THE KINETICS OF RADICAL COPOLYMERIZATION OF ACRYLONITRILE AND METHYLACRYLATE WITH HEXADECYLTRIMETHYLAMMONIUM BROMIDE AS A PHASE-TRANSFER CATALYST

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Abstract – The phase-transfer radical copolymerization of acrylonitrile and methylacrylate with hexadecyltrimethyl ammonium bromide was investigated in $(NH_4)_2S_2O_8$ 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 peroxydisulfate ion in the aqueous phase rather than the fed concentrations of HTAB and $(NH_4)_2S_2O_8$. The observed initial rate of co-polymerization was used to analyze the copolymerization mechanism with a cyclic phase-transfer initiation step.

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

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; Bulacovschi and Mihailescu, 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 dif-fusion 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 methylacrylate (MA) with ammonium peroxydisulfate as initiator and hex-adecyltrimethylammonium bromide (HTAB or QBr) as a PTC in toluene/water two-phase system.

THEORY

Fig. 1 presents the reactions characterizing the copolymerization of $AN(M_1)$ and $MA(M_2)$ initiated by $(NH_4)_2S_2O_4$/HTAB in toluene/water two-phase systems. It is assumed that dissociation of QBr and $(NH_4)_2S_2O_8$, formation of $Q_2S_2O_8$ in aqueous phase, dissociation of $Q_2S_2O_8$ transfered 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 $Q_2S_2O_8$ are defined as follows, respectively,

$$K_1 = \frac{[Q^+]_w [Br^-]_w}{[Q^+Br^-]_w} \tag{6}$$

$$K_2 = \frac{[NH_4^+]_w^2 [S_2O_8^{-2}]_w}{[(NH_4)_2S_2O_8]_w} \tag{7}$$

$$K_3 = \frac{[Q_2S_2O_8]_w}{[Q^+]_w^2[S_2O_8^{-2}]_w} \tag{8}$$

$$\alpha_1 = \frac{[Q^+Br^-]_w}{[QBr]_o} \tag{9}$$

$$\alpha_2 = \frac{[Q_2^+S_2O_8^{-2}]_w}{[Q_2S_2O_8]_o} \tag{10}$$

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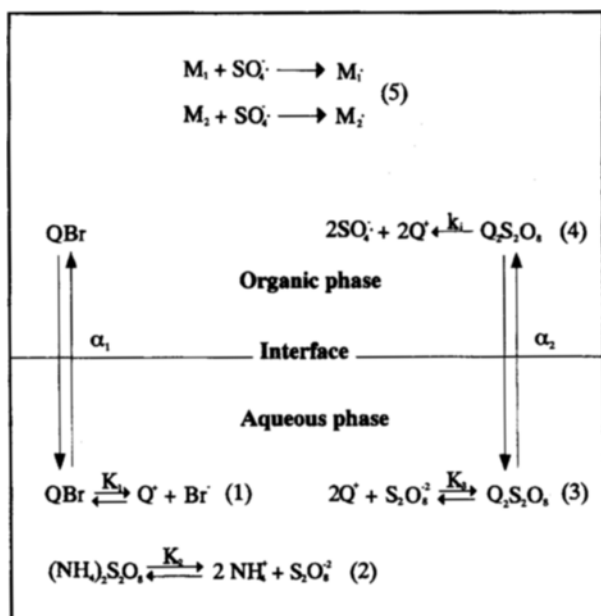E-mail : swparkφ@hyowon.pusan.ac.kr

Fig. 1. Polymerization path with phase-transfer catalyst in an aqueous-organic two-phase system.

