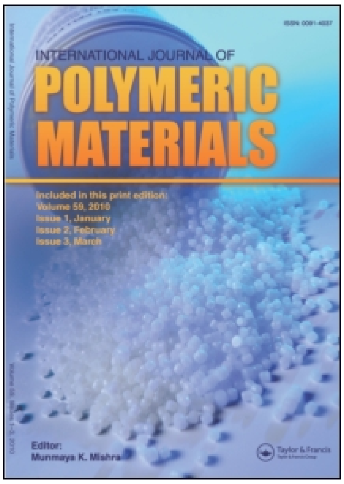

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Polymerization of Butyl Acrylate using Potassium Peroxy Disulfate as Initiator in the Presence of Phase Transfer Catalyst—A Kinetic Study

Savitha Sivapitchai[a]; M. Vajjiravel[a]; M. J. Umapathy[a]
[a] Department of Chemistry, College of Engineering, Anna University, Tamil Nadu, India

To cite this Article Sivapitchai, Savitha , Vajjiravel, M. and Umapathy, M. J.(2006) 'Polymerization of Butyl Acrylate using Potassium Peroxy Disulfate as Initiator in the Presence of Phase Transfer Catalyst—A Kinetic Study', International Journal of Polymeric Materials, 55: 8, 537 — 548

To link to this Article: DOI: 10.1080/009140391001769

URL: http://dx.doi.org/10.1080/009140391001769

International Journal of Polymeric Materials, 55:537–548, 2006
Copyright © Taylor & Francis Group, LLC
ISSN: 0091-4037 print/1563-5333 online
DOI: 10.1080/009140391001769

Polymerization of Butyl Acrylate using Potassium Peroxy Disulfate as Initiator in the Presence of Phase Transfer Catalyst—A Kinetic Study

Savitha Sivapitchai
M. Vajjiravel
M. J. Umapathy
Department of Chemistry, College of Engineering, Anna University,
Tamil Nadu, India

The kinetics and mechanism of free radical polymerization of butyl acrylate (BA), using potassium peroxydisulfate ($K_2S_2O_8$) as initiator in the presence of propiophenonebenzyldimethylammonium chloride (PPBDMAC) as phase transfer catalyst (PTC) has been studied. The reactions were carried out under inert, unstirred conditions and at a constant temperature of 60°C in cyclohexanone/water biphase media. The dependence of the rate of polymerization (R_p) on various experimental conditions such as different concentrations of monomer, initiator, phase transfer catalyst, varying acid and ionic strength, temperature, and volume fraction of aqueous phase were studied. The order with respect to monomer, initiator, and the phase transfer catalyst were found to be 1.5, 0.5, and 0.5, respectively. The rate of polymerization was independent of acid and ionic strength. Based on the results, a mechanism has been proposed for the polymerization reaction.

Keywords: phase transfer catalyst, radical polymerization, kinetics

INTRODUCTION

Phase transfer catalysis is a technique in which two mutually insoluble reagents react with the help of phase transfer catalyst [1]. The main function of the phase transfer catalyst is to facilitate the reaction between a species present often as an anion in an aqueous phase and a

Received 18 April 2005; in final form 29 April 2005.

Address correspondence to Savitha Sivapitchai, Department of Chemistry, College of Engineering, Anna University, Chennai 600025, Tamil Nadu, India. E-mail: saveetha6@yahoo.co.in

hydrophobic species that is often water insoluble. The phase transfer catalyst does the work of extracting the reactive anions from the aqueous phase and transfering them to the organic phase containing the reactant(substrate). Subsequently, a reaction takes place between the transferred reagent or ion-pair with the non-transferred reactant within the organic phase. Polymers prepared by this method include polysulfonates [2], polyphosphonates [3], polyesters [4], and so on.

Rasmussen and Smith demonstrated [5] the use of phase transfer catalyst in the polymerization of vinyl monomers employing water soluble initiators like potassium peroxydisulfate.

In this work, the kinetics of the free radical polymerization of butyl acrylate in the presence of a phase transfer catalyst using potassium peroxydisulfate as initiator was studied. The results were discussed and a mechanism has been proposed.

