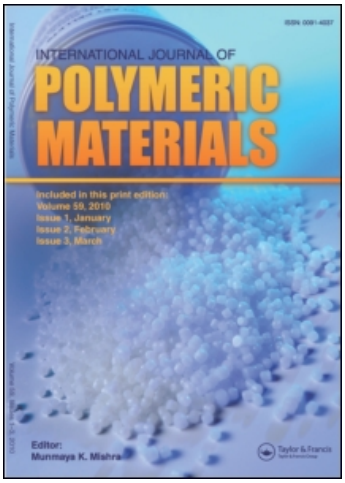

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Phase Transfer Catalyst-Induced Free Radical Polymerization of Acrylonitrile Using Water Soluble Initiator – A Kinetic Study

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In this paper, we report the kinetics and mechanism of phase transfer catalyzed radical polymerization of acrylonitrile (AN) using potassium peroxydisulphate as water-soluble initiator. The polymerization was executed unstirred at 60°C under nitrogen atmosphere. The roles of concentration of monomer, initiator, catalyst, temperature and effect of solvent polarity were evaluated. Based on the results obtained, a viable kinetic scheme and mechanism have been proposed.

Keywords: free radical polymerization, kinetics, phase transfer catalysis

INTRODUCTION

Phase transfer catalysis (PTC) is a technique for conducting heterogeneous reactions where the reagents are located in different phases. It has received widespread attention and attracted considerable scientific and practical interest due to its operational simplicity, mild reaction conditions, high reaction rates, high selectivity, and utilization of inexpensive reagents [1–4]. With a long list of highly desirable benefits achieved in commercial applications, the phase transfer catalysis methodology has been applied to all branches of chemistry, which led to the publication of thousands of research papers and publications [5–10]. The most important phase transfer catalysts, which have been widely used, are quaternary ammonium and phosphonium salts, crown ethers and cryptands.

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This paper will focus on the use of 1,2bis(N,N-dimethyl-N (n-pentyl)ammonium)ethylene dibromide as a phase transfer catalyst for radical polymerization of acrylonitrile using a water-soluble initiator.

EXPERIMENTAL

Materials and Methods

The monomer acrylonitrile (Lancaster, Chennai, India) was washed with 5% sodium hydroxide solution followed by distilled water to remove the inhibitor. The purified monomer was then dried over $CaCl_2$ and distilled under reduced pressure. The middle fraction was used. Potassium peroxydisulphate (Merck, Mumbai, India) was purified by crystallization thrice from double-distilled water. The crystals were dried at room temperature in a vacuum desiccator. Methanol and ethyl acetate solvents were purified by the usual procedure.

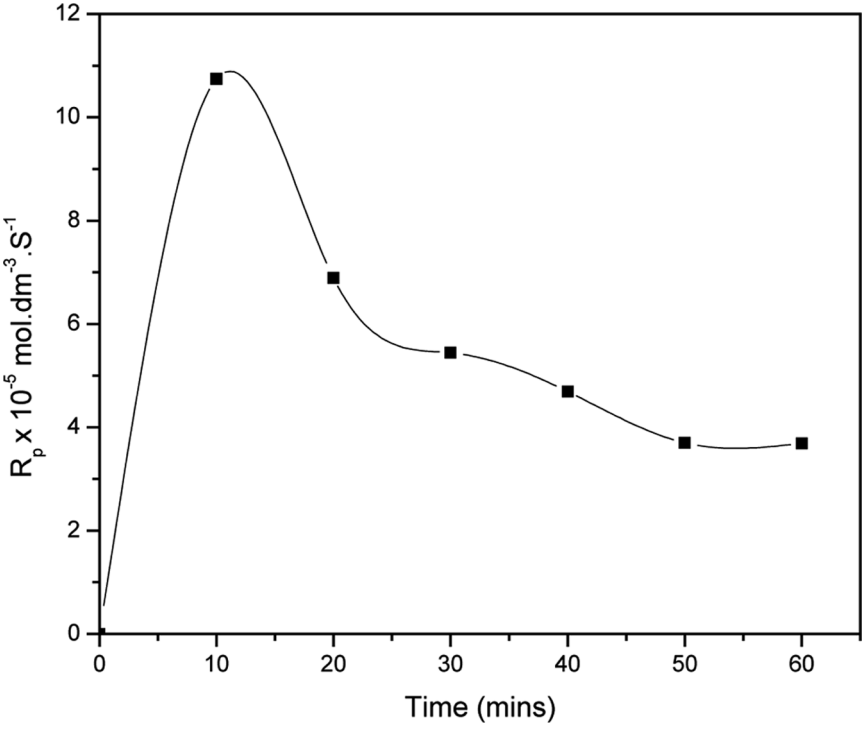

FIGURE 1 Steady-state rate of polymerization.