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

$$r_i = \frac{d[SO_4^-]}{dt} = 2k_i fK_3 [Q^+]_w^2 [S_2O_8^{-2}]_w \tag{11}$$

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

$$M_1 \cdot + M_1 \xrightarrow{k_{11}} \sim M_1 \cdot$$
$$M_1 \cdot + M_2 \xrightarrow{k_{12}} \sim M_2 \cdot$$
$$M_2 \cdot + M_1 \xrightarrow{k_{21}} \sim M_1 \cdot$$
$$M_2 \cdot + M_2 \xrightarrow{k_{22}} \sim M_2 \cdot \tag{12}$$

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

$$r_{p1} = -\frac{d[M_1]}{dt} = k_{11}[M_1 \cdot][M_1] + k_{21}[M_2 \cdot][M_1] \tag{13}$$

$$r_{p2} = -\frac{d[M_2]}{dt} = k_{22}[M_2 \cdot][M_2] + k_{12}[M_1 \cdot][M_2] \tag{14}$$

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,

$$r_{t1} = k_{t1}[M_1 \cdot]^2 \tag{15}$$

$$r_{t2} = 2k_{t2}[M_2 \cdot]^2 \tag{16}$$

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

$$r_{p1} = \left[\left(\frac{k_{11}^2}{k_{t1}} \right)^{1/2} + \left(\frac{k_{21}^2}{2k_{t2}} \right)^{1/2} \right] \left(\frac{2fk_iK_3}{\alpha_2} \right)^{1/2}$$
$$[Q^+]_w [S_2O_8^{-2}]_w^{1/2} [M_1]_\phi \tag{17}$$

$$r_{p2} = \left[\left(\frac{k_{22}^2}{2k_{t2}} \right)^{1/2} + \left(\frac{k_{12}^2}{k_{t1}} \right)^{1/2} \right] \left(\frac{2fk_iK_3}{\alpha_2} \right)^{1/2}$$
$$[Q^+]_w [S_2O_8^{-2}]_w^{1/2} [M_2]_\phi \tag{18}$$

where, $[M_1]_\phi$ and $[M_2]_\phi$ ar 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,

$$r_{pt} = \gamma(b_1 f_1 + b_2) \tag{19}$$

where,

$$f_1 = [M_1]_\phi / [M_2]_\phi \tag{20}$$

$$b_1 = \left[\left(\frac{k_{11}^2}{k_{t1}} \right)^{\frac{1}{2}} + \left(\frac{2k_{21}^2}{k_{t2}} \right)^{\frac{1}{2}} \right] \left(\frac{2fk_iK_3}{\alpha_2} \right)^{\frac{1}{2}} [M_2]_\phi \tag{21}$$

$$b_2 = \left[\left(\frac{k_{22}^2}{2k_{t2}} \right)^{\frac{1}{2}} + \left(\frac{k_{12}^2}{k_{t1}} \right)^{\frac{1}{2}} \right] \left(\frac{2fk_iK_3}{\alpha_2} \right)^{\frac{1}{2}} [M_2]_\phi \tag{22}$$

$$\gamma = \frac{[Q^+]_w^T [S_2O_8^{-2}]_w^{1/2}}{1 + \frac{[Q^+]_w}{K_1} + K_3[Q^+]_w [S_2O_8^{-2}]_w} \tag{23}$$

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

$$r_{pco} = k_{21}[M_2 \cdot][M_1] + k_{12}[M_1 \cdot][M_2] \tag{24}$$

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.

$$r_{pco} = F_{co} \gamma [M_2]_\phi \tag{25}$$

$$F_{co} = \left[\left(\frac{2fk_iK_3}{\alpha_2} \right)^{1/2} \left(\frac{k_{21}^2}{2k_{t2}} \right)^{1/2} f_1 + \left(\frac{2fk_iK_3}{\alpha_2} \right)^{1/2} \left(\frac{k_{21}^2}{k_{t1}} \right)^{1/2} \right] \tag{26}$$

$$\gamma = \frac{[Q^+]_w^T [S_2O_8^{-2}]_w^{1/2}}{1 + \frac{[Q^+]_w}{K_1} + K_3 [Q^+]_w [S_2O_8^{-2}]_w} \tag{27}$$

where,

$$[Q^+]_w^T = [Q^+]_w + [QBr]_w + [Q_2S_2O_8]_w \tag{28}$$

EXPERIMENTAL

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

chemicals were of reagent grade. Polymerization was carried out with stirring in a four-necked flask under nitrogen atmosphere at 55 °C by the polymerization procedure reported before [Park et al., 1993a].

