

# Polymerization of Acrylonitrile Using Potassium Peroxydisulfate as an Initiator in the Presence of a Multisite Phase-Transfer Catalyst: A Kinetic Study

Murugesan Vajjiravel, M. J. Umapathy, M. Bharathbabu

Department of Chemistry, College of Engineering, Anna University, Chennai 600 025, India

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**ABSTRACT:** In this article, the kinetics and mechanism of the free-radical polymerization of acrylonitrile (AN) using potassium peroxydisulfate (PDS) as a water-soluble initiator in the presence of synthesized 1,4-bis(triethyl methyl ammonium) benzene dichloride (DC-X) as a phase-transfer catalyst (PTC) were studied. The polymerization reactions were carried out under inert and unstirred conditions at a constant temperature of  $60 \pm 1^\circ\text{C}$  in cyclohexane/water biphasic media. The rate of polymerization ( $R_p$ ) increased with an increase in the concentrations of AN, PTC, and PDS. The

order with respect to the monomer, initiator, and PTC was found to be 1.0, 0.5, and 0.5, respectively.  $R_p$  was independent of the ionic strength and pH of the medium. However, an increase in the polarity of the solvent slightly increased the  $R_p$  value. On the basis of the obtained results, a mechanism is proposed for the polymerization reaction. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3634–3639, 2007

**Key words:** kinetics (polym.); phase transfer catalysis; radical polymerization

## INTRODUCTION

Phase-transfer catalysis is a powerful technique involving the transport of an inorganic reagent from a solid or aqueous phase into an organic liquid in which a reaction with an organic-soluble substrate takes place. Its applications have attracted considerable interest because of its excellent performance, simplicity, safety, and ecofriendliness.<sup>1–3</sup>

The study of free-radical polymerization aided by phase-transfer catalysts (PTCs) is a field that has attracted considerable interest in the recent past. A number of single-site-PTC-assisted free-radical polymerizations of vinyl monomers have been reported with peroxy salts as initiators, such as butyl acrylate,<sup>4</sup> acrylonitrile (AN),<sup>5,6</sup> methyl methacrylate,<sup>7,8</sup> glycidyl methacrylate,<sup>9</sup> butyl methacrylate,<sup>10</sup> and methacrylate.<sup>11</sup>

A systematic literature survey has revealed that so far no reports are available in multisite-PTC-assisted free-radical polymerizations of vinyl monomers. This prompted us to investigate the kinetics of the free-radical polymerization of AN using potassium peroxy disulfate as a water-soluble initiator and newly synthesized 1,4-bis(triethyl

methyl ammonium) benzene dichloride (DC-X) as a multisite PTC in cyclohexane/water biphasic media.

## EXPERIMENTAL

### Materials

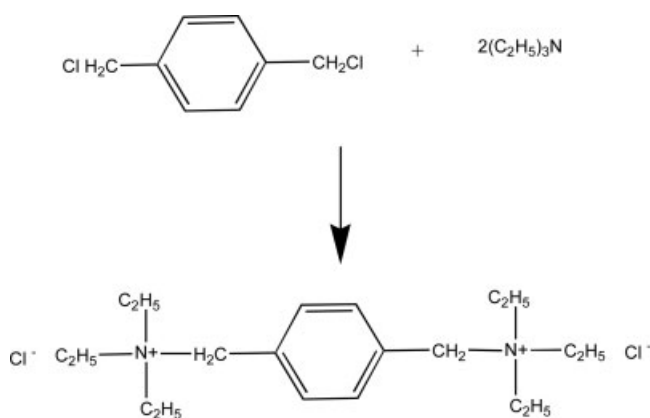
The following chemicals were used as received: AN (Lancaster, Chennai, India), potassium peroxydisulfate (PDS; Merck, Mumbai, India), cyclohexane (New Delhi, India) (CDH), and methanol (Mumbai, India) (SRL).

DC-X (PTC) was synthesized with the following procedure.

### Synthesis of the two-sited PTC (DC-X)

A measured quantity of  $\alpha,\alpha'$ -dichloro-*p*-xylene (0.01 mol) was introduced into a 150-mL flask. Triethylamine (0.01 mol), dissolved in ethanol (30 mL), was then introduced into the flask for the reaction with  $\alpha,\alpha'$ -dichloro-*p*-xylene under an agitation speed of 800 rpm at  $60^\circ\text{C}$  for 24 h. The organic solvent ethanol and triethylamine were stripped in a vacuum evaporator. White precipitates of DC-X were obtained. A white, solid crystal of the product was obtained by recrystallization of the product in an ethanol solvent.<sup>12</sup>

Correspondence to: M. Vajjiravel (chemvel@rediffmail.com).



