Phase-Transfer Catalysis: Free-Radical Polymerization of Acrylonitrile using Potassium Peroxomonosulphate–Tetrabutyl Phosphonium Chloride Catalyst System: A Kinetic Study

T. BALAKRISHNAN, S. DAMODARKUMAR

Department of Physical Chemistry, University of Madras, A.C. College, Guindy Campus, Chennai 600 025, India

Received 14 May 1999; accepted 15 October 1999

ABSTRACT: This article presents the systematic study of kinetics and mechanism of phase-transfer-catalyzed free-radical polymerization of acrylonitrile (AN) and water-soluble initiator potassium peroxomonosulphate (PMS) coupled with tetrabutyl phosphonium chloride (TBPC) in ethyl acetate/water biphase system in the temperature range 45–55°C at fixed pH and ionic strength. The rate of polymerization increases with an increase in concentrations of AN, PMS, and phase transfer catalyst, PTC. It was observed that R_p is proportional to $[\mathrm{AN}]^{1.5}$, $[\mathrm{KHSO5}_5^-]^{0.5}$, and $[\mathrm{TBPC}]^{0.5}$. A suitable kinetic scheme has been proposed to account for the experimental observations and its significance was discussed. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1564–1571, 2000

Key words:

INTRODUCTION

Phase-transfer catalysis is a novel and fascinating method which has been extensively employed as an attractive subject of current research in recent years.[1,2] Phase-transfer-catalyzed free-radical polymerization of vinyl monomers with water-soluble initiators, such as potassium peroxydisulphate, ammonium peroxydisulphate, and potassium peroxymonosulphate, is a relatively new area of research and has become a unique research interest to chemists all over the world owing to its high-reaction rates at lower temperatures. Moreover, water-soluble initiators such as potassium and ammonium peroxydisulphates offer more advantages over the organic soluble initiators like AIBN and benzoyl peroxide (BPO). It was found that such water-soluble initiators could be used effectively for bulk or solution polymerization with phase-transfer catalysis such as quaternary ammonium salts $[Q^+X^-]$ and macrocyclic polyethers (crown ethers).[3–9] Balakrishnan and Muniraj[10] reported the kinetics of polymerization *ortho*-, *meta*-, and *para*-tolylmethacrylates and $K_2S_2O_8$/TBBA-assisted free-radical polymerization. The present article describes the kinetics of polymerization of acrylonitrile (AN) by using potassium peroxomonosulphate/phase-transfer catalyst [tetrabutylphosphonium chloride (TBPC)] in ethyl acetate/water two-phase system.

EXPERIMENTAL

Materials

Acrylonitrile (SD's, Bombay, India) was washed with 5 wt % NaOH solution to remove the inhib-

---

Correspondence to: T. Balakrishnan.

Journal of Applied Polymer Science, Vol. 76, 1564–1571 (2000)

itor and with double-distilled water to remove the basic impurities and then dried over calcium chloride and distilled under reduced pressure. The middle fraction of the distillate was used. The sample of potassium peroxomonosulphate (PMS; trade name Oxone)[11] was obtained from E. I. Dupont de Nemours & Co. (Wilmington, DE) and used as received. The phase-transfer catalyst [viz., TBPC (Fluka, Buchs, Switzerland)] and other chemicals were used as received.

Polymerization Procedure

The polymerization reactions were carried out in Pyrex glass tubes with inlets and outlets for nitrogen. The reaction mixture consists of 10 mL of aqueous phase and 10 mL of organic phase (ethyl acetate). The reaction mixture was thoroughly deaerated for 45 min. All reactions were carried out at 50 ± 0.1°C. When PMS was added to the reaction mixture, polymerization occurred and polyacrylonitrile precipitated continuously during polymerization. At higher concentrations of AN, PMS, and PTC, polymers were distributed in the aqueous as well as the organic phase. The reactions were arrested by pouring the reaction mixture into ice-cold methanol containing traces of hydroquinone. The polymer was collected on a sintered glass crucible, washed with water and methanol, and then dried in vacuum at 60°C. The rate of polymerization was calculated from the weight of the polymer formed. The conversion was restricted to $< 10\%$ in all kinetic studies. All polymerizations were carried out in polymerization tubes (100 mL) without any agitation. The molecular weights of the purified polymers were determined by viscometry by using the appropriate Mark–Houwink relationship[13]

$$[\eta] = K\bar{M}_v^a$$

where η denotes intrinsic viscosity and $\bar{M}_v$ denotes the viscosity-averaged molecular weight of the polymer.