AN and MA dissolved in toluene, and $(NH_4)_2S_2O_8$ and HTAB dissolved in distilled water were placed in a 300 cm³, four-necked flask equipped with a mechanical stirrer, an inlet-tube of N_2, a Dimroth condenser with an outlet-tube of N_2, and a dropping funnel. The mixture was stirred at a constant speed for a given reaction time, and the contents were poured into a large amount of aqueous methanol. The precipitated content was filtered, washed several times with water and methanol, and dried *in vacuo*. The dried content was assumed to be a mixture of polyacrylonitrile (PAN), polymethylacrylate (PMA) and copolymer of AN and MA. Then, the dried polymer was poured into acetone to separate PMA. After filtering, the dried polymer was poured into 50 % HNO_3 aqueous solution to separate PAN. After filtering, the filtrate was poured into aqueous methanol to get copolymer. The conversions of homo- and copolymer were calculated from the weight of polymer obtained during the each separation procedure, and the structures and the components of polymers were confirmed by FT-IR spectrophotometer and organic element analyzer, respectively. The initial rate of polymerization was computed from the conversions into polymers obtained at various reaction times.

RESULTS AND DISCUSSION

The conversions of copolymer of AN and MA were calculated from the weights of copolymer measured according to the change of reaction time. The conversions of copolymer were plotted against the reaction time in Fig. 2 at the reaction temperature, 55 °C, and the speed of agitation, 1,000 rev/min,

under the reaction condition such as amounts of HTAB, 0.5 mmol, $(NH_4)_2S_2O_8$, 15 mmol, AN, 9.2 ml, MA, 0.8 ml, toluene, 10 ml and water, 80 ml, typically. As shown in Fig. 2, the linear relationship between the conversions of copolymer and the reaction time was satisfied. Thus, the rates of copolymerization were experimentally obtained from the amounts of copolymer produced for one hour reaction.

It is necessary to indicate the experimental conditions for the diffusion effect to be neglected if the chemical reaction occurs in the heterogeneous phase like a liquid-liquid system [Doraiswamy and Sharma, 1984]. The conversions of copolymer were calculated from the weights of copolymer measured according to the change of agitation speed under the reaction conditions listed in Fig. 2. The conversions of copolymer were plotted against the speed of agitation in the range of 400-1,200 rev/min in Fig. 3. As shown in Fig. 3, the conversions were constant for the change of agitation speed. Therefore, it could be considered that the controlling step for the copolymerization of AN and MA was the chemical reaction in the range of agitation speed between 400 and 1,200 rev/min. The speed of agitation was fixed at the value of 1,000 rev/min in all the experiments mentioned below.