1,2bis(N,N-dimethylN(n-pentyl)ammonium)ethylene dibromide was synthesized in the laboratory [11,12].

Polymerization Technique

Polymerization was performed unstirred in a closed long Pyrex polymerization tube under nitrogen atmosphere. The reaction mixture contained 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). Polymerization was initiated by transferring a calculated amount of peroxydisulphate to the reaction mixture and a stop watch was simultaneously started. Polymerization was stopped by pouring the reaction mixture into a beaker containing acidified ice–cold methanol. The polymer formed was separated through a sintered crucible (G–4), washed several times with double-distilled water and methanol, and dried in a vacuum oven to

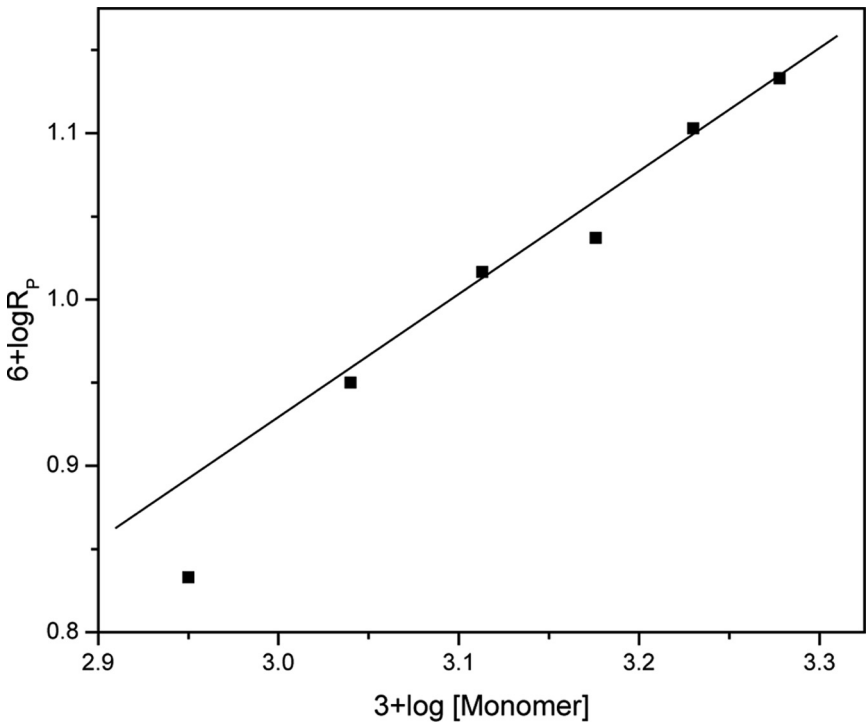

FIGURE 2 Effect of monomer concentration on rate of polymerization.

constant weight. The rates of polymerization (Rp) were determined gravimetrically [13].

RESULTS AND DISCUSSION

The kinetics of free radical polymerization of acrylonitrile using the water-soluble initiator potassium peroxydisulphate with the phase transfer catalyst viz. 1, 2 bis (N,N dimethyl N,(n-pentyl) ammonium) ethylene dibromide at 60°C were studied.

Steady-State Rate on Polymerization

The steady-state rate of polymerization (R_p) was ascertained by carrying out the experiments at different time intervals. The steady-state rate of polymerization of acrylonitrile was obtained after 50 min. A sharp increase in R_p was observed initially which decreased thereafter and then attained a constant value (Figure 1).

