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### Kinetics of Phase Transfer Agent-aided Free-Radical Polymerization of Acrylonitrile and Methyl Methacrylate Using Water-Soluble Initiator

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## Kinetics of Phase Transfer Agent-aided Free-Radical Polymerization of Acrylonitrile and Methyl Methacrylate Using Water-Soluble Initiator

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*This paper deals with the kinetics of radical polymerization of acrylonitrile (AN) and methyl methacrylate (MMA), using water-soluble potassium peroxydisulphate initiator in the presence of cetyldimethylbenzylammonium chloride (PTC), at 60°C under oxygen-free atmosphere. The role of concentrations of monomer, initiator, catalyst and temperature on the rate of polymerization were ascertained. Based on the results obtained, a suitable kinetic scheme has been proposed to account for the experimental observation.*

**Keywords:** free-radical polymerization, kinetics, phase transfer catalysis

### INTRODUCTION

Phase transfer catalysis is a technique involving transport of an organic/inorganic salt from a solid/aqueous phase into an organic liquid where reaction with an organic soluble substrate takes place [1–4]. Phase transfer catalysis has emerged as a broadly useful tool due to its significant advantages such as high yield, increased reaction rates, sometimes leading to enhanced selectivity, mild reaction conditions, and compatibility with a broad range of solvents. It has been effectively exploited in the field of synthetic organic chemistry, pharmaceutical chemistry, synthesis of agricultural chemicals, perfumes, and flavorants. In polymer chemistry the application was subdivided into several categories dealing with the production of monomers,

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polymerization, chemistry on already-formed polymers and chemistry at the surface of a polymer/solid. A number of reports on the free-radical polymerization of vinyl monomer under phase transfer catalyst have appeared in the last few years [5–12]. This paper will focus on the use of phase transfer catalysis for free-radical polymerization of acrylonitrile and methyl methacrylate using a water-soluble initiator.

## EXPERIMENTAL

### Materials and Methods

The monomers acrylonitrile (Lancaster, Chennai, India), and methyl methacrylate (Lancaster, Chennai, India) were washed with 5% sodium hydroxide solution and water to remove the inhibitor, dried over  $\text{CaCl}_2$ , and distilled under reduced pressure. The middle fraction was used. Potassium peroxydisulphate (Merck, Mumbai, India) was thrice purified by crystallization from water. The crystals were dried at room temperature in a vacuum desiccator. Methanol and ethyl acetate solvents were purified by standard procedure. Cetyltrimethylammonium chloride (SRL, Mumbai, India) was used as received.

### Polymerization Procedure

Polymerization was carried out without stirring in a closed long Pyrex glass tube. The reaction mixtures consist of equal volumes of aqueous and organic phases. The aqueous phase consists of phase transfer agents, sodium bisulphate (for adjusting the ionic strength) and sulphuric acid (for maintaining acid strength). A calculated quantity of peroxydisulphate was added to the reaction mixture and simultaneously a stopwatch was started. Polymerization started and precipitate formed continuously during polymerization. Polymerization was quenched by pouring each reaction mixture into a beaker containing acidified ice-cold methanol. The polymers formed were isolated by filtering in a sintered crucible (G-4), washed several times with double-distilled water, methanol, and dried in a vacuum oven to constant weight. The rate of polymerization ( $R_p$ ) was determined gravimetrically.

## RESULTS AND DISCUSSION

The kinetics of free-radical polymerization of acrylonitrile and methyl methacrylate using water-soluble peroxydisulphate with single-site phase transfer catalyst were studied under different experimental

conditions to evaluate various parameters, which influence the polymerization rate.

### Steady State Approximation

The rate of polymerization for the acrylonitrile and methyl methacrylate was determined at different intervals of time. Initially, the rate of polymerization increases, then decreases rapidly and then remains constant. The time at which the rate of polymerization remains constant was taken as steady-state rate of polymerization, and was found to be 40 min for both the monomers (Figure 1). The polymerization reaction time was fixed for 40 min to carry out the experiments with variation of other parameters.