MATERIALS AND METHODS

The monomer butyl acrylate, potassium peroxydisulfate, methanol, cyclohexanone and acetone were purified by standard procedures. The phase transfer catalyst, propiophenonebenzyldimethylammonium chloride [6], was synthesized for this study.

The polymerization reactions were carried out in an inert and unstirred condition at constant temperature of 60°C. The reaction mixture consists of aqueous and organic phases. The organic phase consists of monomer in cyclohexanone and the aqueous phase consists of phase transfer catalyst, sodium bisulfate (for adjusting the ionic strength), and sulfuric acid (for maintaining acid strength). A calculated amount of peroxydisulfate was added to the reaction mixture and simultaneously a stop watch was started. Polymerization started and precipitate formed continuously during polymerization. The reaction was arrested by pouring the reaction mixture into ice-cold methanol containing traces of hydroquinone. The polymer formed was filtered quantitatively through a sintered crucible (G-4), washed several times with double distilled water and methanol, and dried at 50–65°C, in a vacuum oven to constant weight. The rate of polymerization was determined by gravimetry [7].

Viscosity measurements of the fractionated polymer were carried out in acetone at 25°C using Ubbelohde suspended level viscometer. Intrinsic viscosity were evaluated from the linear plots of specific viscosity/concentration (γ_{sp}/C) versus concentration (C). Average degree, of polymerization ($\overline{P}_n$) were calculated from the intrinsic viscosity data by making use of Mark-Houwink equation [8].

RESULTS AND DISCUSSION

The steady-state rate of polymerization was first arrived at by determining the rate of polymerization at different time intervals (see Figure 1) and it was found to be 50 min. Thus, the reaction time was fixed at 50 min to carry out the experiments with variation in other parameters.

Effect of Initiator Concentration on Rate of Polymerization

The effect of potassium peroxydisulfate concentration on the rate of polymerization was studied in the concentration range of 0.008 to 0.018 mol dm^{-3} at fixed concentrations of monomer, phase transfer catalyst, acid strength, ionic strength, and volume fraction of the aqueous phase constant. With an increase in the concentration of potassium peroxydisulfate, the rate of polymerization also showed an increase (Figure 2). A plot of log R_p versus log $[K_2S_2O_8]$ is found to be linear with a slope of 0.53 indicating a half order dependence of

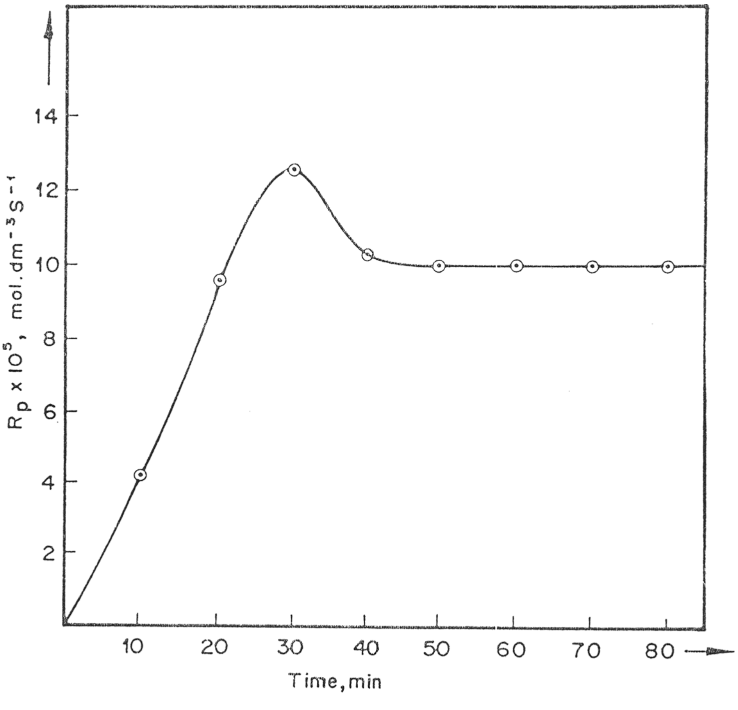

FIGURE 1 BA-PPBDMAC-$K_2S_2O_8$ system steady state.