The conversions of copolymer were measured while the HTAB concentration was varied in order to investigate the effect of phase-transfer catalyst on the rate of copolymerization. Fig. 4 shows a plot of the measured conversion into copolymer and the rates of copolymerization against amounts of HTAB in the range of 0-1 mmol under the reaction conditions such as amounts or $(NH_4)_2S_2O_8$, 15 mmol, AN, 9.2 ml, MA, 0.8 ml, toluene, 10 ml and water, 80 ml. As shown in Fig. 4, the conversions into copolymer and the rates of copolymerization increased as the concentrations of HTAB, and the relationship between conversion or copolymerization rate and concentration of HTAB were nonlinear. As shown in Eq. (25), the rate of copolymerization is influenced by the concentration of sev-
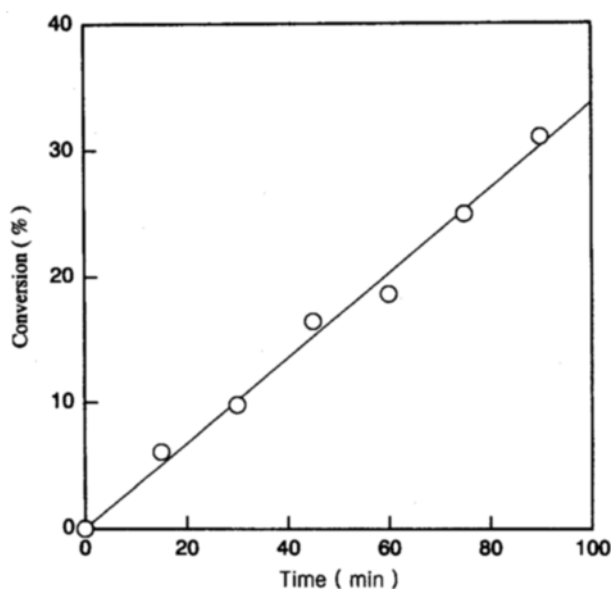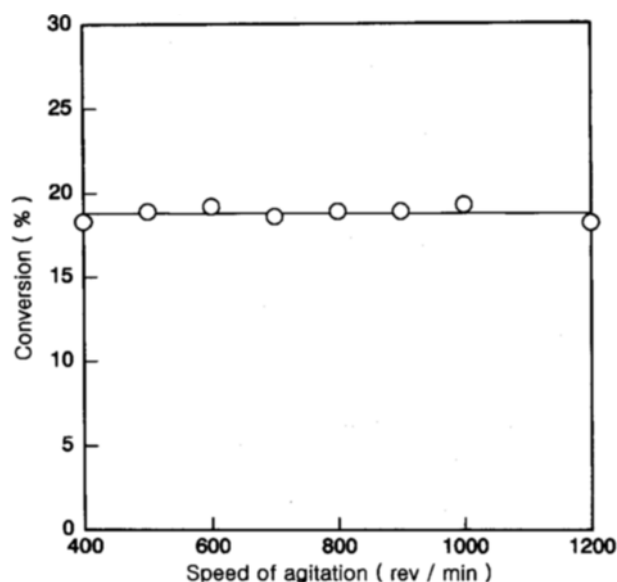

Fig. 2. Effect of reaction time on the conversion of copolymerization.
(55 °C, speed of agitation; 1,000 rev/min, AN; 9.2 ml, MA; 0.8 ml, HTAB; 0.5 mmol, $(NH_4)_2S_2O_8$; 15 mmol, toluene; 10 ml, H_2O; 80 ml)

Fig. 3. Effect of revolution of stirrer on the conversion of copolymerization at 55 °C.
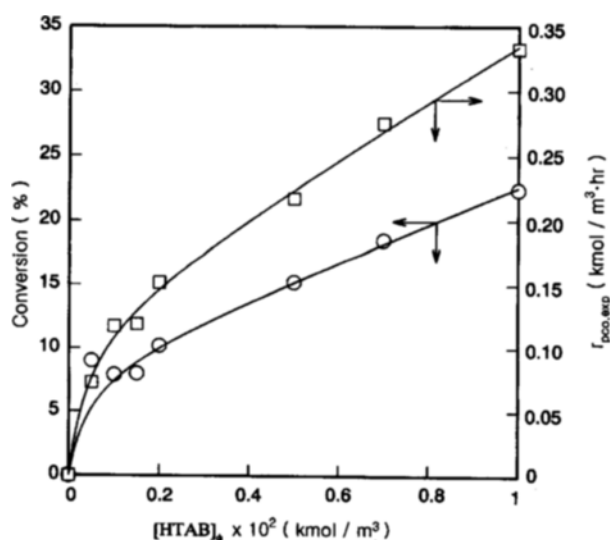(reaction conditions are listed in Fig. 2)

Fig. 4. Effect of concentration of HTAB on the conversion into copolymer and the rate of copolymerization.
(AN; 9.2 ml, MA; 0.8 ml, $(NH_4)_2S_2O_8$; 15 mmol, toluene; 10 ml, H_2O; 80 ml).

eral ions in the aqueous phase.

One attempts to observe the effect of concentration of ions on the rate of copolymerization as below.