The viscosity of the polymer samples were determined by using a Ubbelohde viscometer. The solvent taken for the measurements of viscosity was dimethylformamide. From the molecular weight of the polymer, the degree of polymerization ($\bar{X}_n$) values were calculated.

RESULTS AND DISCUSSION

The kinetics of the phase-transfer catalyst-assisted free-radical polymerization of AN by using PMS (as the initiator) with phase-transfer catalyst TBPC was investigated at 50°C in ethyl acetate/water two-phase systems under unstirred conditions. In the control experiments without catalyst, there was no polymerization.

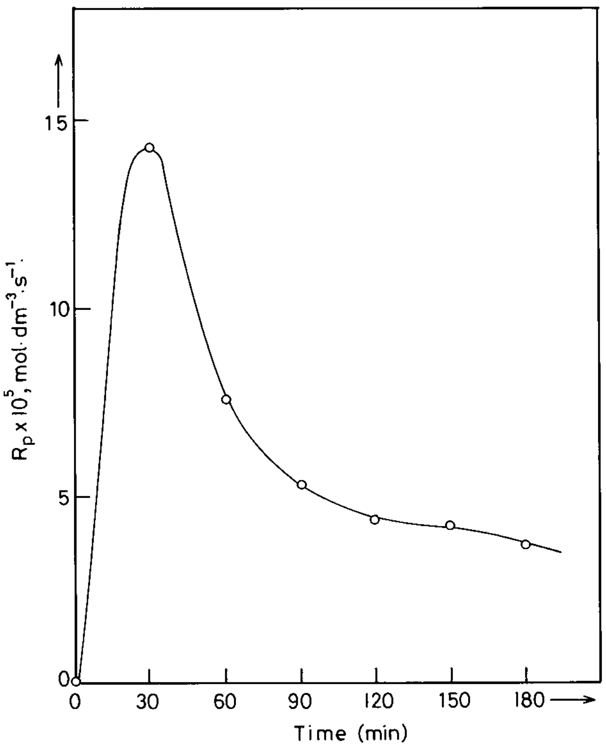

Figure 1 AN–PMS–TBPC system: steady state rate of polymerization. Line: $R_p \times 10^5$, mol dm^{-3} S^{-1}, Time in minutes. [Monomer]: 2.0*M;* [TBPC]: 0.02*M;* [PMS]: 0.02*M;* μ: 0.05*M;* Temp: 50°C.

The steady state rate of polymerization (R_p) was ascertained first by carrying out the experiments for various durations. A sharp increase in R_p was observed initially, which then reached a maximum, decreased subsequently, and then reached a steady value. The time taken for the establishment of steady state R_p was found to be 90 min for polymerization of AN (Fig. 1).

Effect of Monomer Concentration on R_p

The effect of [monomer] on the R_p was studied by varying the concentration in the range 1.0–3.0 mol dm^{-3} at fixed concentrations of PMS, PTC, and 0.05*M* [KHSO$_4$] ionic-strength system. R_p increased with an increase in the concentration of AN. The order of the reaction was found to be 1.5, from a plot of log R_p versus log [AN] (Fig. 2).