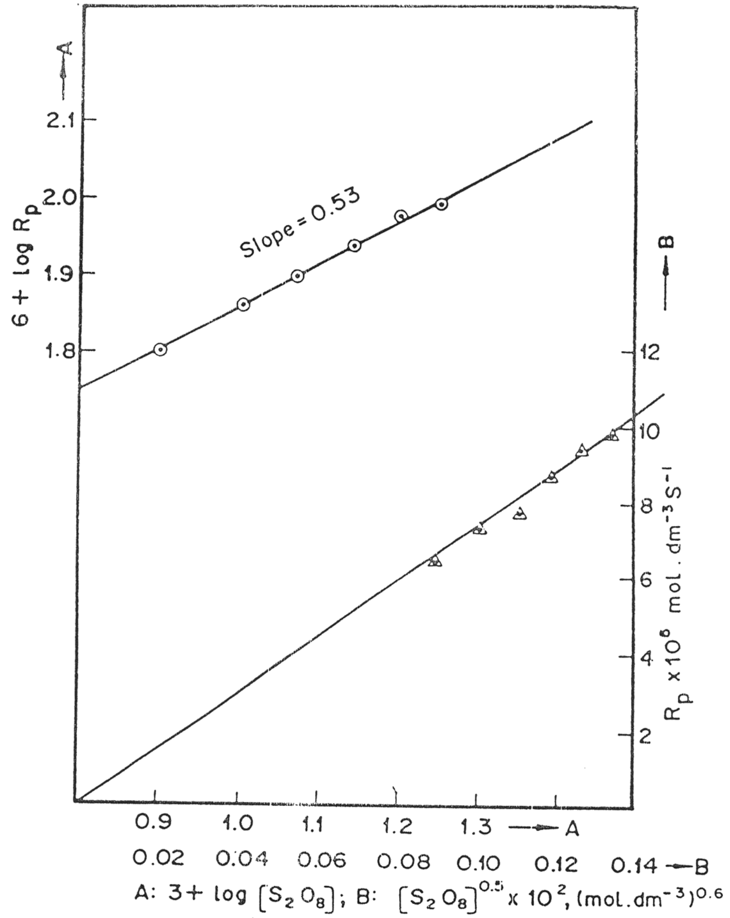

FIGURE 2 BA-PPBDMAC-$K_2S_2O_8$ system variation of [$K_2S_2O_8$].

R_p on [$K_2S_2O_8$]. A plot of R_p versus $[K_2S_2O_8]^{0.5}$ is linear passing through the origin supporting the earlier observation. Generally, the rate of polymerization is proportional to the square root of initiator concentration when the termination is bimolecular and this observation reconfirms the same theory.

Effect of Monomer Concentration on Rate of Polymerization

At fixed concentration of initiator, phase transfer catalyst, acid strength, ionic strength, and volume fraction of the aqueous phase, the effect of monomer concentration on rate of polmerization has been studied in the concentration range 1.7 to 2.7 mol dm^{-3}. The rate of polymerization was found to increase with increasing monomer concentration. The order with respect to monomer was deduced from a plot of log R_p versus log [BA], which is linear and the order was found to be 1.5. Further, a plot Figure 3 of R_p versus $[BA]^{3/2}$ was found to be linear passing through the origin, confirming the earlier observation. A reaction order greater than unity is not uncommon among vinyl monomers [9–13].

The reaction order greater than unity may be due to the dependence of initiator rate on monomer concentration, primary radical termination