### Polymerization procedure

The polymerization reactions were carried out in an inert atmosphere at 60°C. The reaction mixture consisted of equal volumes of aqueous and organic phases (10 mL each). The monomer in cyclohexane was the organic phase. The catalyst, sodium bisulfate (for adjusting the ionic strength), and sulfuric acid (for maintaining  $[H^+]$ ) were taken in the aqueous phase. A calculated amount of peroxydisulfate was added to the reaction mixture. The polymerization started, and a precipitate formed continuously during the polymerization.

The reaction was arrested by the pouring of the reaction mixture into ice-cold methanol containing traces of hydroquinone. The polymer was filtered quantitatively through a sintered crucible, washed with methanol and double-distilled water, and then dried in a vacuum oven at 50°C. The rate of polymerization ( $R_p$ ) was determined by gravimetry.

The conversion was restricted to 10% in all kinetic studies because above 10% age kinetics would not obeyed.

$R_p$  was calculated from the weight of the polymer with the following formula:

$$R_p = 1000W/V \times t \times M$$

where  $W$  is the weight of the polymer (g),  $V$  is the volume of the reaction mixture (mL),  $t$  is the reaction time (s), and  $M$  is the molecular weight of the monomer.

### Measurements

The viscosity-average molecular weight ( $M_v$ ) of the polymer was determined in dimethylformamide at  $30 \pm 1^\circ\text{C}$  with an Ubbelohde viscometer via the Mark-Houwink equation:<sup>13</sup>

$$[\eta] = K(M_v)^\alpha$$

where  $K$  is  $20.9 \times 10^{-3}$ ,  $\alpha$  is 0.75, and  $[\eta]$  is the intrinsic viscosity.

From the molecular weight of the polymer, the values of the degree of polymerization ( $\bar{P}_n$ ) were calculated.

## RESULTS AND DISCUSSION

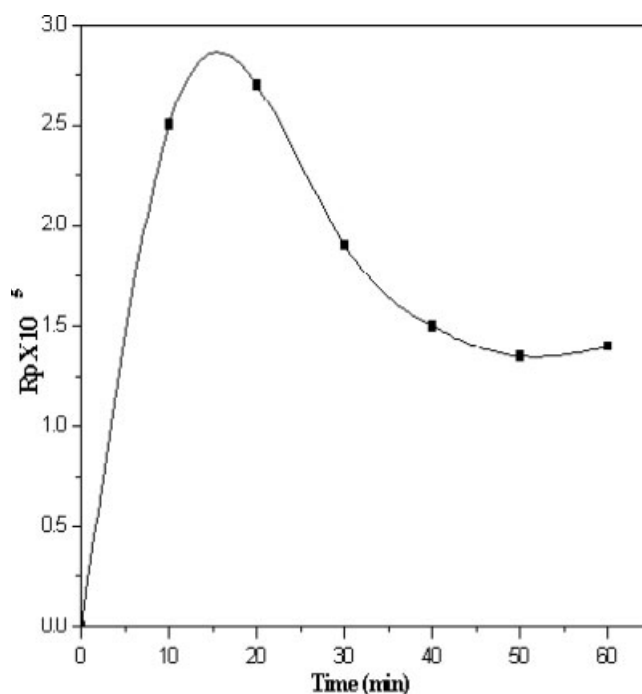
The polymerization of AN initiated by PDS-PTC in a cyclohexane/water biphase was studied under different experimental conditions to evaluate the various parameters that influence the polymerization reaction.