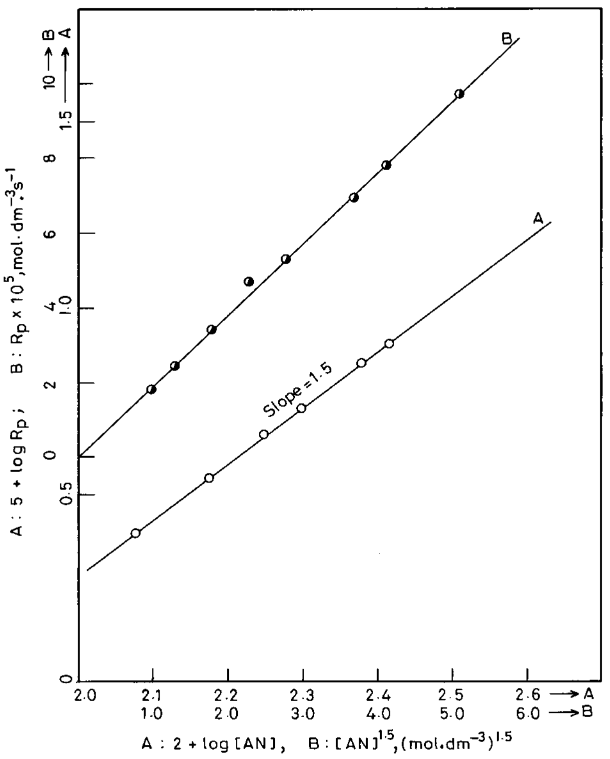

Figure 2 AN–PMS–TBP$_c$ system: variation of [monomer]. Line A: 5 + log R_p versus 2 + log[AN]. Line B: R_p × 10^5, mol dm^{-3} S^{-1} versus $[AN]^{1.5}$ (mol dm^{-3})$^{1.5}$. Influence of [Monomer] on R_p: [PMS]: 0.02*M;* [TBPC]: 0.02*M;* μ: 0.05*M;* Temp: 50°C.

The homogeneous polymerization of AN-initiated oil-soluble initiators is a subject of interest for many investigators, mainly due to the abnormal kinetic behavior of AN.[14–19] Generally, in most free-radical polymerization of vinyl monomers, the order, with respect to the monomer and initiator concentrations, is found to be 1.0 and 0.5, respectively. The deviation from the normal first order on monomer concentration may be attributed to any one of the factors (viz., concentration of monomer involved in the initiation step, the primary radical termination, occlusion phenomenon, or gel effect).

These factors are known to influence both homogeneous and heterogeneous polymerizations. In the case of heterogeneous systems, as the polymerization proceeds, the polymer is formed in poor solvent media and precipitation of the polymer occurs. Because AN is undergoing precipitation polymerization, the occlusion phenomenon,[18,19] which is the main contributing factor in heterogeneous conditions, is also expected to influence the overall rate of polymerization. However, at temperatures of 50°C or above, the extent of occlusion was so diminished[20] that bimolecular termination becomes increasingly important due to a drastic decrease in concentration of occluded radicals. Hence, the polymerization of AN carried out at 50°C, the importance of occlusion, and its concomitant influence on the kinetic feature can be ignored. Thus the higher monomer order in the present study can be attributed to dependence of initiation rate on monomer concentration. Maruthamuthu and Manivannan[12] observed the order of reaction with respect to [M] to be 1.5 in the homogeneous polymerization of AN by PMS as the initiator catalyzed by Thiols.

Effect of PMS Concentration on R_p

The polymerization rate increases with increased concentration of PMS (0.01–0.026 mol dm^{-3}) at a fixed concentration of phase-transfer catalyst, pH, AN, and at constant ionic strength. A plot of log R_p versus log[PMS] is found to be linear with a slope of 0.5 (Fig. 3), indicating the half-order dependence of R_p on the initiator concentration.

Generally, R_p is proportional to the square root of initiator concentration, whenever termination is bimolecular. Its termination takes place by combination with primary radicals. The order with respect to initiator is expected to deviate from 0.5 and approach 0 and the exponent of monomer may also approach a value very close to 2.[20] Because the initiator exponent is found to be 0.5 in the present investigation, the possibility of primary radical termination may be ruled out. A square-root-order dependence of [initiator] was reported in the polymerization of methyl methacrylate (MMA) with $K_2S_2O_8/Bu_4N^+Br^-$ catalyst system by Ghosh and Mandal.[7] Balakrishnan and Muniraj[10] observed an initiator exponent of 0.5 with respect to initiator in the polymerization of tolylmethacrylates initiated by $K_2S_2O_8$–Q^+X^- catalyst systems in ethyl acetate/water media, which indicates bimolecular termination.