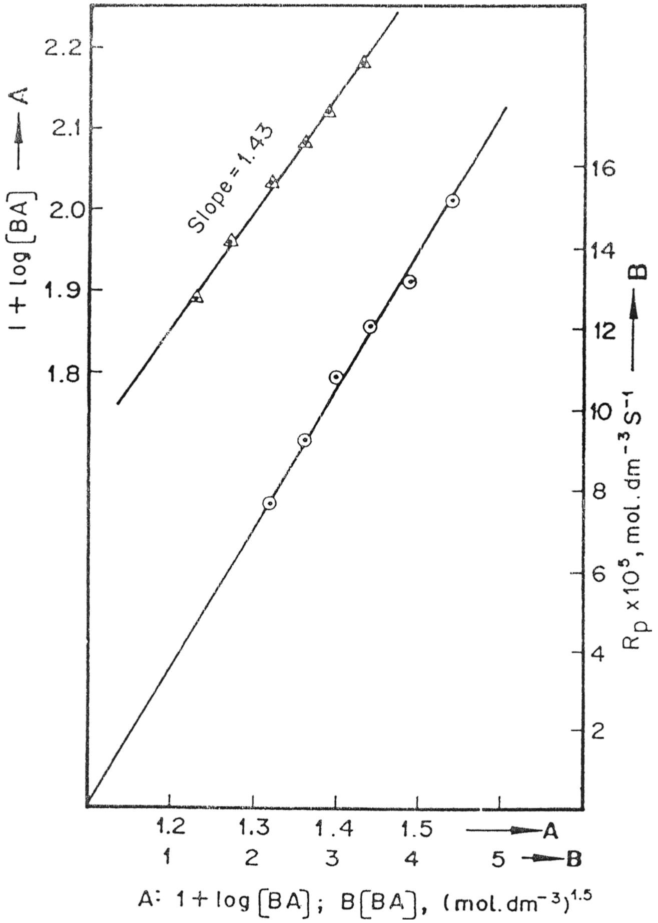

FIGURE 3 BA-PPBDMAC-$K_2S_2O_8$ system variation of [BA].

or the occlusion phenomena [14,15] occurring in the polymerization reaction. Since the reaction is carried out at 60°C, the incidence of occlusion cannot account for the higher monomer order. The order of 0.5 with respect to initiator instead of zero order rules out the possibility of primary radical termination. Hence, the higher monomer order in the present study may be attributed to the dependence of initiation rate on monomer concentration. It is also to be considered that variation in diffusion-controlled termination rate significantly influence monomer order even at very small polymerization conversion [16]. Any one or both of these factors could have contributed to the monomer exponent of 1.5 in the polymerization reaction of butyl acrylate.

Effect of Phase Transfer Catalyst Concentration on Rate of Polymerization

The dependence of rate of polymerization on concentration of phase transfer catalyst propiophenonebenzyldimethylammonium chloride was examined by varying the concentration of phase transfer catalyst in the range 0.003 to 0.013 mol dm^{-3} at fixed concentration of monomer, potassium peroxydisulfate, acid strength, ionic strength, and volume fraction of aqueous phase. Rate of polmerization increases with increase in the concentration of the phase transfer catalyst and the results are plotted in Figure 4. From the slope of the linear plot obtained by plotting log R_p versus log [PTC], the order with respect to [PTC] is found to be 0.5. The observed order of 0.5 is confirmed from the straight line passing through origin in a plot of R_p versus $[PTC]^{0.5}$. Polymerization did not occur in the absence of phase transfer catalyst even after several hours.

Effect of Acid and Ionic Strength on Rate of Polymerization

Variation in either acid or ionic strength of the medium had no discernable effect on the rate of polymerization.

Effect of Variation of Volume Fraction of Aqueous Phase on Rate of Polymerization

Polymerization reactions were conducted with a constant volume of organic phase and different volumes of aqueous phase ($V_w/V_o = 0.17$ to 1.0) at fixed concentration of monomer, potassium peroxydisulphate, phase transfer catalyst, acid strength, and ionic strength. A small increase in rate of polymerization was observed with an increase in