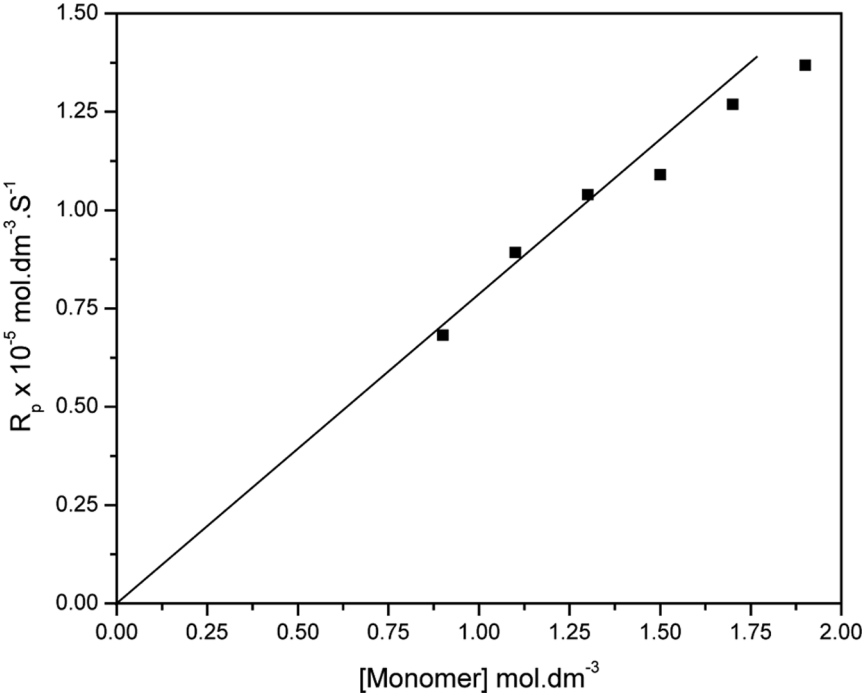

FIGURE 3 Derivative graph for monomer variation.

Influence of Monomer Concentration on the Rate of Polymerization (R_P)

The effect of monomer concentration on the rate of polymerization (R_p) was studied by varying monomer concentration in the range $0.9 - 1.9\,\text{mol dm}^{-3}$ at the fixed concentration of initiator and catalyst. The rate of polymerization increases with increasing monomer concentration. The reaction order was obtained from a plot of log R_p vs. log [AN] and the value was found to be unity (Figure 2). A plot of R_p vs. $[AN]^{1.0}$ is linear passing through the origin (Figure 3) [14,15].

Influence of Initiator Concentration on the Rate of Polymerization (R_P)

With varying concentrations of potassium peroxydisulphate, the effect on R_p has been studied in the concentration range of 0.015 to $0.025\,\text{mol dm}^{-3}$ at fixed concentration of other parameters. The rate of polymerization increased with an increase of initiator concentration

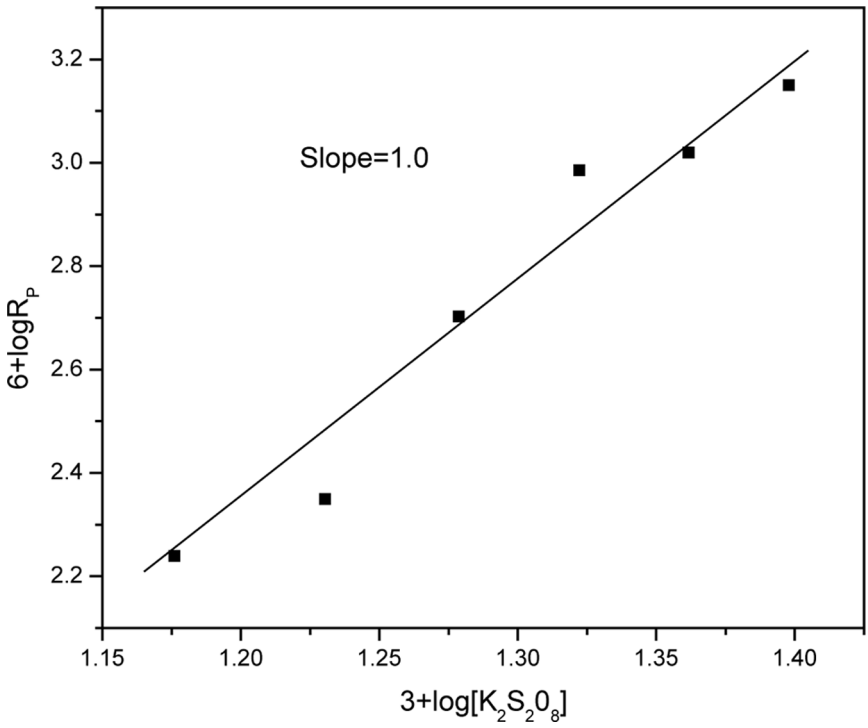

FIGURE 4 Effect of initiator concentration on rate of polymerization.

and the order is found to be unity from plot of log R_p vs. log [PDS] (Figure 4). A plot of R_p vs. $[PDS]^{1.0}$ is also linear passing through the origin (Figure 5).