Effect of PTC Concentration on R_p

The dependence of R_p on the concentration of PTC was examined by varying PTC in the range 0.01–0.026 mol dm^{-3} at fixed concentration of monomer and PMS, pH, and ionic strength. R_p increases with an increase in the concentration of phase-transfer catalyst [TBPC]. A plot of log R_p

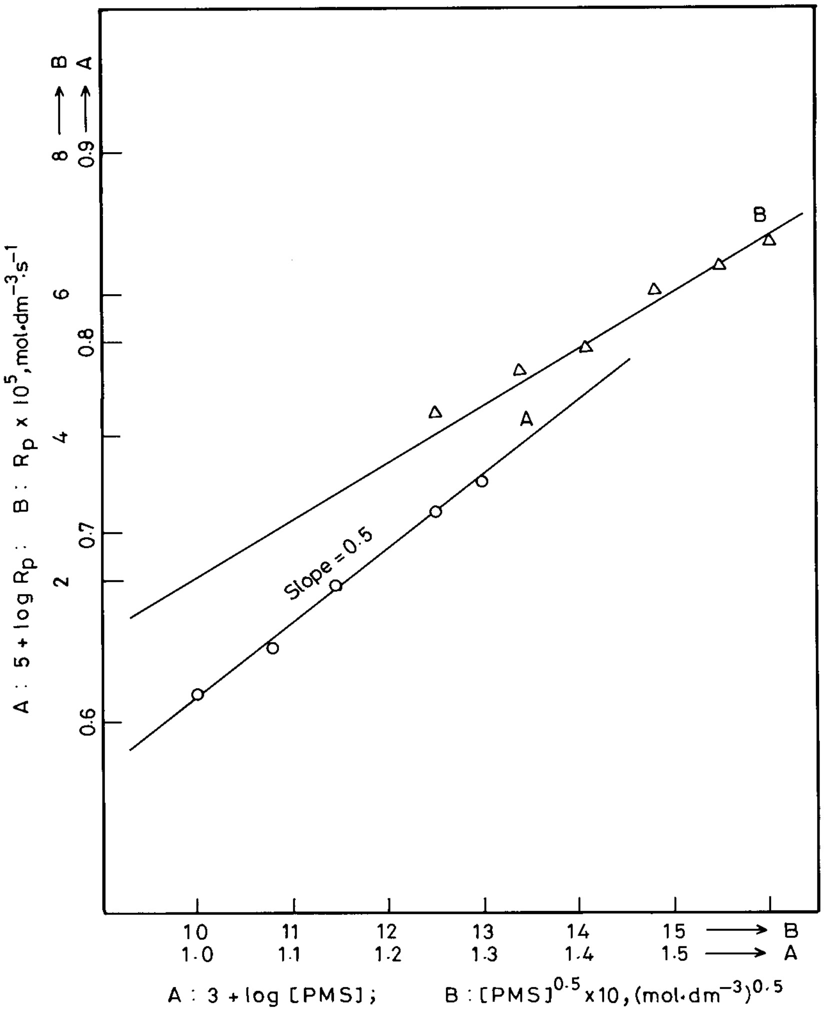

Figure 3 AN–PMS–TBP$_c$ system: variation of [PMS]. Line A: 5 + log R_p versus 3 + log[PMS]. Line B: $R_p \times 10^5$, mol dm^{-3} S^{-1} versus [PMS]$^{0.5} \times 10$ (mol dm^{-3})$^{0.5}$. Influence of [PMS] on R_p: [AN]: 2.0*M;* [TBPC]: 0.02*M;* μ: 0.05*M;* Temp: 50°C.

versus log[TBPC] was found to be linear with a slope 0.5 (Fig. 4), indicating a half-order dependence on PTC. In the phase-transfer catalyzed free-radical polymerization reaction, the catalyst order 0.5 was reported by Balakrishnan and Jayachandramani.[21] Identical reports were also given by Jayakrishnan and Shah[5,6] and Choi and Lee[8] that the phase-transfer catalyst rate exponent was 0.5 in the free-radical polymerization.

