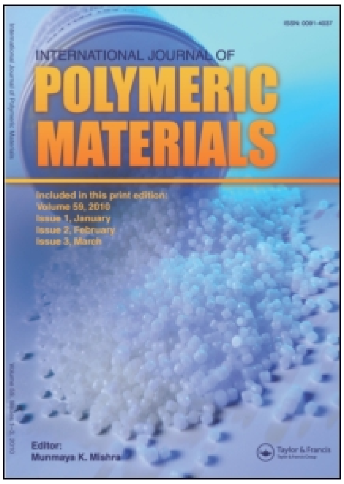

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Free Radical Polymerization of Acrylonitrile Using Potassium Peroxy Disulphate Initiator and a Phase Transfer Catalyst

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Free radical polymerization of acrylonitrile with the di-site phase transfer catalyst 1,4-bis(tetramethylhexyl)ethylenediammonium bromide (TMHEDAB) was investigated using the water-soluble initiator PDS (potassium peroxydisulphate) and water-insoluble solvent ethylacetate in an aqueous-organic biphase system at 60 ± 1°C under nitrogen atmosphere at fixed pH and ionic strength. Rp increased with the increase in concentration of the monomer, initiator and catalyst. The order of R_p, with respect to monomer and catalyst concentration was found to be unity and with respect to initiator was found to be 0.5. A suitable mechanism has been proposed and its significance was discussed. The polymers obtained were characterized by spectral studies such as FTIR, ^{1}H-NMR, XRD, DSC, and TGA.

Keywords: free radical polymerization, kinetics, phase transfer catalysis

INTRODUCTION

The phase-transfer catalysis (PTC) is widely used in industrial application in the synthesis of various organic chemicals such as dyes, pharmaceuticals, perfumes, flavorants, agricultural chemicals, monomers, polymers, and for many other applications, and thus shows a plausible growth in the chemical field. Free radical polymerization of acrylonitrile (AN) is carried out applying this technique. Many industrial applications have been carried out based on enhanced reaction rates, high yields of products and the convenience found with this method. Nontoxicity, excellent performance, thermal

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stability, safety and ecofriendliness are all some of the characteristics of a phase transfer catalyst, which prompted us to make an investigation in free radical polymerization of AN with the di-sited phase transfer catalyst (TMHEDAB) using $K_2S_2O_8$ as an initiator.

An interesting aspect of phase transfer catalysis is reactions in which the reactants are highly immiscible with each other and when continued for unlimited periods of time are unable to proceed to completion, but upon adding a pinch of PTC, they react completely and also produce the desired results. This occurs by the transfer of the nucleophilic anion from the aqueous phase to the organic phase with the help of the PTC, which is lipophilic in nature. The choice of organic solvent and an anion, structure of the catalyst and degree of hydration of anions are some of the factors that affect the reactivity of a phase transfer catalyzed reaction. These reactions were reviewed by Starks and Liotta [1] and Dehmlow and Dehmlow [2] in detail. Two main reactants, one being an organic substrate dissolved in an organic solvent and the other being an organic or inorganic salt from an aqueous phase, are involved in phase transfer catalysis. PTC forms a complex [3–5] with the initiator in the aqueous phase and carries it to the organic phase in order to perform the reaction.

Quaternary salts have the general formula $[Q^+]_nX^{n-}$, where Q^+ represents an organically soluble residue of a phase transfer agent and X^{n-} represents the anionic residue of the initiator which is capable of producing free radicals [6–13] and n is an integer, usually 1 or 2. In this work, a kinetic study of free radical polymerization of AN using potassium peroxydisulphate as an initiator is performed and a suitable mechanism is proposed [14]. The polymers are characterized [15–17] and confirmed by various spectral techniques (FTIR, NMR, XRD, DSC and TGA).

MATERIALS AND METHODS

The monomer acrylonitrile, potassium peroxydisulphate, methanol and ethylacetate were purified by standard procedures. The phase transfer catalyst, 1,4-bis(tetramethylhexyl)ethylenediammonium bromide [18] was involved in the free radical polymerization of AN.

Polymerization Procedure

Under undisturbed conditions, the polymerization procedure was earned out at 60 ± 1°C in an oxygen-free atmosphere with equal volumes of aqueous and organic phases (10 ml each). PTC, initiator, potassium bisulphate for maintaining ionic strength and sulphuric acid for maintaining uniform acid strength are all in the aqueous phase, and monomer dissolved in solvent is in the organic phase. The polymerization reaction was carried out in a N_2 atmosphere by adding initiator of known concentration to the reaction mixture. As soon as the initiator was added, polymerization started and precipitation of polymer was observed. The reaction was arrested by pouring the reaction mixture into ice-cold methanol. In case of colloidal polymer formation, the polymer was coagulated by the controlled addition of a few drops of concentrated HC1. The polymers formed were then filtered quantitatively through a G-4 sintered crucible, washed several times with distilled water followed by anhydrous methanol and finally dried at 50°C in a vacuum oven to constant weight.

