^{\frac{1}{2}}[S_2O_5^{-}]_{w}^{\frac{1}{2}}}{1 + \frac{[Q]_{w}^{\frac{1}{2}}}{K_1} + k_5[Q]_{w}^{\frac{1}{2}}[S_2O_5^{-}]_{w}^{\frac{1}{2}}}$$

(23)

Using reaction (12), the rate of copolymerization of AN and MA at steady state may be written

$$r_{peo} = k_{21}[M_2]_{o}^{\frac{1}{2}}[M_1]_{o}^{\frac{1}{2}} + k_{12}[M_1]_{o}^{\frac{1}{2}}[M_2]_{o}^{\frac{1}{2}}$$

(24)

The rate of copolymerization of AN and MA may be derived as Eq. (25) from Eq. (24) by using the procedures as similar as those for derivation of total rate of polymerization.

$$r_{peo} = F_{co} \gamma[M_1]_{o}$$

(25)

$$F_{co} = \left[\frac{2f_kk_3}{\alpha_2} \left(\frac{k_{22}}{k_{12}} \right)^{\frac{1}{2}}\right]^{\frac{1}{2}} + \frac{2f_kk_3}{\alpha_2} \left(\frac{k_{22}}{k_{12}} \right)^{\frac{1}{2}}[M_1]_{o}^{\frac{1}{2}}[M_2]_{o}^{\frac{1}{2}}$$

(26)

$$\gamma = \frac{[Q]_{w}^{\frac{1}{2}}[S_2O_5^{-}]_{w}^{\frac{1}{2}}}{1 + [Q]_{w}^{\frac{1}{2}} + K_6[Q]_{w}^{\frac{1}{2}}[S_2O_5^{-}]_{w}^{\frac{1}{2}}}$$

(27)

where, $[Q]_{w}^{\frac{1}{2}} = [Q]_{w} + [QBr]_{w} + [Q_2S_2O_5^{-}]_{w}$

(28)

EXPERIMENTAL

AN (Junsei Chem. Co.) and MA (Junsei Chem. Co.) were purified by the vacuum distillation method. HTAB (Aldrich Chem. Co.) was used without further purification. All other