### Effect of Monomer Concentration on Rate of Polymerization

The effect of monomer concentration on the rate of polymerization was studied at various concentrations of acrylonitrile and methyl methacrylate ranging from 1.0 to 1.8 mol dm<sup>-3</sup>, keeping the concentrations of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, phase transfer catalyst, ionic strength and pH constant. The reaction order with respect to [monomer] concentration was determined from the slope of log Rp vs. log [monomer] (Figure 2). The reaction order with respect to monomer concentration of acrylonitrile

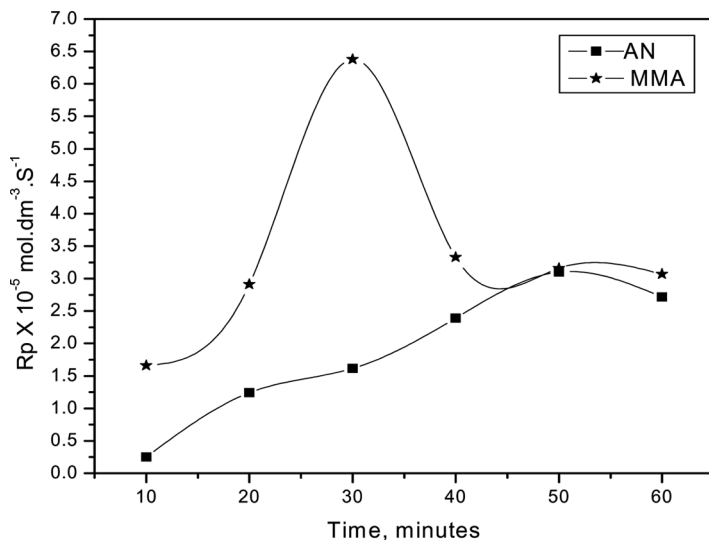
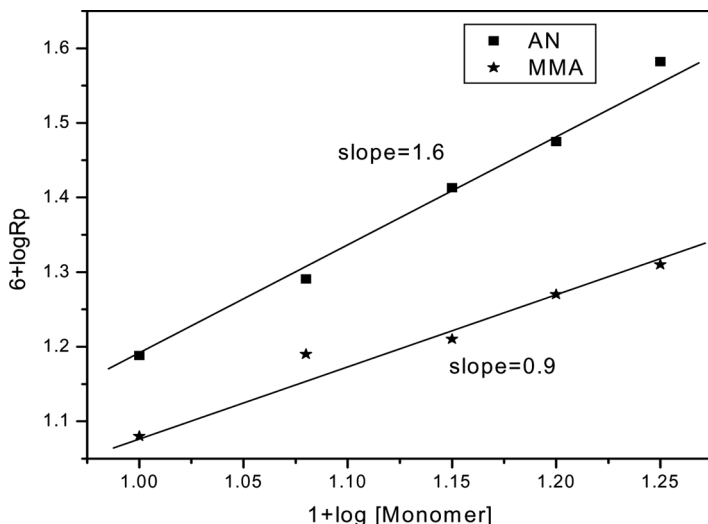
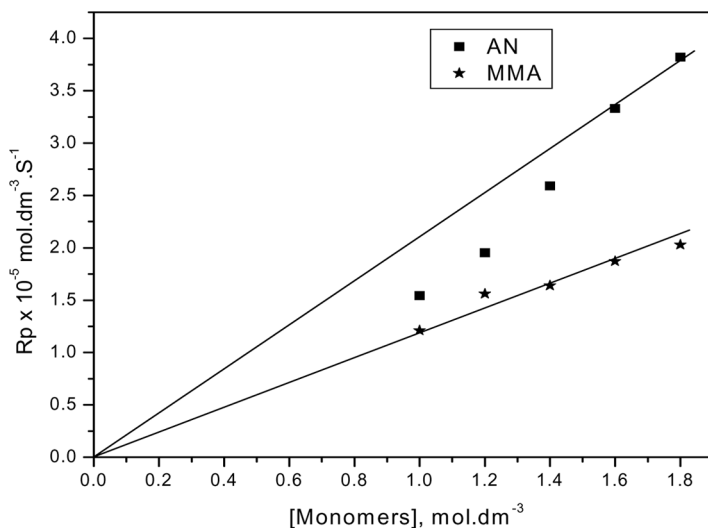


FIGURE 1 Steady-state rate of polymerization.