Rate Measurements

From the molecular weight of the monomer used, the weight of the polymer obtained in each experiment and the volume of the reaction mixture, rate of polymerization (Rp) was calculated from the equation.

$$R_\mathrm{p} = 1000 * \mathrm{W/V.t.M}$$

where W is the weight of the polymer in g, M is the molecular weight of the monomer, V is the volume of the reaction mixture in ml, and t is the reaction time in seconds.

In almost all kinetic studies, the conversion of the polymer was restricted to be within 15 percent as the higher percentage conversion did not obey the above equation. Apparent deviation from linear relationship in the figures may be attributes to gravimetric data handling analysis.

RESULTS AND DISCUSSION

Kinetics of Free Radical Polymerization

The kinetics of free radical polymerization of AN using PDS with TMHEDAB has been studied as follows.

Steady State Rate of Polymerization

Polymerization reactions have been carried out at 60 ± 1°C with AN dissolved in ethylacetate solvent as organic phase and the initiator and PTC in the aqueous phase. By the determination of R_p at different time intervals and by keeping the concentration of monomer, initiator and the phase transfer catalyst constant, the steady state rate of polymerization was ascertained. A sharp increase in R_p was observed initially which then reached a maximum, slightly decreased and thereafter remained constant. The time taken to attain the steady-state rate of polymerization to carry out further experiments with variation in other parameters was found to be 40 min (Figure 1).

Variation of [Monomer] Over R_p

At fixed concentration of all other parameters, the effect of monomer on R_p was studied in the range of 0.9–1.9 mol dm^{-3}. R_p increased with increase in [AN]. Order with respect to the monomer was found to be unity from the graph plotted against $6 + \log R_p$ Vs $3 + \log[AN]$, and the observation was confirmed by plotting R_p vs. [AN]. A plot of R_p Vs. $[AN]^1$ was also found to be linear passing through the origin. The free radicals precipitate from the liquid phase before termination (Figure 2).

Variation of [Initiator] Over R_p

The effect of initiator concentration on R_p was studied by varying the concentration range (0.015–0.025 mol dm^{-3}) at fixed monomer concentrations of AN, PTC and ionic strength. With an increase in the concentration of $K_2S_2O_8$, R_p also showed an increase. The plot of R_p vs. log [PDS] was found to be linear with a slope equal to 0.5 indicating the half order dependence of R_p on $[K_2S_2O_8]$. A plot of R_p

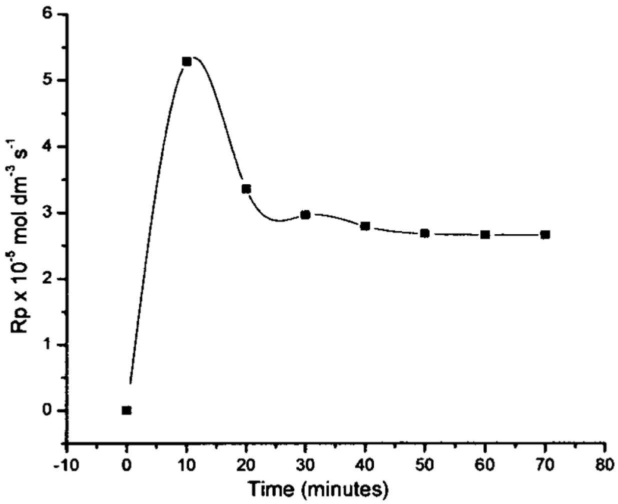

FIGURE 1 Steady state rate of polymerization.