The mass balance of component, Q in the organic and aqueous phase is

$$[QBr]_\phi = [QBr]_w + [Q^+]_w + [Q_2S_2O_8]_w + [Q_2S_2O_8]_o + [QBr]_o \quad (29)$$

Combining Eq. (29) with Eq. (6)-(10), Eq. (29) is given by

$$[QBr]_\phi = \frac{[Q^+]_w^2}{K_1} + \frac{[Q^+]_w}{\alpha_1 K_1} + [Q^+]_w + K_3[S_2O_8^{-2}]_w [Q^+]_w^2$$

$$+ \frac{K_3[S_2O_8^{-2}]_w [Q^+]_w^2}{\alpha_2} \quad (30)$$

Also, the mass balance of component, $S_2O_8^{-2}$ using Eqs. (6)-(10) is given by

$$[S_2O_8^{-2}]_\phi = [S_2O_8^{-2}]_w + K_3[S_2O_8^{-2}]_w [Q^+]_w^2 + \frac{K_3}{\alpha_2}[S_2O_8^{-2}]_w [Q^+]_w^2 \quad (31)$$

The values of K_1 and K_3 to be used for calculation of γ in Eq. (27), and those of α_1 and α_2 for $[Q^+]_w$ and $[S_2O_8^{-2}]_w$ in Eq. (30) and (31) were calculated by the same procedure reported before [Park et al., 1993a]. The values of K_1 and K_3 calculated for the $QBr - (NH_4)_2S_2O_8$ system were 2.03×10^{-6} kmol/ m^3 and 4.5×10^9 $(m^3/kmol)^2$, respectively.

The empirical equations of α_1 and α_2 were following:

$$\log\left(\frac{\alpha_1}{2.6604}\right) = -0.056[(NH_4)_2S_2O_8]_\phi \quad (32)$$

$$\log\left(\frac{\alpha_2}{0.1704}\right) = -1.6743[(NH_4)_2S_2O_8]_\phi \quad (33)$$

The concentrations of Q^+ and $S_2O_8^{-2}$ in the aqueous phase were calculated from Eqs. (30) and (31) with the values of K_1, K_3, α_1 and α_2 by using Eq. (32) and (33) at the given con-

centration of QBr and $(NH_4)_2S_2O_8$ to get γ values in Eq. (27). Fig. 5 shows a plot of copolymerization rate against γ in the range of $[QBr]_\phi$ between 0 and 1 mmol under the reaction condition listed in Fig. 4. As shown in Fig. 5, the linear relationship between rate of copolymerization and γ was satisfied.

Conversions into copolymer were measured according to the change of concentrations of $(NH_4)_2S_2O_8$ in the range of 0-0.25 $kmol/m^3$ under the reaction condition such as AN, 9.2 ml, MA, 0.8 ml, HTAB, 0.5 mmol, toluene, 10 ml, and H_2O, 80 ml from which the rates of copolymerization were calculated in order to observe the effect of $(NH_4)_2S_2O_8$ on the conversion into copolymer and the rate of copolymerization. Fig. 6 shows a plot of conversion of copolymer or rate of copolymerization against the concentration of $(NH_4)_2S_2O_8$. As
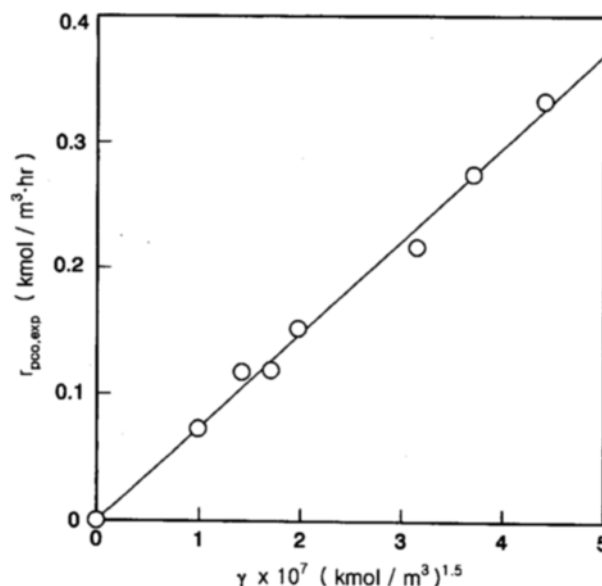