### Steady-state $R_p$

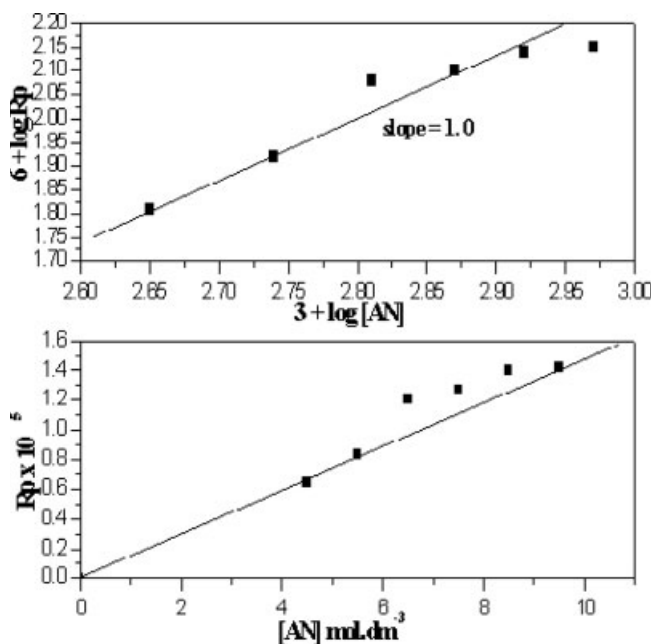
The steady-state  $R_p$  value for AN was studied by the determination of  $R_p$  at different intervals of time. A plot of  $R_p$  versus time shows an increase to some extent, a slight decrease thereafter, and then a constant value. The steady-state  $R_p$  value of AN was obtained at 40 min (Fig. 1).

### Effect of the monomer concentration on $R_p$

The effect of the concentration on  $R_p$  was studied at various concentrations of the monomers, from 0.45 to



**Figure 1** Steady-state  $R_p$  ( $[AN] = 2.0 \text{ mol/dm}^3$ ,  $[K_2S_2O_8] = 2.0 \times 10^{-2} \text{ mol/dm}^3$ ,  $[PTC] = 2.0 \times 10^{-2} \text{ mol/dm}^3$ ,  $[H^+] = 0.5 \text{ mol/dm}^3$ , ionic strength =  $0.2 \text{ mol/dm}^3$ , temperature =  $60 \pm 1^\circ\text{C}$ ).



**Figure 2** Effect of the monomer concentration on  $R_p$  ( $[K_2S_2O_8] = 2.0 \times 10^{-2} \text{ mol/dm}^3$ ,  $[PTC] = 2.0 \times 10^{-2} \text{ mol/dm}^3$ ,  $[H^+] = 0.5 \text{ mol/dm}^3$ , ionic strength =  $0.2 \text{ mol/dm}^3$ , temperature =  $60 \pm 1^\circ\text{C}$ ).

$0.95 \text{ mol/dm}^3$ , with the concentration of PDS (initiator), the PTC, the ionic strength, and the pH kept constant.  $R_p$  increases with an increase in the concentration of the monomer. The reaction order with respect to the monomer concentration was determined from the slope of  $\log R_p$  versus  $\log [AN]$ , and the reaction order with respect to the monomer concentration was found to be 1.0. The plot of  $R_p$  versus  $[AN]$  passing through the origin confirms the previous observations with respect to  $[AN]$  (Fig. 2).

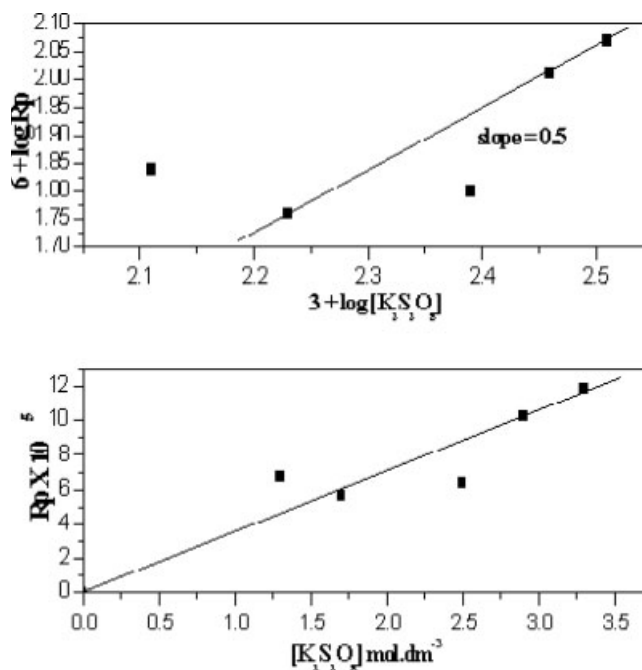
A similar order of unity with respect to the concentration of the monomer has been reported for the polymerization of AN with another PTC using potassium peroxy disulfate as an initiator.<sup>5</sup>

#### Effect of the PDS concentration on $R_p$

At fixed concentrations of other parameters, the effect of the concentration of  $K_2S_2O_8$  on  $R_p$  of AN was studied by the variation of the concentration of  $K_2S_2O_8$  in the range  $0.15\text{--}0.25 \text{ mol/dm}^3$ .  $R_p$  was found to increase with an increasing concentration of  $K_2S_2O_8$  in the AN system. From the plot of  $R_p$  versus  $\log [K_2S_2O_8]$ , the slope was found to be 0.5. As expected, a plot of  $R_p$  versus  $[K_2S_2O_8]$  is linear passing through the origin, supporting the previous deduction (Fig. 3).