Dependence of R_p on Temperature

The free-radical polymerization of AN using PMS coupled with TBPC catalyst was studied at three different temperatures (viz., 45, 50, and 55°C). In all the experiments, the concentrations of AN, PMS, and PTC, and the ionic strength and pH were kept constant. The rate of polymerization of the monomer is found to increase with an increase in temperature. The overall activation energy of polymerization (E_a) obtained from the plot of log R_p versus $1/T$ is 69.5 kJ/mol (Fig. 5) for AN system.

Dependence of Ionic Strength on R_p

The effect of ionic strength on R_p was investigated by varying ionic strength in the range 0.04–0.07 mol dm^{-3}, keeping other variables, such as [monomer], [PMS], [PTC], and pH, constant. The variation of ionic strength is found to exert no appreciable effect on R_p for AN.

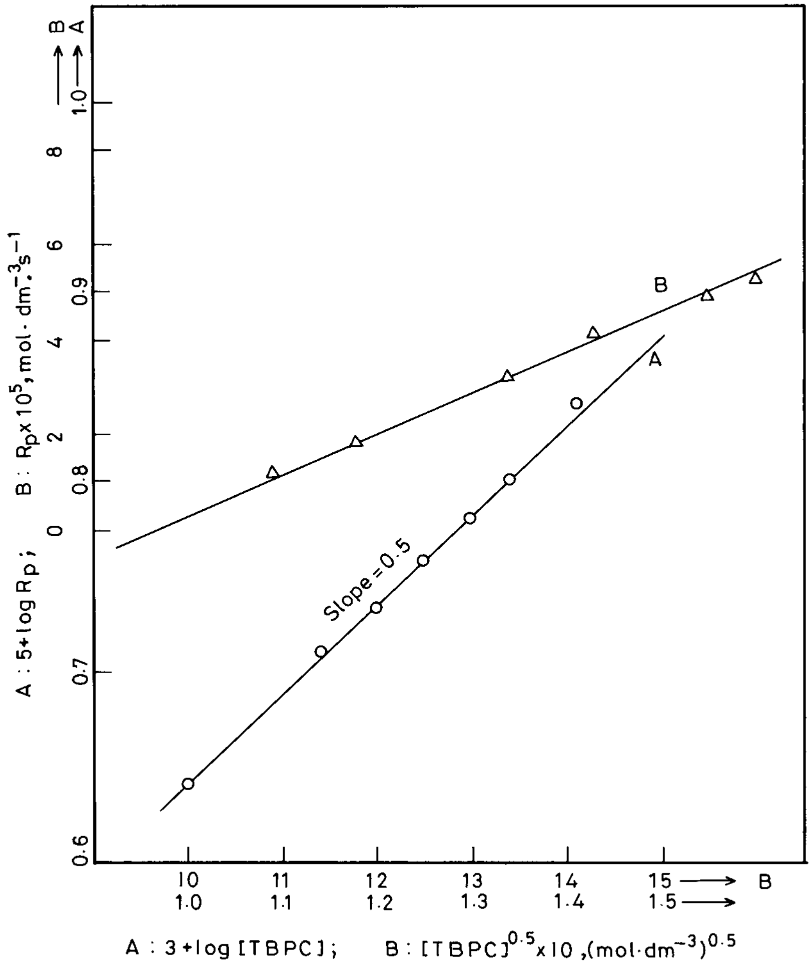

Figure 4 AN–PMS–TBPC system: variation of [TBPC]. Line A: 5 + log R_p versus 3 + log[TBPC]. Line B: $R_p \times 10^5$, mol dm^{-3} S^{-1} versus [TBPC]$^{0.5} \times 10$ (mol dm^{-3})$^{0.5}$. Influence of [PTC] on R_p: [AN]: 2.0*M;* [PMS]: 0.02*M;* μ: 0.05*M;* Temp: 50°C.