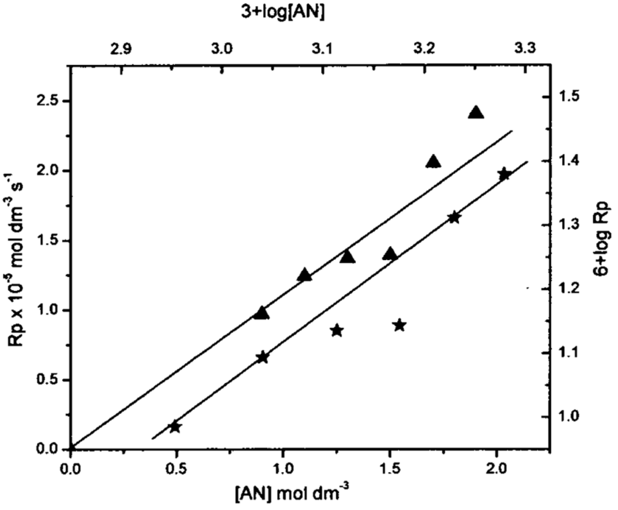

FIGURE 2 Effect of monomer concentrations on R_p.

Vs $[PDS]^{0.5}$ was also found to be linear passing through the origin. Thus, R_p is found to be directly proportional to the square root of initiator concentration (Figure 3).

Variation of [PTC] Over R_p

The effect of concentration of di-site phase transfer catalyst TMHEDAB on the rate of polymerization was studied by varying its concentration from 0.0075–0.0125 mol dm^{-3}. R_p was found to be directly proportional to catalyst concentration. Polymerization was conducted in the range of 60 ± 1°C. Due to the catalytic efficiency, increase in concentration of the PTC further increases the rate of polymerization of AN. Hence the R_p was found to increase with the increase in concentration of TMHEDAB (Figure 4).

Temperature Variation

The effect of temperature on the rate of polymerization was studied and varied from 50–65°C. With an increase in temperature, the R_p also intensified (Table 1). The activation energy for the overall R_p was calculated from the Arrhenius plot of $\log R_p$ vs. 1/T. The thermodynamic parameters such as entropy of activation ($\Delta S^{\#}$), enthalpy of activation ($\Delta H^{\#}$) and free energy of activation ($\Delta G^{\#}$) have also been evaluated (Figure 5).

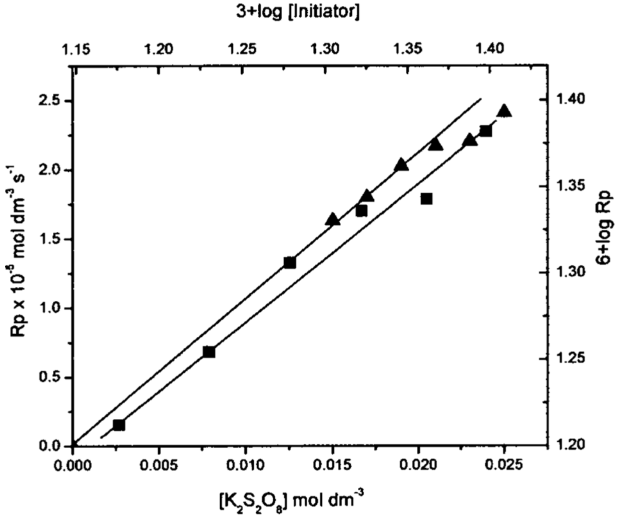

FIGURE 3 Effect of initiator concentrations on the R_p.

Variation of Solvents

The effect of solvent on R_p was examined by carrying out the polymerization reaction for AN in three solvents, ethylacetate, cyclohexane and toluene, having the dielectric constants of 6.02, 2.02 and

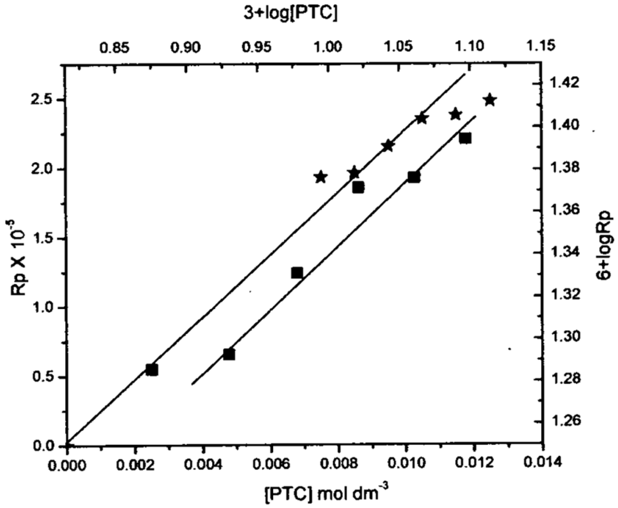

FIGURE 4 Effect of PTC concentrations on R_p.