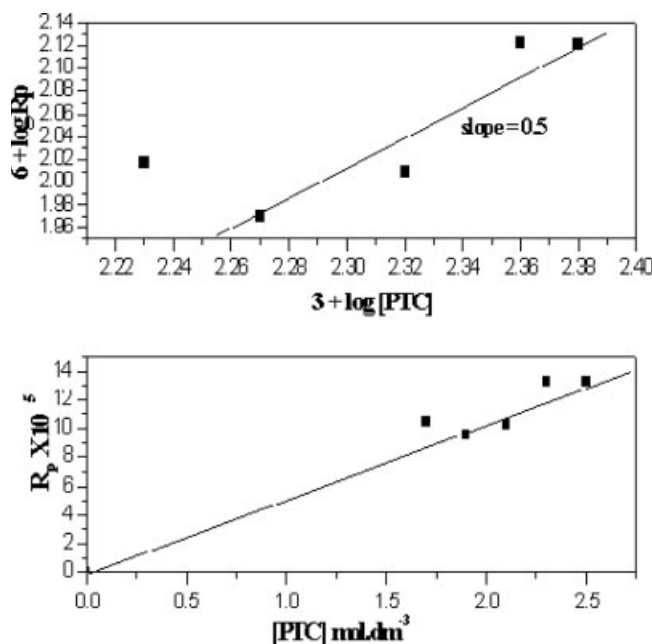
#### Effect of the PTC concentration on $R_p$

The effect of the concentration of DC-X (PTC) on  $R_p$  was studied by the variation of its concentration in the range of  $0.15\text{--}0.25 \text{ mol/dm}^3$  at fixed concentrations of

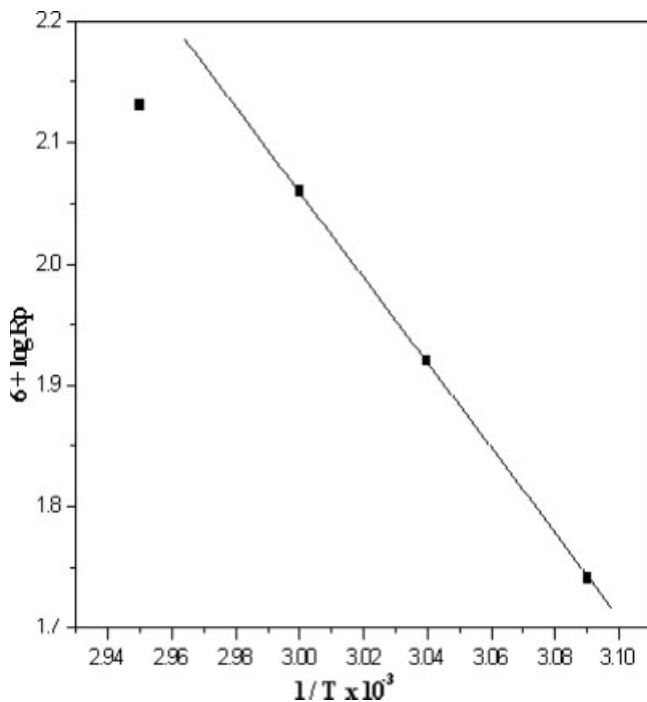


**Figure 3** Effect of the initiator concentration on  $R_p$  ( $[AN] = 2.5 \text{ mol/dm}^3$ ,  $[PTC] = 2.0 \times 10^{-2} \text{ mol/dm}^3$ ,  $[H^+] = 0.5 \text{ mol/dm}^3$ , ionic strength =  $0.2 \text{ mol/dm}^3$ , temperature =  $60 \pm 1^\circ\text{C}$ ).

the other parameters.  $R_p$  increases with an increase in the concentration of PTC. A plot of  $\log R_p$  versus  $\log [PTC]$  was found to be linear with a slope of 0.5 (Fig. 4). Also, the plot of  $R_p$  versus  $[PTC]$  passing through the origin confirms the previous observations with respect to  $[PTC]$ .