**FIGURE 2** Effect of monomer concentration on rate of polymerization.

and methacrylate was 1.6 and 0.9, respectively. Further, plots of rate of polymerization ( $R_p$ ) vs.  $[\text{AN}]^{1.6}$  and  $[\text{MMA}]^{0.9}$  were found to be linear passing through the origin, confirming the above observation (Figure 3). An order of unity with respect to monomer concentration



**FIGURE 3** Derivative graph for monomer variation.

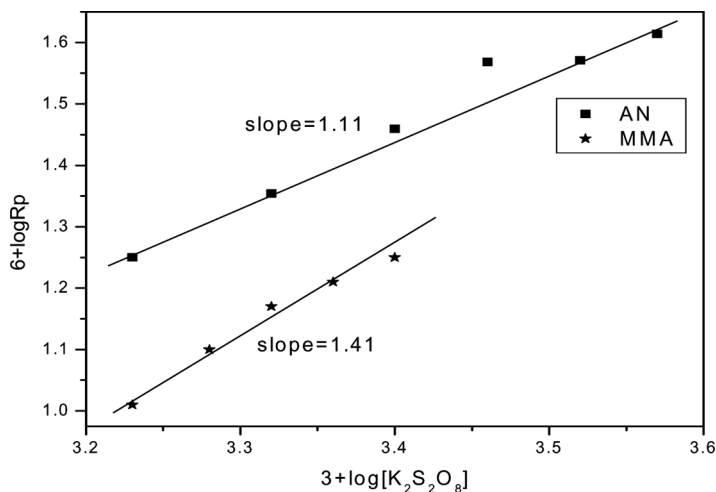
has been reported by many authors [13–16]. The high order with respect to monomer concentration may be due to gel effect [17].

### Effect of Initiator Concentration on Rate of Polymerization

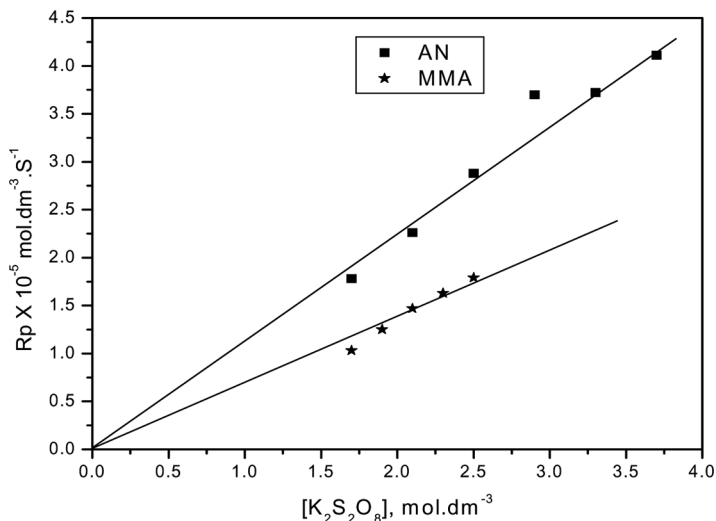
Figure 4 shows the effect of initiator concentration on the rate of polymerization by varying its concentration in the range 1.7 to 3.7 mol dm<sup>-3</sup> for acrylonitrile and 1.7 to 2.5 mol dm<sup>-3</sup> for methyl methacrylate at fixed value of other parameters. For both monomers, the rate of polymerization increases with increased concentration of initiator. The orders with respect to acrylonitrile and methyl methacrylate were found to be 1.11 and 1.41, respectively. A plot of rate of polymerization (Rp) versus concentration of initiator was found to be linear, passing through the origin (Figure 5) for both monomers. The higher than first order of polymerization may be due to either induced decomposition of the initiator or decreased termination rate constant.

### Effect of PTC Concentration on Rate of Polymerization

At constant values of other parameters, the effect of concentration of phase transfer catalyst on the rate of polymerization was studied by varying the concentration of two monomers in the range 1.7 to 3.7 mol dm<sup>-3</sup> for acrylonitrile and 1.7 to 2.5 mol dm<sup>-3</sup> for methyl methacrylate. Rate of polymerization was found to increase with an increase in concentration of methyl methacrylate and decrease in