Fig. 5. Plot of $r_{DCO,exp}$ vs. γ on the various concentration of HTAB.
(reaction conditions are listed in Fig. 4)

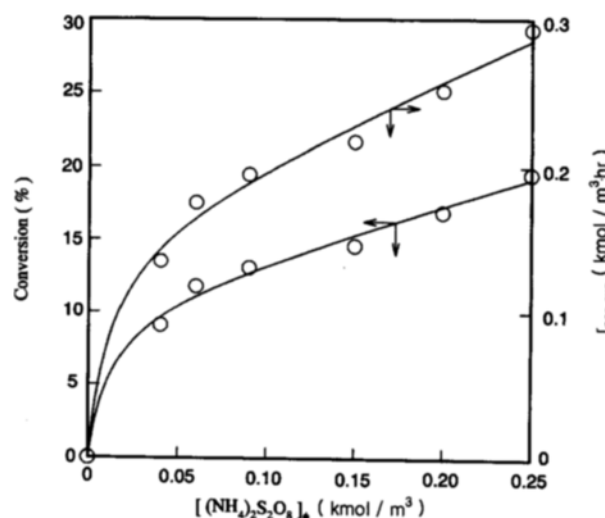**Fig. 6. Effect of concentration of $(NH_4)_2S_2O_8$ on the conversion into copolymer and the rate of copolymerization.**
(AN; 0.9 ml, MA; 0.8 ml, HTAB; 0.5 ml, toluene; 10 ml, H_2O; 80 ml)

shown in Fig. 6, the conversion of copolymer and the rate of copolymerization increased as the concentration of $(NH_4)_2S_2O_8$ increased, but the relationship between the rate of copolymerization and concentration of $(NH_4)_2S_2O_8$ was not linear.

The effect γ on the rate of copolymerization was investigated in order to observe quantitatively the relationship between the concentration of $(NH_4)_2S_2O_8$ and the rate of copolymerization as same as those of HTAB. Fig. 7 shows a plot of copolymerization rate against γ calculated from Eq. (27), where $[Q^+]_w$ and $[S_2O_8^{-2}]_w$ were obtained from Eqs. (30) and (31) at the given values of $[QBr]_\phi$ and $[(NH_4)_2S_2O_8]_\phi$. The linear relationship between rate of copolymerization and γ was satisfied. It was evident that the rate of copolymerization might be ex-
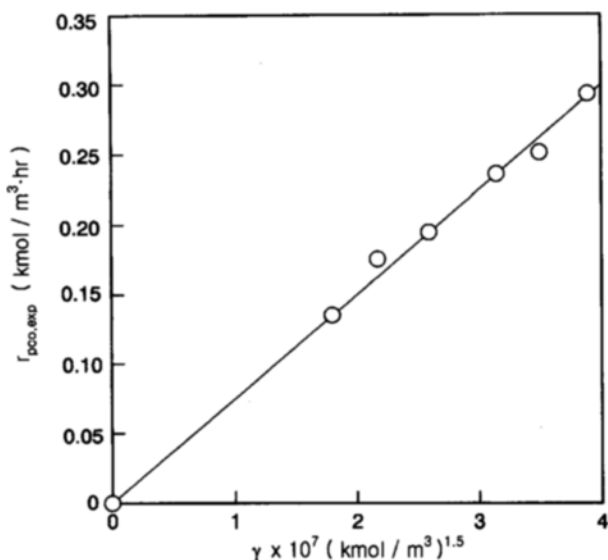

Fig. 9. Comparison of the experimental values with the theoretical ones for the rate of copolymerization.
(AN; 9.2 ml, MA; 0.8 ml, HTAB; 0-1.0 mmol, $(NH_4)_2S_2O_8$; 0-25 mmol, toluene; 10 ml, H_2O; 8 ml)

pressed in terms of $[Q^+]_w$ and $[S_2O_8^{-2}]_w$ rather than the initial concentrations of HTAB and $(NH_4)_2S_2O_8$, i.e., it might be dependent on the ionic concentrations of Q^+ and $S_2O_8^{-2}$ as shown in Fig. 5, 7 and Eq. (25).