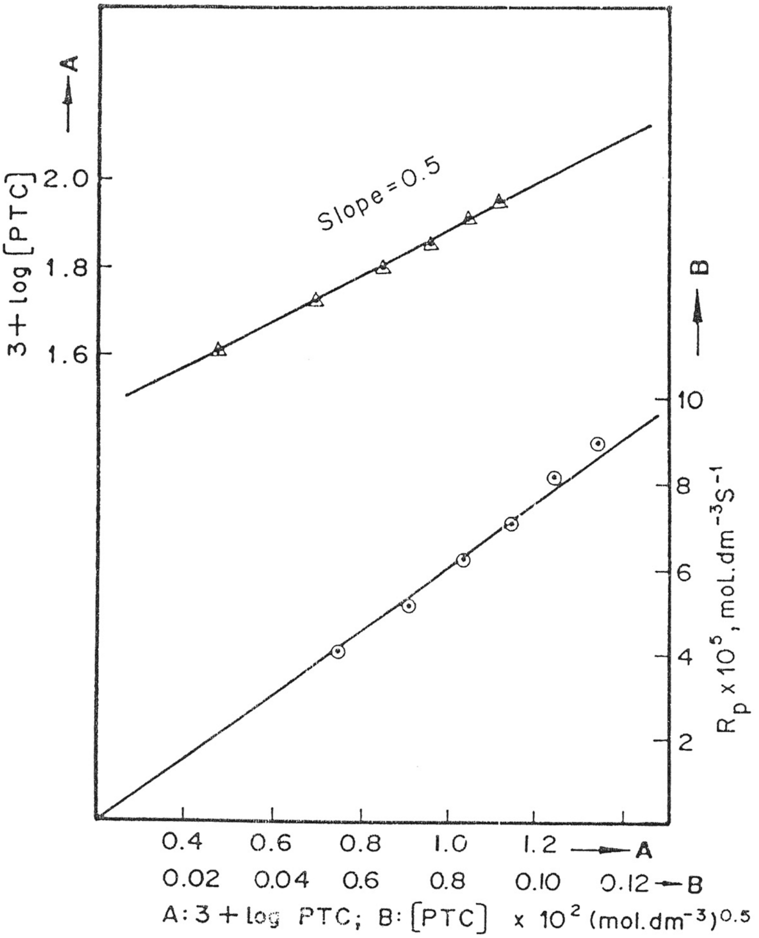

FIGURE 4 BA-PPBDMAC-K_2 S_2 O_8 system variation of [PPBDMAC].

the volume of aqueous phase. From the slope of linear plot of log R_p versus log(V_w/V_o) in Figure 5, the reaction order with respect to (V_w/V_o) was found to be 0.08.

Effect of Solvent Polarity on Rate of Polymerization

An increase in polymerization rate was observed with an increase in the polarity of the solvent employed. For example, when polymerization of butyl acrylate was conducted in three different solvents such as cyclohexane, ethyl acetate, and cyclohexanone, an increase in rate of