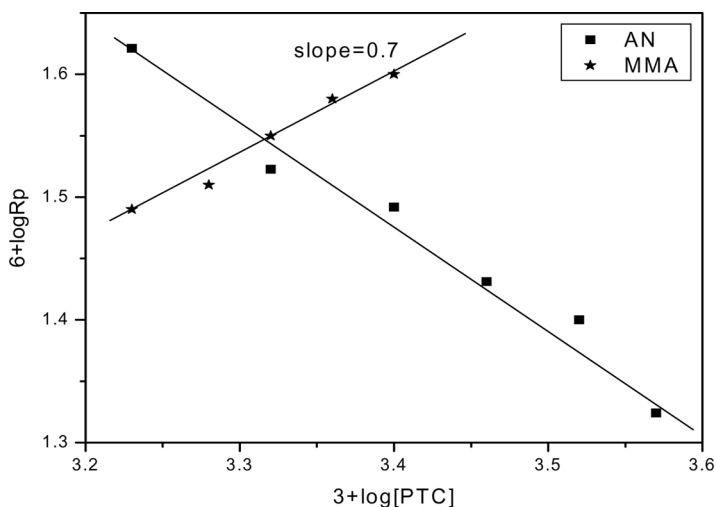


**FIGURE 4** Effect of initiator concentration on rate of polymerization.

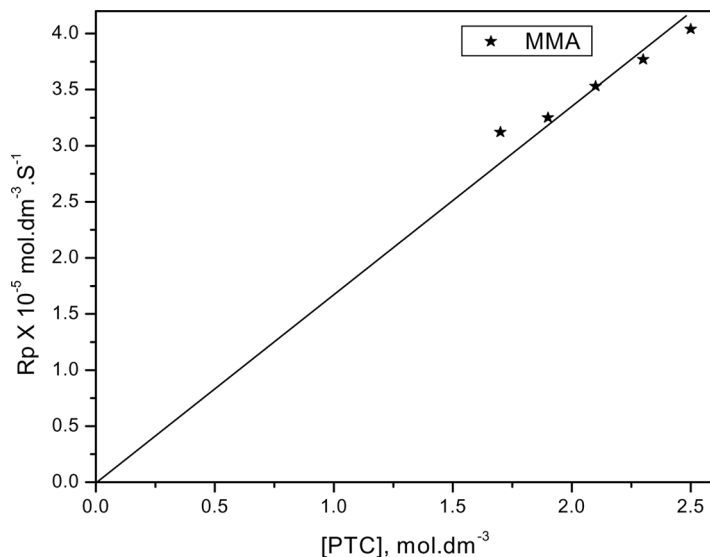


**FIGURE 5** Derivative graph for initiator variation.

the case of acrylonitrile. The order with respect to concentration of catalyst is found to be around 0.7 from a plot of  $\log R_p$  vs.  $\log [PTC]$  for methyl methacrylate (Figure 6). A plot of rate of polymerization ( $R_p$ ) vs.  $[PTC]$  is linear passing through the origin, confirming the above results (Figure 7).



**FIGURE 6** Effect of catalyst concentration on rate of polymerization.



**FIGURE 7** Derivative graph for catalyst variation.

### Arrhenius Plot

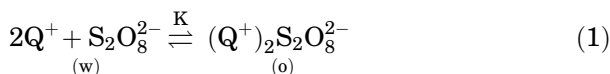
Polymerization reactions were carried out at four different temperatures to evaluate the energy of activation ( $E_a$ ) using the Arrhenius equation (Figure 8). The overall energy of activation for acrylonitrile and methyl methacrylate is  $24.51 \text{ KJ mol}^{-1}$  and  $24.32 \text{ KJ mol}^{-1}$ , respectively.

### Effect of Acid Strength and Ionic Strength on Rate of Polymerization

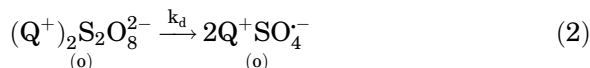
Variation in acid and ionic strength of the medium had no discernable effect on the rate of polymerization for both monomers.

### Kinetic Scheme and Mechanism

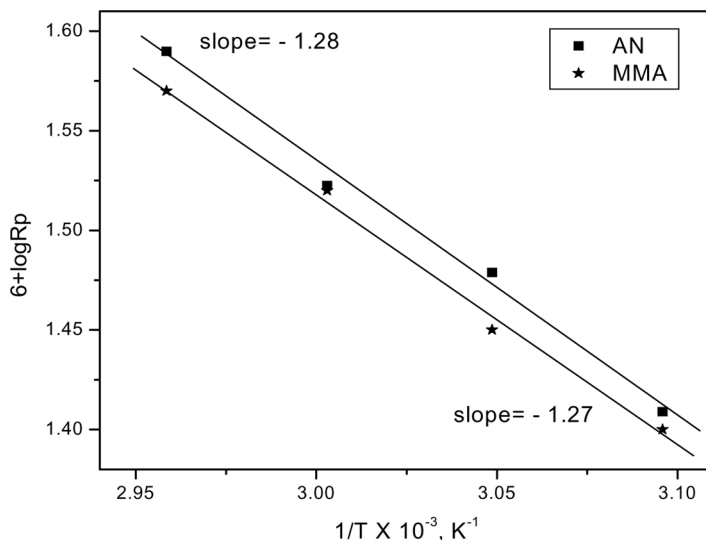
#### Phase Transfer



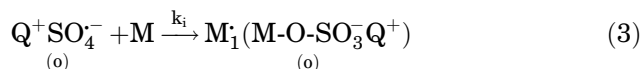
#### Initiation







**FIGURE 8** Effect of temperature on the rate of polymerization.



*Propagation*



.....  
.....