Influence of Catalyst Concentration on Rate of Polymerization (R_P)

R_p was studied by varying the catalyst concentration from 7.5×10^{-3} to 12.5×10^{-3} mol dm^{-3} at fixed concentration of other parameters. A plot of log R_p vs. log [PTC] was found to increase with an increase in concentration of PTC (Figure 6) and the order was found to be 0.7 (Figure 7).

Influence of Temperature on the Rate of Polymerization (R_P)

The graph (Figure 8) indicates that an increase in temperature from $50 - 65^{\circ}C$ leads to an increase in the rate of polymerization. Activation energy was found to be 6.5 K Joule/mol.

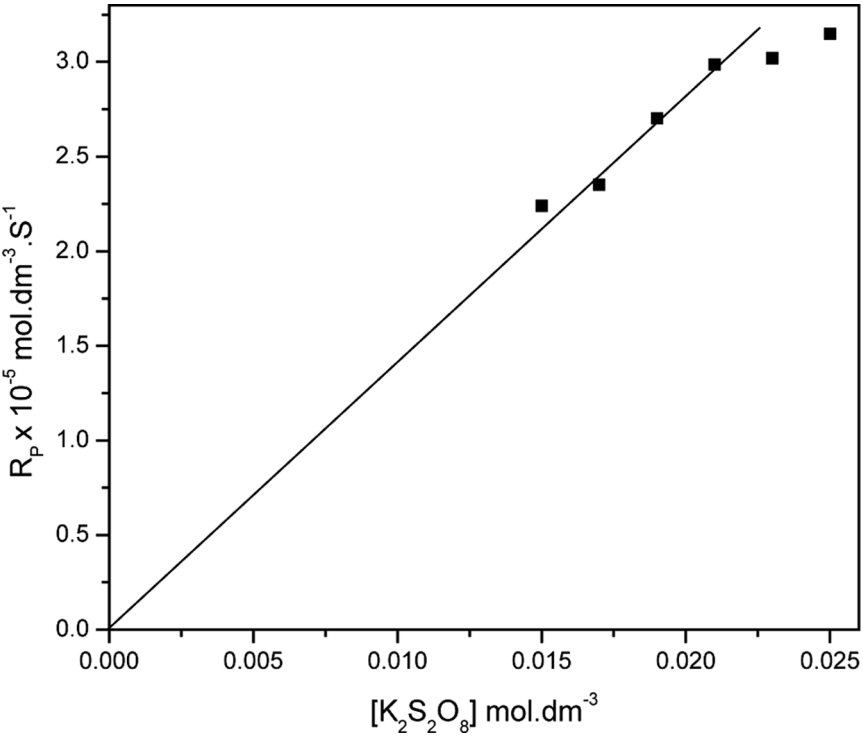

FIGURE 5 Derivative graph for initiator variation.