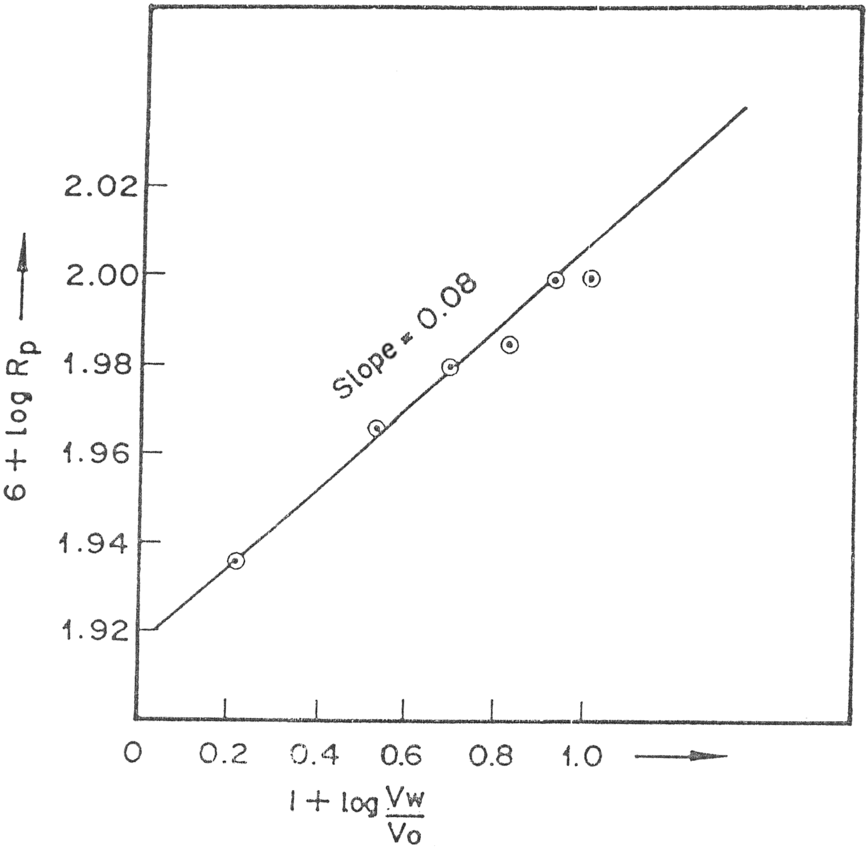

FIGURE 5 BA-PPBDMAC-$K_2S_2O_8$ system variation of aqueous phase volume.

polymerization was observed (Table 1). This may be attributed to the greater transportation of PDS to organic phase due to increasing solvent polarity.

Effect of Temperature on Rate of Polymerization

The effect of variation of temperature in the range 50 to 65°C on the rate of polymerization of butyl acrylate was studied at fixed concentration of monomer, initiator, catalyst, acid strength, ionic strength, and aqueous phase volume. The rate of polymerization increases with temperature. The activation energy for the overall rate of polymerization has been calculated from the slope of the Arrhenius plot of log R_p versus 1/T in Figure 6. From the value of activation energy, the other thermodynamic parameters are computed (Table 2).

TABLE 1 Butyl Acrylate-PPBDMAC-$K_2S_2O_8$ System Dependence of R_p on Solvent Polarity

	$R_p \times 10^5$, mol dm^{-3} s^{-1}		
Experimental conditions	Cyclohexane (=2.5)	Ethylacetate (=6.5)	Cyclohexanone (=18.3)
[BA] = 2.0 mol dm^{-3} s^{-1} [$K_2S_2O_8$] = 0.015 mol dm^{-3} s^{-1} [PPBDMAC] = 0.015 mol dm^{-3} s^{-1} Temperature = 60°C	1.13	3.91	10.03

Mechanism and Rate Law

To explain the aforementioned experimental observations, a mechanism has been proposed. The phase transfer catalyst transfers the reactive species, divalent peroxodisulfate, from the aqueous to the

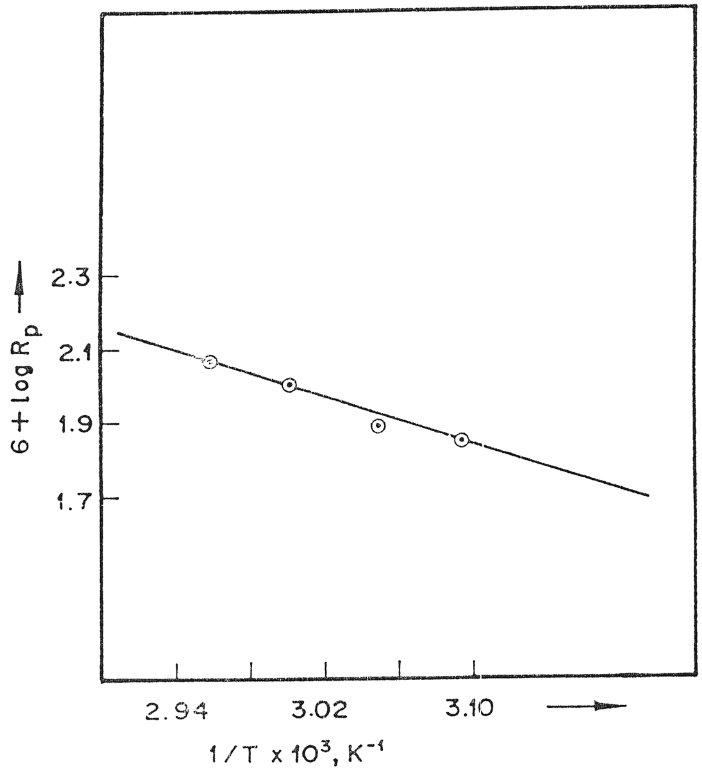

FIGURE 6 BA-PPBDMAC-$K_2S_2O_8$ system arrhenius plot.