Mechanism and Rate Law

The kinetic results obtained in the polymerization of AN initiated by PMS–tetrabutylphosphonium salt (Q^+X^-) catalyst is as follows. The rate of polymerization shows (i) a 1.5-order dependence of [PMS], (ii) a 0.5-order dependence on [PMS], (iii) 0.5-order dependence on [PTC], and (iv) that R_p is found to be independent of ionic strength under the given experimental condition. The mechanism is proposed to explain the abovementioned experimental observations. In this investigation, PMS, which is a water-soluble initiator, is transferred from the aqueous phase to the monomer phase. This is achieved with the aid of the quaternary phosphonium salt (TBPC), which functions as the phase-transfer catalyst. Because studies involving PMS as initiator in the TBPC- (PTC) assisted polymerization is not available in the literature, the typical studies in which peroxydisulphate was used as initiator with PTC are discussed.

The first report of Rasmussen and Smith[3,4] on phase-transfer catalyst-assisted polymerizations states that the presence of 18-crown-6 as the phase-transfer agent accelerated the rate of transfer of potassium peroxydisulphate from the aqueous phase to the monomer phase. These studies established that the formation of quaternary peroxydisulphate complex ($Q^{2+}S_2O_8^{2-}$), which was soluble in the organic medium, was responsible for the polymerization of monomers such as butylacrylate.[4,17] The results obtained in this study indicate the formation of an ion pair

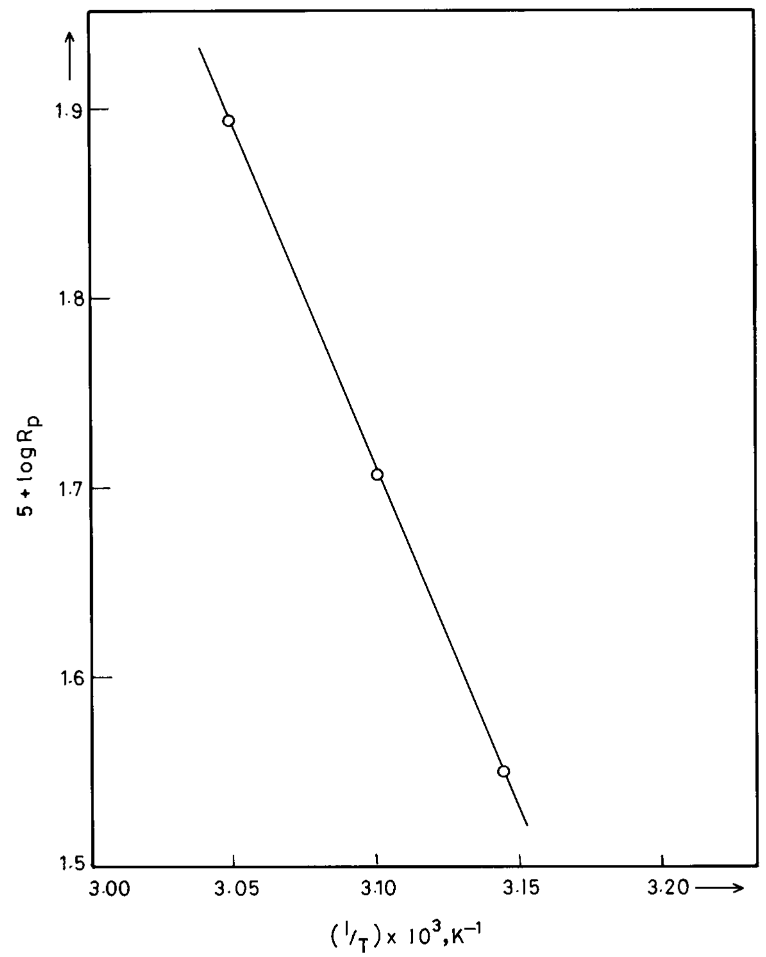

Figure 5 AN–PMS–TBPC system: temperature variation. Line: Plot of log R_p versus $1/T$. Arrhenius Plot: [TBPC]: 0.02*M;* [PMS]: 0.02*M;* [AN]: 2.0*M;* μ: 0.05*M.*

($Q^+HSO_5^-$) and then migration to the organic phase, where it decomposes and initiates polymerization. Based on the kinetic results, we proposed the following mechanism for the polymerization of AN:

Phase Transfer

$$Q^+_{(w)} + HSO^-_{5(w)} \overset{K}{\rightleftarrows} Q^+HSO^-_{5(0)} \qquad (1)$$

Initiation

$$Q^+HSO^-_{5(o)} + M_{(o)} \xrightarrow{k_d} \begin{cases} Q^+SO_4^{0-} + OH^- + M^0 & (2)\\ OH^0 + M^0 + SO_4^{2-} & (3)\end{cases}$$

$$Q^+SO_4^{0-} + M \xrightarrow{k_i1} Q^+SO_4^-{—}M^0 \qquad (4)$$

$$^0OH + M \xrightarrow{k_i2} OH{—}M^0 \qquad (5)$$

Propagation

$$\begin{array}{ccc} M_1^0 + M & \xrightarrow{k_p} & M_2^0 \\ — & & — \\ — & & — \\ — & & — \\ M_{n-1}^0 + M & \rightarrow & M_n^0 \end{array} \qquad (6)$$

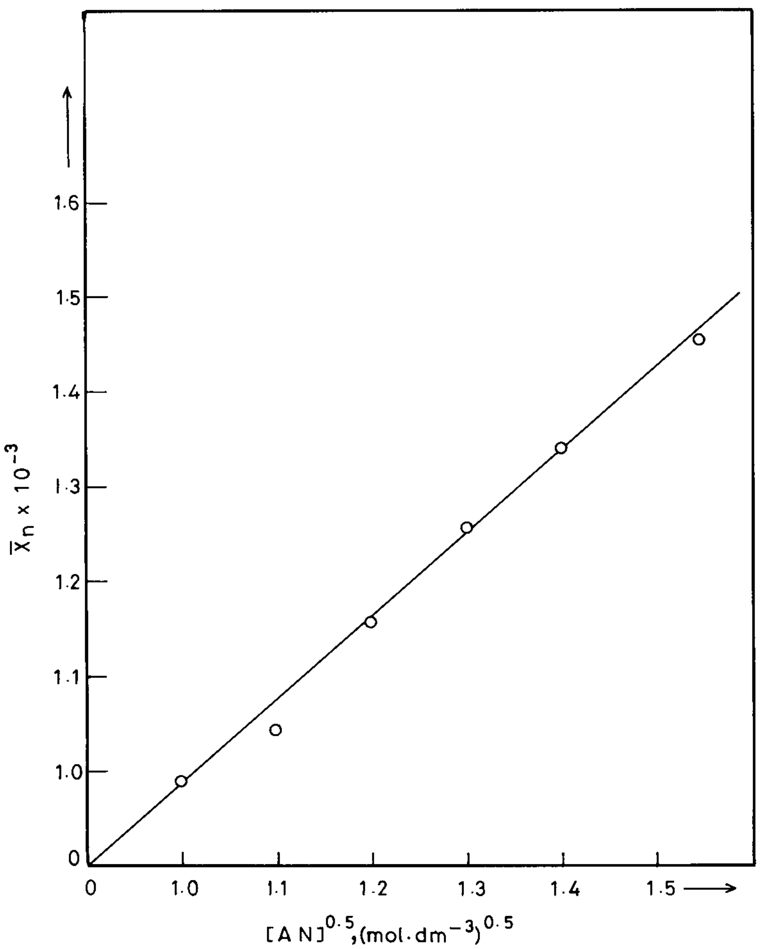

Figure 6 AN–PMS–TBPC system: variation of [AN] degree of polymerization. Line: $\bar{X}_n \times 10^{-3}$ versus $[\mathrm{AN}]^{0.5}$ $(\mathrm{mol\ dm}^{-3})^{0.5}$. Degree of polymerization.

where $\mathrm{M}_n^0 = Q^+\mathrm{SO}_4^-$—$\mathrm{M}^0$ or HO—M^0.