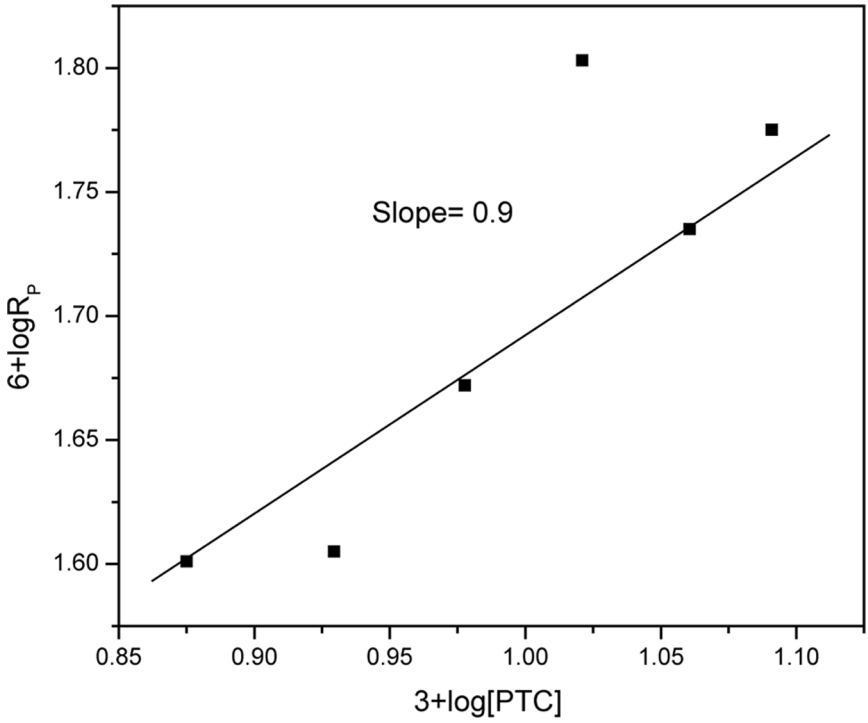

FIGURE 6 Derivative graph for catalyst variation.

Influence of Solvent on the Rate of Polymerization (R_P)

The polarity of the organic solvent plays a vital factor in affecting the rate of polymerization in phase transfer catalysis. The order of relative activities of solvents is

Ethyl acetate > Toluene > Cyclohexane

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 $[(Q^+)_2S_2O_8^{2-}]$ 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 $Q^+SO_4^-$. Applying the general principles of free radical polymerization and stationary-state hypothesis to the radical species, the rate law for this mechanism

Phase Transfer

$$2Q^+ + S_2O_8^{2-} \underset{}{\overset{K}{\rightleftharpoons}} (Q^+)_2S_2O_8^{2-} \quad (1)$$

(w) (o)

Initiation

$$(Q^+)_2S_2O_8^{2-} \xrightarrow{k_d} 2Q^+SO_4^{\bullet -} \quad (2)$$

(o) (o)

$$Q^+SO_4^{\bullet -} + M \xrightarrow{k_i} M_1^{\bullet} \ (M\text{-}O\text{-}SO_3^-Q^+) \quad (3)$$

(o) (o)

Propagation

$$M_1^{\bullet} + M \xrightarrow{k_p} M_2^{\bullet} \quad (4)$$

.....

.....

$$M_{n-1}^{\bullet} + M \xrightarrow{k_p} M_n^{\bullet} \quad (5)$$

Termination

$$2M_n^{\bullet} \xrightarrow{k_t} \text{Polymer} \quad (6)$$

SCHEME 1 Kinetic Scheme and Mechanism.