TABLE 1 Thermodynamic Parameters

Ea, $kJ\,mol^{-1}$	$\Delta G^{\#}$, $kJ\,mol^{-1}$	$\Delta H^{\#}$, $kJ\,mol^{-1}$	$\Delta S^{\#}$, $kJ\,mol^{-1}$
18.075	52.042	20.843	−156.35

1.25, respectively. It was found that the R_p (Table 2) decreased in the following order: ethylacetate > cyclohexane > toluene. The increase in the rate of polymerization may be due to the increase in polarity of the medium, which plays an active role in facilitating greater transfer of the nuclophilic anion from the aqueous phase into the organic phase with the AID of TMHEDAB.

Kinetic Scheme and Mechanism

To explain the aforementioned experimental observations, a mechanism is herein being proposed. PTC transfers the reactive species, divalent PDS, from the aqueous to the organic phase containing the monomer and initiates the reaction. AN induces the decomposition of the initiator and produces radical ions. This initiation is followed by the propagation and termination. Based on these conclusions, the mechanism is given as follows:

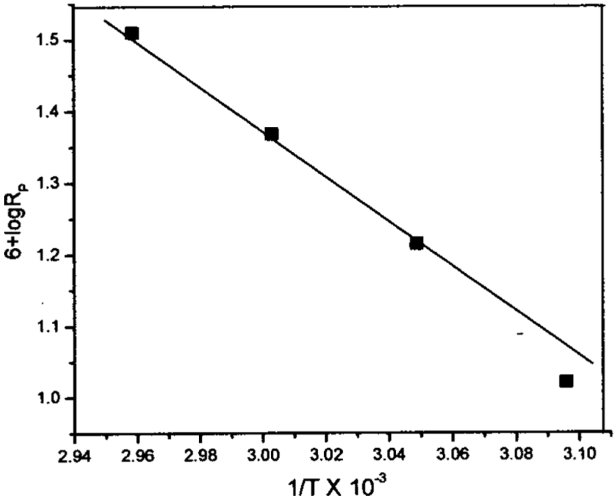

FIGURE 5 Effect of temperature on the R_p.

TABLE 2 Effect of Solvent Polarity on R_p

Experimental conditions	$R_p \times 10^{-5}$ mol dm^{-3} s^{-1}		
	Ethyl acetate	Cyclohexane	Toulene
[AN] = 4.0 mol dm^{-3} [PDS] = 0.2 mol dm^{-3} [PTC] = 0.1 mol dm^{-3} Temperature = 60 ± 1°C	7.195	6.8161	6.5641

Phase Transfer

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

Initiation

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

$$\underset{(o)}{Q^+SO_4^-} + M \xrightarrow{k_i} \underset{(o)}{M_{1^-}} \tag{3}$$

Propagation

$$M_{1^-} + M \xrightarrow{k_i} M_{2^-} \tag{4}$$

$$\vdots$$

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

Termination

$$2M_{n^-} \xrightarrow{k_t} \text{Polymer} \tag{6}$$

In Eqs. (1–6), the subscripts (o) and (w) refer to the organic and aqueous phase, k_i, k_p and k_t all refer to the rate of initiation, propagation and termination constants, respectively, and Q refers to PTC. Applying the general principles of free radical polymerization and steady-state hypothesis to the radical species, the rate law for this mechanism can be derived as

$$R_p = k_p\left(\frac{k_d k}{k_t}\right)^{0.5}\left(\frac{[M^0]^1[S_2O_8^{2-}]^{0.5}[Q^+]^1_{Total}}{1 + k[Q^+]_w[S_2O_8^{2-}]_w}\right) \tag{7}$$

Equation (7) for R_p satisfactorily explains the experimental observations.

Spectral Studies of PAN

FTIR Spectrum

Peak around 2246 cm^{-1} confirms the nitrile group which shows the presence of polymer. Out-of- plane bending of the methylene group is confirmed by the peak at 940 cm^{-1}. Peaks around 2986 cm^{-1} and 2898 cm^{-1} are due to the presence of asymmetric and symmetric stretchings of the methylene group (Figure 6).

^{1}H-NMR Spectrum

Signal at 1.48 ppm corresponds to methylene proton and that positioned around 1.2 ppm confirms the proton of the CH group attached to the nitrile group (Figure 7).

XRD Analysis

The XRD pattern confirms that the polymer is amorphous and not crystalline.