Fig. 8 shows a plot of the rates of copolymerization against γ $[M_A]_\phi$ by using the measured conversions of copolymer in the range of $[QBr]_\phi$ between 0-0.01 kmol/m^3 and $[(NH_4)_2$ $S_2O_8]_\phi$ between 0 and 0.25 kmol/m^3. As shown in Fig. 8, the plots showed a linear relationship. The value of F_∞ obtained from comparison of the slope of the plots in Fig. 8 with Eq. (25) was 8.271×10^6 $(kmol/m^3)^{-1.5}$ hr^{-1}.

Fig. 9 shows a plot of the experimental value of copolymerization rate against the theoretical one calculated from Eq. (25) for the concentration change of $[QBr]_\phi$ and $[(NH_4)_2S_2O_8]_\phi$ mentioned above. As shown in Fig. 9, the measured values approached reasonably to the theoretical ones within the standard error with 6.2 %.

Fig. 7. Plot of $r_{pco,exp}$ vs. γ on the various concentration of $(NH_4)_2$-S_2O_8.
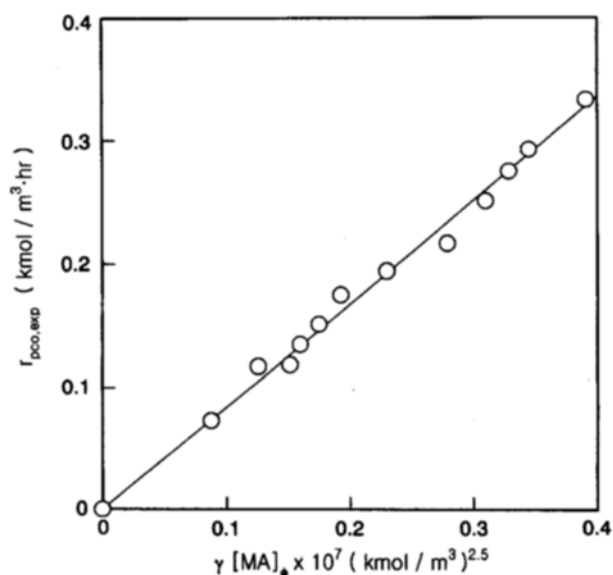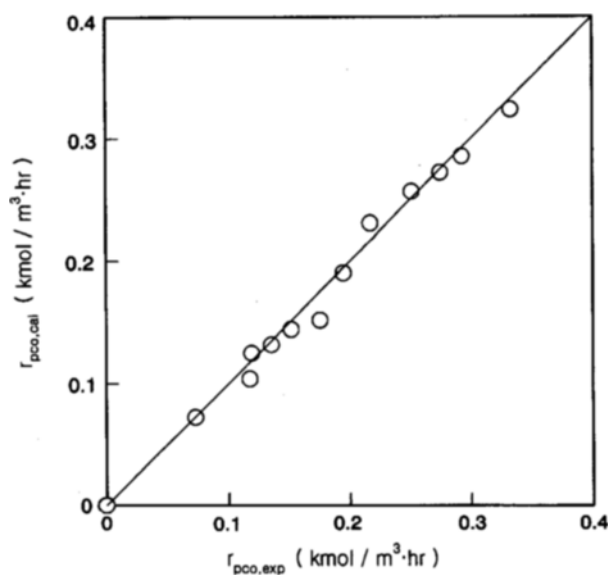(reaction conditions are listed in Fig. 6)

CONCLUSION

The kinetics of the radical copolymerization of acrylonitrile and methylacrylate was investigated by using ammonium peroxydisulfate as initiator and hexadecyltrimethylammonium bromide as a phase-transfer catalyst in toluene/water two-phase system at 55 °C and under nitrogen circumstances.