TABLE 2 Thermodynamic Parameters

Monomer	Ea, kcal mol^{-1}	S$^{\#}$ eu	H$^{\#}$ kcal mol^{-1}	G$^{\#}$ kcal mol^{-1}
Butyl acrylate	7.82	–53.48	7.08	24.75

organic phase containing the monomer and initiates the reaction. The higher reaction order of the monomer indicates the participation of monomer in the radical forming process, that is, monomer-induced decomposition of ion-paired peroxo disulfate dianion ($Q_2S_2O_8$).

Hence, it is clear that the decomposition of quaternary peroxodisulfate induced by the monomer molecule produces sulfate radical ions that exist in the form of $Q^+SO_4^{\overset{\bullet}{-}}$. The initiation is followed by the propagation steps with bimolecular reaction of two polymer chains as the termination step. Based on these conclusions, the mechanism is given as follows:

a) *Phase Transfer*

$$\underset{(w)}{2Q^+} + \underset{(w)}{S_2O_8^{2-}} \xrightarrow{k} (Q^+)_2S_2O_8^{2-} \tag{1}$$

b) *Initiation*

$$\underset{(o)}{(Q^+)_2S_2O_8^{2-}} + \underset{(o)}{M} \xrightarrow{k_d} M_1 + Q^+SO_4^- \tag{2}$$

$$\underset{(o)}{Q^+SO_4^-} + M \xrightarrow{k_i} \underset{(o)}{M_1\cdot} \tag{3}$$

c) *Propagation*

$$M_1\cdot + M \xrightarrow{k_p} M_2\cdot \tag{4}$$

$$\vdots$$

$$M_{n-1}\cdot + M \xrightarrow{k_p} M_n\cdot \tag{5}$$

d) *Termination*

$$2\,M_n\cdot \xrightarrow{k_t} \text{Polymer} \tag{6}$$

The subscripts (o) and (w) refer to the organic and aqueous phase, respectively. Q refers to the phase transfer catalyst (PPBDMAC).

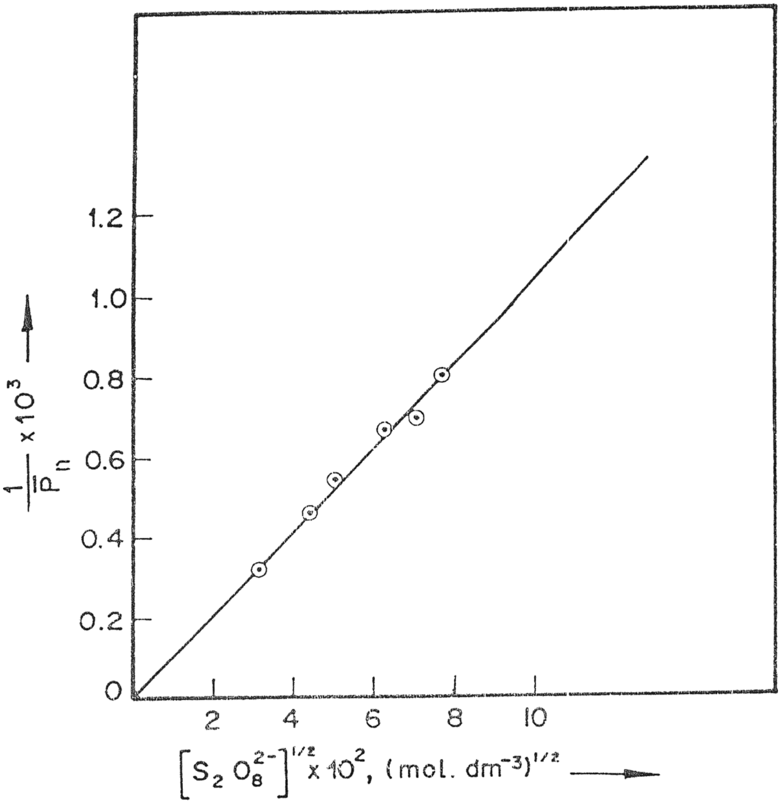

FIGURE 7 BA-PPBDMAC-$K_2S_2O_8$ system dependence of $\overline{P}_n$ on $[K_2S_2O_8]$.