Termination

$$\mathrm{M}_n^0 + \mathrm{M}_n^0 \xrightarrow{k_t} \text{polymer} \qquad (7)$$

The subscripts (o) and (w) refer to the organicand aqueous phases, respectively. Applying general principles of free-radical polymerization, the steady state hypothesis for all the radicals formed, the derived rate expression for R_p is

$$R_p = k_p\left(\frac{Kk_d}{k_t}\right)^{0.5}[Q^+]_{(w)}^{0.5}[\mathrm{HSO}_5^-]_{\mathrm{total}}^{0.5}[\mathrm{M}]^{1.5}$$

According to this rate expression, the order with respect to [M] is 1.5 and the order with respect to [PMS] and [PTC] is 0.5. The above equation satisfactorily explains all the experimental observations.

The expression for the degree of polymerization is

$$\bar{X}_n = \frac{\text{rate of propagation}}{\text{rate of termination}} = \frac{R_p}{R_t}$$

$$\bar{X}_n = \frac{k_p[\mathrm{M}]^{0.5}}{2(Kk_tk_d)^{0.5}[Q^+]_{(w)}^{0.5}[\mathrm{HSO}_5]_{(w)}^{0.5}}$$

This equation for the degree of polymerization $\bar{X}_n$ is directly proportional to $[\mathrm{M}]^{0.5}$. It is found that a plot of $\bar{X}_n$ versus $[\mathrm{M}]^{0.5}$ gives a straight line passing through the origin for AN system (Fig. 6). This observation lends support to the mechanism proposed.

REFERENCES

1. Starkes, C. M.; Liotta, C. Phase Transfer Catalysis: Principles and Techniques; Academic Press: New York, 1994.
2. Dehmlow, E. V.; Dehmlow, S. S. Phase Transfer Catalysis, 3rd Ed.; Verlag Chemie: Weinheim, 1993.
3. Rasmussen, J. K.; Smith, H. K., II. J Am Chem Soc 1981, 103, 730.
4. Rasmussen, J. K.; Smith, H. K., II. Makromol Chem 1981, 182, 701.
5. Jayakrishnan, A.; Shah, D. O. J Polym Sci, Polym Chem Ed 1983, 21, 3201.
6. Jayakrishnana, A.; Shah, D. O. J Appl Polym Sci 1984, 29, 2937.
7. Ghosh, N. N.; Mandal, B. M. Macromolecules 1986, 19, 19.
8. Choi, K. Y.; Lee, C. Y. Ind Eng Chem Res 1987, 26, 2079.
9. Bulacovschi, V.; Mihailescu, C.; Ioan, S.; Simionescu, B. C. J Macromol Sci Chem 1991, 28(7), 613.
10. Balakrishnan, T.; Muniraj, S. Macromol New front, Proceedings of the IUPAC. International Symposium of Advanced Polymer Science Technology, 1998, 1, 153.
11. Technical Data on Oxone, E. I. Dupont de Nemours & Co., Wilmington, DE, 1979.
12. Maruthamuthu, P.; Neta, P. J Phys Chem 1977, 81, 937.
13. Brandrup, J.; Immergut, E. H., Eds.; Polymer Handbook, Wiley–Interscience: New York, 1975.
14. Patron, L.; Mazzolini, C.; Moretti, A. J Polym Sci Sym 1973, 42, 405.
15. Misra, G. S.; Mathice, V. R. B. Makromol Chem 1967, 1005.
16. Horikx, M. W.; Hermans, J. J. J Polym Sci 1953, 11, 325.
17. Rasmussen, J. K.; Heilmann, S. M.; Krepski, L. R.; Smith, H. K., II in Phase Transfer Catalysis: New Chemistry, Catalysis and Applications, Starks, C. M., Ed.; ACS Symposium Series 326; American Chemical Society: Washington, DC, 1987; Chapter 10.
18. Bamford, C. H.; Jenkins, A. D. Proc R Soc London, Series A 1953, 216, 515.
19. Lewis, O. G.; King, R. M. In Advanced Chemical Series 91, American Chemical Society: Washington, DC, 1969; p 25.
20. Odian, G. Principles of Polymerization, 2nd ed.; Wiley–Interscience: New York, 1981; pp 190–199.
21. Balakrishnan, T.; Jayachandramani, N. J Macromol Sci, Pure Appl Chem 1994, A31, 841.