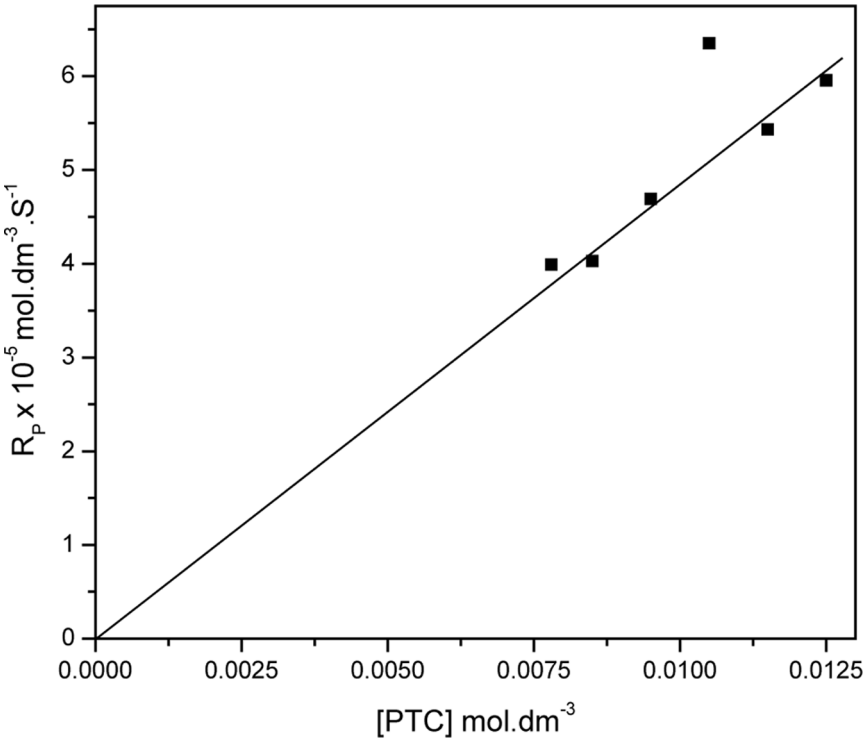

FIGURE 7 Effect of catalyst concentration on rate of polymerization.

can be derived as:

$$R_P = k_p\left(\frac{k_d K}{k_t}\right)^{0.5}\left(\frac{[M]^{1.0}[S_2O_8^{2-}]^{1.0}[Q^+]_{Total}}{1 + k[Q^+]_w[S_2O_8^{2-}]_w}\right) \quad (7)$$

This expression satisfactorily explains all the experimental results and observations.

CONCLUSION

In this work the kinetics and mechanism of the radical polymerization of acrylonitrile were studied by employing a potent phase transfer catalyst. The unstirred polymerization reactions were carried out under nitrogen at a constant temperature of 60°C in ethyl acetate/water biphase media using potassium peroxydisulphate as the water-soluble initiator.

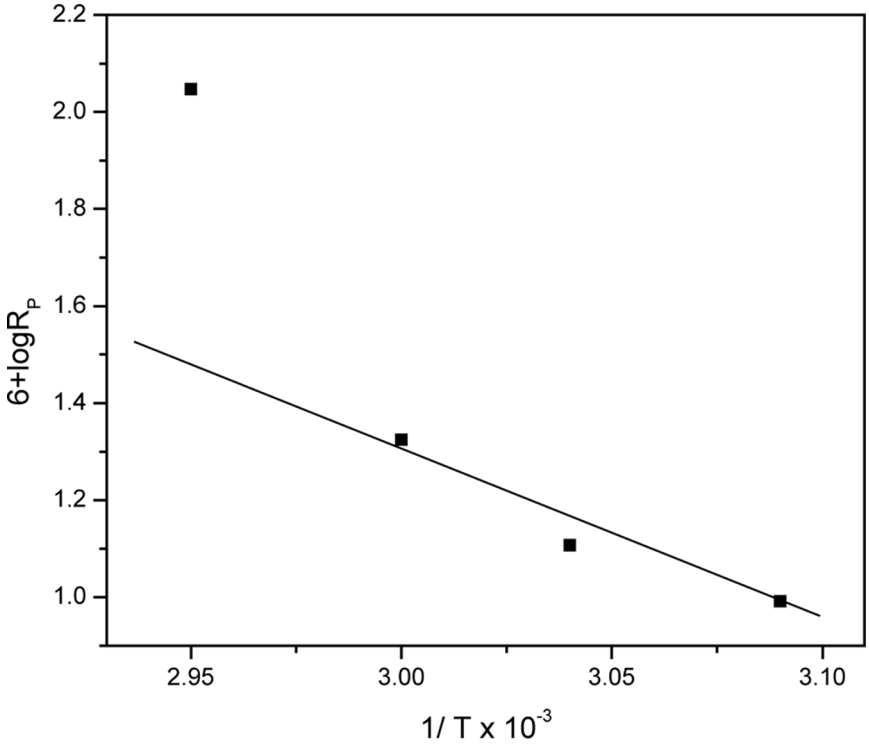

FIGURE 8 Effect of temperature on the rate of polymerization.

Kinetic variations in the polymerization of acrylonitrile has been performed using 1,2bis(N,N-dimethyl-N(n-pentyl)ammonium)ethylene dibromide as PTC. The dependence of the rate of polymerization on various experimental conditions, such as different concentrations of monomer, initiator, PTC and temperature is discussed. The order for acrylonitrile was found to be 1.0. The order with respect to the initiator for acrylonitrile was found to be 1.0. Activation energy for the polymerization of acrylonitrile was calculated from the slope of log R_p vs. 1/T in the temperature range 55 to 70°C. The dependence of the rate of polymerization on solvent polarity is dealt with.

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