Applying the general principles of free radical polymerization and stationary state hypothesis to the radical species, the rate law for this mechanism can be derived as

$$R_p = k_p\left(\frac{k_dK}{k_t}\right)^{1/2}\frac{[M^\circ]^{3/2}[S_2O_8^{2-}]^{1/2}[Q^+]_{Total}}{1 + K[Q^+]_w[S_2O_8^{2-}]_w} \qquad (7)$$

This equation satisfactorily explains the experimental observations. The kinetic results are supplemented with viscosity studies.

The degree of polymerization of poly(butylacrylate) was evaluated from the intrinsic viscosity data and an inverse square-root relationship is found to exist between the degree of polymerization and initiator concentration. A straight line passing through the origin in a plot of $1/\overline{P}_n$ versus $[K_2S_2O_8]$ (see Figure 7). Provides additional evidence for the proposed mechanism.

CONCLUSION

The kinetic features, such as the rate of polymerization (R_p) of free radical polymerization of butyl acrylate, increase with the increasing concentration of monomer, initiator, catalyst, and aqueous volume fractions. The hydrogen ion concentration and ionic strength of the medium do not show any appreciable effect on the (R_p). The reaction rate increases with increasing temperature.

The reaction order of the polymerization of butyl acrylate is in accordance with the general rate law of radical polymerization with respect to the concentration of initiator and catalyst, which is 0.5 in each case. However, the order with respect to the concentration of the monomer is greater than unity and it is 1.5. The higher reaction order with respect to monomer concentration has been explained in terms of heterogeneous nature of polymerization of butyl acrylate, hydrogen bonding, and so on, and it was concluded that the higher order may be partialy due to the dependence of the initiator rate on monomer concentration.

A mechanism for the polymerization of butyl acrylate has been proposed, taking into account the deactivation of $SO_4^{\cdot}$ radical ions in addition to initiation, propagation, and termination steps. The proposed mechanism has been confirmed by the degree of polymerization and [$K_2S_2O_8$].

REFERENCES

[1] Starks, C. M., *J. Am. Chem. Soc.* **93**, 195 (1971).

[2] Imai, Y., Sato, N., and Li, M., *J. Polym. Sci. Polym Lett.* **17**, 85 (1979).

[3] Imai, Y., Sato, N., and Ueda, M., *Makromol. Chem., Rapid Commun.* **1**, 419 (1980).

[4] Cameron, G. G., Buchan, G. M., and Law, K. S., *Polymer* **22**, 558 (1981).

[5] Rasmussen, J. K. and Smith, H. K., *Makromol. Chem.* **182**, 101 (1981).

[6] Umapathy, M. J., Studies on phase transfer catalyzed polymerization of vinyl monomers, Ph.D. Thesis, Anna University, India (1997).

[7] Umapathy, M. J. and Balakrishnan, T., *J. Polym. Mater.* **15**, 275 (1998).

[8] Valley, R. J., *J. Polym. Sci.* **A3**, 3853 (1965).

[9] Morgan, J. L., *Trans. Faraday. Soc.* **42**, 169 (1946).

[10] Thomas, W. M., Gleason, E. H., and Pellon, J. J., *J. Polym. Sci.* **17**, 275 (1955).

[11] Dainton, F. S., Seaman, P. H., James, D. G. L., and Eaton, R. S., *J. Polym. Sci.* **34**, 209 (1959).

[12] Parts, A. G., *J. Polym. Sci.* **37**, 131 (1959).

[13] Balakrishnan, T. and Jayachandramani, N., *Ind. J. Chem.* **35A**, 201 (1995).

[14] Bamford, C. H., Jenkins, A. D., Symons, M. C. R., and Townsend, M. G., *J. Polym. Sci.* **34**, 181 (1959).

[15] Odian, G. (1981). *Principles of Polymerization*, Wiley Interscience, New York, 2nd ed., p. 190.

[16] Benson, S. W. and North, A. M., *J. Am. Chem. Soc.* **84**, 935 (1962).