*Termination*



The subscripts (w) and (o) refer to the water and organic phases, respectively. Q refers to the catalyst. This mechanism involves the formation of quaternary ammonium peroxydisulphate complex  $[(\text{Q}^+)_2\text{S}_2\text{O}_8^{2-}]$  in the aqueous phase, which is then transferred to the organic phase. The decomposition of this ion-pair takes place in the organic phase, leading to the formation of  $\text{Q}^+\text{SO}_4^-$ . Applying the

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

$$R_p = k_p \left( \frac{k_d K}{k_t} \right)^{0.5} \left( \frac{[M]^{1.6} [S_2O_8^{2-}]^{1.11} [Q^+]_{\text{Total}}}{1 + k[Q^+]_w [S_2O_8^{2-}]_w} \right) \quad (7)$$

$$R_p = k_p \left( \frac{k_d K}{k_t} \right)^{0.5} \left( \frac{[M]^{0.9} [S_2O_8^{2-}]^{1.41} [Q^+]_{\text{Total}}^{0.7}}{1 + k[Q^+]_w [S_2O_8^{2-}]_w} \right) \quad (8)$$

This expression satisfactorily explains all the experimental results and observations.

## CONCLUSION

The kinetics of free-radical polymerization of acrylonitrile and methyl methacrylate were determined by employing  $K_2S_2O_8$  as a water-soluble initiator and Cetyldimethylbenzylidiammonium chloride as phase transfer catalyst in cyclohexanone/water biphasic system at  $60 \pm 1^\circ\text{C}$  under oxygen-free atmosphere. The rate of polymerization ( $R_p$ ) increases with an increasing concentration of monomer, initiator and temperature. With respect to catalyst, the rate of polymerization increased with an increase in concentration of catalyst for methyl methacrylate and decreased for acrylonitrile. Based on the obtained results, a suitable mechanism has been proposed.

## REFERENCES

- [1] Starks, C. M. *Spec. Pub. R. Soc. Chem.* **77**, 165 (1990).
- [2] Starks, C. M. and Liotta, C. (1994). *Phase Transfer Catalysis: Principles and Techniques*, Academic Press, New York, p 1.
- [3] Dehmlow, E. V. and Dehmlow, S. S. (1993). *Phase Transfer Catalysis*, 3rd ed., Verlag Chemie, Weinheim, p. 1.
- [4] Rasmussen, J. K. and Smith, H. K., *Makromol. Chem.* **182**, 701 (1981).
- [5] Murugesan V., Umamathy, M. J., and Bharathbabu, M., *J. App. Polym. Sci.* **105**, 3634 (2007).
- [6] Murugesan V. and Umamathy, M. J., *J. Poly. Res.* **15**, 27 (2007).
- [7] Murugesan V. and Umamathy, M. J., *Colloid and Poly. Sci.* **286**, 729 (2007).
- [8] Umamathy, M. J., "Studies on Phase Transfer Catalysed Polymerization of Vinyl Monomers," Ph.D. Thesis, Anna University, India (1997).
- [9] Umamathy, M. J. and Balakrishnan, T., *J. Polym. Mater.* **15**, 275 (1998).
- [10] Umamathy, M. J. and Mohan, D., *Ind. J. Chem. Technol.* **8**, 510 (2001).
- [11] Umamathy, M. J., Malaisamy, R., and Mohan, D., *J. Macromol. Sci. Part A: Pure. App. Chem.* **37**, 1437 (2000).
- [12] Savitha, S., Vajjiravel, M., and Umamathy, M. J., *Int. J. Polym. Mater.* **55**, 537 (2006).

- [13] Morgan, L. B., *Trans. Faraday. Soc.* **42**, 169 (1946).
- [14] Thomas, W. M., Gleason, E. H., and Pellon, J.J., *J. Polym. Sci.* **17**, 275 (1955).
- [15] Dainton, F. S., Seaman, P. H., James, D. G. L., and Eaton, R. S., *J. Polym. Sci.* **34**, 209 (1959).
- [16] Parts, A. G., *J. Polym. Sci.* **37**, 131 (1959).
- [17] Gowariker, V. R., Viswanathan, N. V., and Sreedhar, J. (2003). *Polymer Science*, New Age International (P) Limited, New Delhi, p. 71.