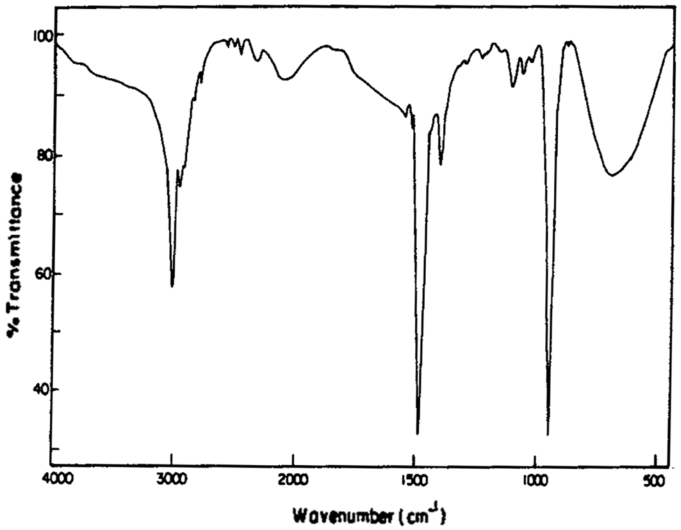

FIGURE 6 FTIR spectrum of PAN.

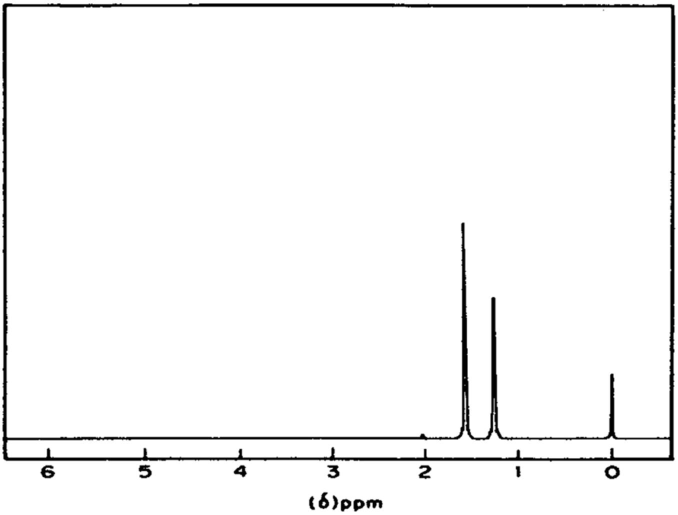

FIGURE 7 ^{1}H-NMR spectrum of PAN.

TGA and DSC Studies

Thermogravimetric analysis was carried out between 30 and 800°C, and the resulting traces indicate a major decomposition around 360°C and then leave a residue (Figure 8). The DSC trace also gave a sharp endotherm around 360°C, matching the decomposition observed in the TGA trace. Hence this endotherm is assigned to the degradation of the polymer.

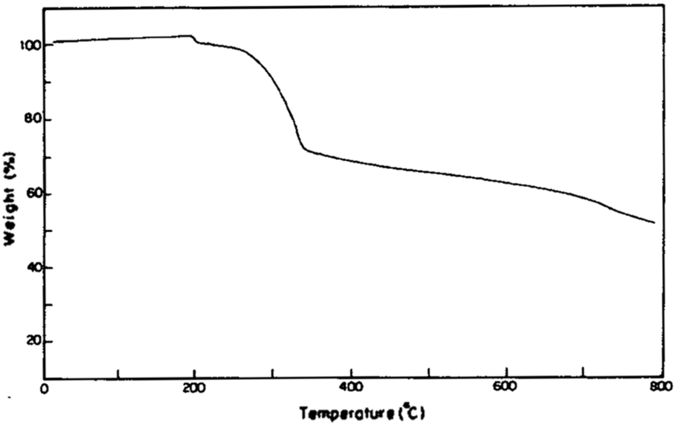

FIGURE 8 TGA of PAN.

CONCLUSION

Free radical polymerization of AN using PDS as an initiator with the di-sited PTC (TMHEDAB) in aqueous organic biphase system was successfully performed and the studies on the rate of polymerization (R_p) over various concentrations of monomer, initiator, catalyst and aqueous phase were carried out. R_p was found to increase with an increase in concentrations of monomer, catalyst and the initiator. Hydrogen ion concentration and ionic strength do not show any appreciable change in R_p. Based upon the kinetic studies, a suitable mechanism has been proposed which was found to exactly match the experimental results. The polymer obtained was characterized and confirmed by spectral techniques such as FTIR, ^{1}H-NMR, XRD, TGA and DSC analyses. Thus, with the results obtained from the lively free radical polymerization of AN using $K_2S_2O_8$ as an initiator and ethylacetate as water-insoluble solvent, the efficiency of the phase transfer catalyzed free radical polymerization of AN using PDS as an initiator and ethylacetate as a solvent in aqueous organic biphase system was found to be satisfactory and rich in industrial applications.

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