The measured values of K_1 and K_3 were 2.03×10^{-6} kmol/ m^3 and 4.5×10^9 (m^3/kmol)^2, respectively.

The empirical equations of α_1 and α_2 were as follows:

$$\log\left(\frac{\alpha_1}{2.6604}\right) = -0.056[(NH_4)_2S_2O_8]_\phi$$

Fig. 8. Plot of $r_{pco,exp}$ vs. γ $[MA]_\phi$.
(AN; 9.2 ml, MA; 0.8 ml, $(NH_4)_2S_2O_8$, 0-25 mmol, HTAB; 0-1.0 mmol, Toluene; 10 ml, H_2O; 80 ml)

$$\log\left(\frac{\alpha_2}{0.1704}\right) = -1.6743[(NH_4)_2S_2O_8]_\phi$$

The conversions of copolymer increased as the concentrations of initiator and catalyst increased.

It was reasonable to express the rate of copolymerization as the combined terms of concentrations of Q^+ and $S_2O_4^{-2}$ in aqueous phase rather than the fed concentrations of HTAB and $(NH_4)_2S_2O_8$, and the observed rates of copolymerization were used to analyze the copolymerization mechanism proposed with a cyclic phase-transfer initiation step.

The rate of copolymerization was proposed as the following equation.

$$r_{pco} = F_{co}\gamma[M_2]_o$$

$$F_{co} = \left[\left(\frac{2fk_iK_3}{\alpha_2}\right)^{1/2}\left(\frac{k_{21}^2}{2k_{t2}}\right)^{1/2}f_1 + \left(\frac{2fk_iK_3}{\alpha_2}\right)^{1/2}\left(\frac{k_{21}^2}{k_{t1}}\right)^{1/2}\right]$$

$$\gamma = \frac{[Q^+]_w^T[S_2O_8^{-2}]_w^{1/2}}{1 + \frac{[Q^+]_w}{K_1} + K_3[Q^+]_w[S_2O_8^{-2}]_w}$$

ACKNOWLEDGEMENTS

NOMENCLATURE

b_1 : quantity defined in Eq. (22) $[(kmol/m^3)^{0.5}/hr]$
b_2 : quantity defined in Eq. (23) $[(kmol/m^3)^{0.5}/hr]$
F_{co} : quantity defined by Eq. (26) $[(m^3/kmol)^{1.5}/hr)]$
f : efficiency of initiator
f_1 : molar ratio of monomers in feed defined by Eq. (20)
K_1 : equilibrium constant defined by Eq. (1) $[kmol/m^3]$
K_2 : equilibrium constant defined by Eq. (2) $[kmol/m^3]^2$
K_3 : equilibrium constant defined by Eq. (3) $[m^3/kmol]^2$
k_i : reaction rate constant of the $Q_2S_2O_8$ in Eq. (4) $[1/hr]$
k_{ij} : reaction rate constants of propagation of i and j species $[m^3/kmol \cdot hr]$
k_{ti} : terminate rate constant of i species $[m^3/kmol \cdot hr]$
M_i : monomer of i species
Q^+ : quaternary ammonium ion of phase transfer catalyst
r_i : initiation rate defined by Eq. (11) $[kmol/m^3 \cdot hr]$
r_{pco} : copolymerization rate defined by Eq. (24) $[kmol/m^3 \cdot hr]$
r_{pi} : propagation rate of i species of monomer defined by Eq. (13) and (14) $[kmol/m^3 \cdot hr]$
r_{pt} : total rate of polymerization defined by Eq. (19) $[kmol/m^3 \cdot hr]$
r_{ti} : termination rate of i species of monomer defined by Eq. (15) and (16) $[kmol/m^3 \cdot hr]$
t : reaction time $[hr]$

Greek Letters

α_1 : distribution coefficient defined by (9)
α_2 : distribution coefficient defined by (10)
γ : quantity defined by Eq. (27) $[(kmol/m^3)^{1.5}]$

Subscripts

cal : calculated value

exp : experimental value
o : organic phase
w : aqueous phase
ϕ : initial value
T : total value

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