**Figure 4** Effect of the PTC concentration on  $R_p$  ( $[AN] = 2.5 \text{ mol/dm}^3$ ,  $[K_2S_2O_8] = 2.0 \times 10^{-2} \text{ mol/dm}^3$ ,  $[H^+] = 0.5 \text{ mol/dm}^3$ , ionic strength =  $0.2 \text{ mol/dm}^3$ , temperature =  $60 \pm 1^\circ\text{C}$ ).



**Figure 5** Effect of the temperature on  $R_p$  ( $[AN] = 2.5 \text{ mol/dm}^3$ ,  $[K_2S_2O_8] = 2.0 \times 10^{-2} \text{ mol/dm}^3$ ,  $[PTC] = 2.0 \times 10^{-2} \text{ mol/dm}^3$ ,  $[H^+] = 0.5 \text{ mol/dm}^3$ , ionic strength =  $0.2 \text{ mol/dm}^3$ ).

#### Effect of the ionic strength on $R_p$

The effect of the ionic strength was observed by the variation of the ionic strength in the range of  $0.4\text{--}0.6 \text{ mol/dm}^3$ . The variation of the ionic strength was found to exert no significant change in  $R_p$ .

#### Effect of the $[H^+]$ variation on $R_p$

The effect of the  $[H^+]$  variation was observed by the variation of the  $H^+$  ion concentration in the range of  $0.1\text{--}0.3 \text{ mol/dm}^3$ . The variation of  $[H^+]$  was found to exert no significant change in  $R_p$ .

#### Effect of the temperature on $R_p$

The effect of the variation of the temperature from  $50$  to  $65^\circ\text{C}$  on  $R_p$  was studied, with the other parameters kept constant.  $R_p$  increases with an increase in the temperature (Fig. 5). The energy of activation ( $E_a$ ) was found to be  $13.27 \text{ kcal/mol}$  with the Arrhenius equation. The thermodynamic parameters were computed with the following equations (Table I):

$$\Delta H^\ddagger = -2.303 \times R \times \text{Slope} \quad (1)$$

$$\Delta S^\ddagger = [\text{Intercept} - 10.32] \times 19.15 \quad (2)$$

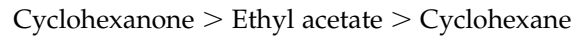
$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (3)$$

The slope and intercept for eqs. (1) and (2) are determined graphically by the plotting of  $\log(R_p \times 1/T)$

versus  $1/T$  (this equation is reached on the basis of the Arrhenius equation).  $R$  is the gas constant.

#### Effect of the solvent polarity on $R_p$

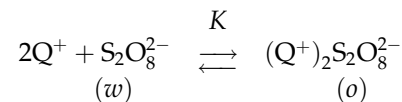
The effect of solvents on  $R_p$  was examined through the polymerization reactions of AN in the solvents cyclohexane, ethyl acetate, and cyclohexanone, which have dielectric constants of  $2.02, 6.02$ , and  $18.03$ , respectively.  $R_p$  decreases in the following order:



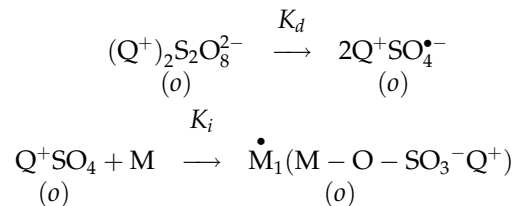
The decrease in  $R_p$  may be due to the increase in the polarity of the medium, which facilitates greater transfer of peroxydisulfate to the organic phase.

#### Mechanism and rate law

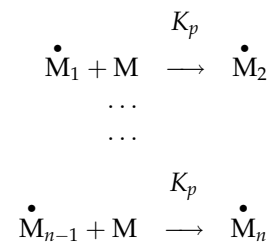
1. Phase transfer:



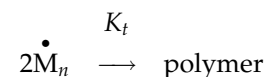
2. Initiation:



3. Propagation:



4. Termination:

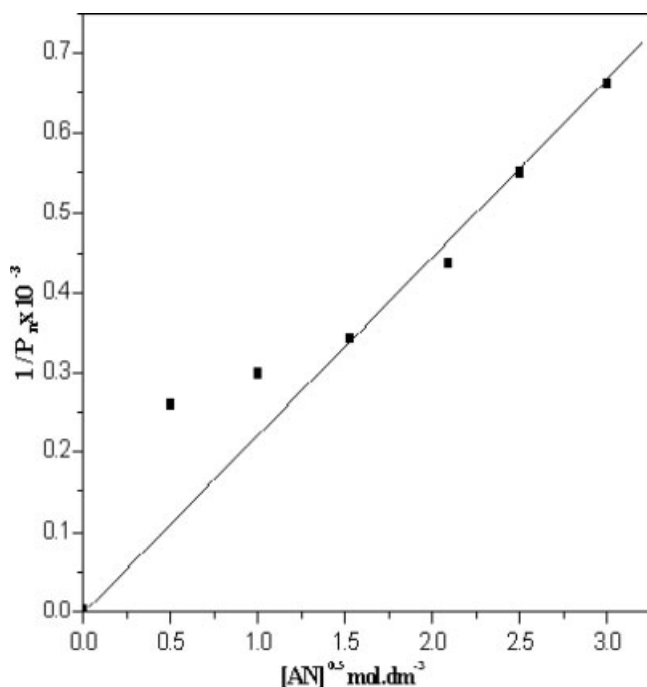


where  $K$  is equilibrium constant,  $K_d$ , the reaction rate constant of decomposition,  $K_i$ , the reaction rate constant of initiation,  $K_p$ , the reaction rate constant of propagation, and  $K_t$ , the reaction rate of termination.

**TABLE I**  
Thermodynamic Parameters

$E_a$ (kcal/mol)	$\Delta G^\ddagger$ (kcal/mol)	$\Delta H^\ddagger$ (kcal/mol)	$\Delta S^\ddagger$ (kcal/mol)
13.27	67.44	45.76	-65.11

$E_a$ , energy of activation.



**Figure 6** AN-PTC-K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> system dependence of  $1/\bar{P}_n$  on [AN].

The subscripts (*w*) and (*o*) refer to the water phase and organic phase, respectively. Q refers to the catalyst.

This mechanism involves the formation of a quaternary ammonium peroxydisulfate complex  $[(Q^+)_2 S_2O_8^{2-}]$  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  $Q^+SO_4^{\bullet-}$ .

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 follows:

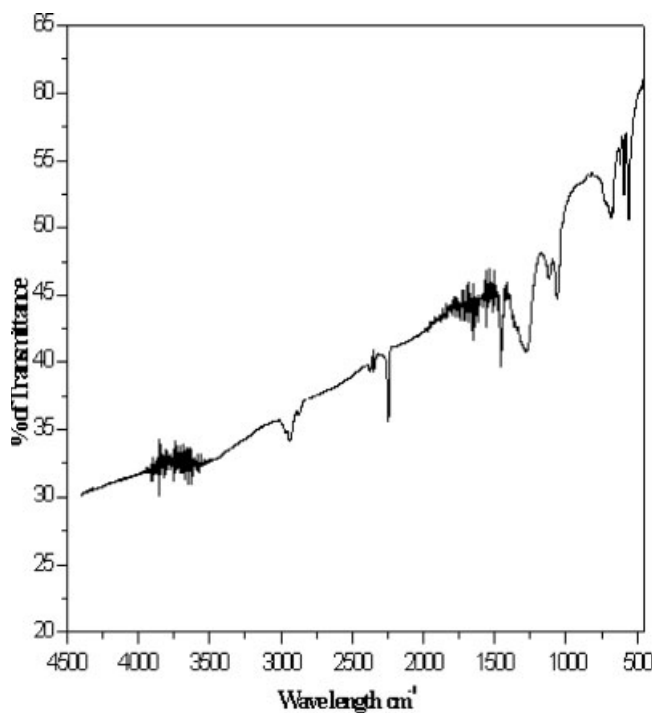
$$R_p = k_p \left( \frac{k_d K}{k_t} \right)_{1+K} \frac{[M][S_2O_8^{2-}][Q^+]_{Total}}{[Q^+]_w [S_2O_8^{2-}]_w}$$

$\bar{P}_n$  of polyacrylonitrile was evaluated from the  $[\eta]$  data, and an inverse square-root relationship was found to exist between  $\bar{P}_n$  and the monomer concentration. A straight line passing through the origin in a plot of  $1/\bar{P}_n$  versus  $[AN]^{0.5}$  [(mol/dm<sup>3</sup>)<sup>0.5</sup>; Fig. 6] provides additional evidence for the proposed mechanism.

### Characterization of the polymer

#### Fourier transform infrared (FTIR) spectroscopy

The FTIR spectrum of polyacrylonitrile was recorded with a PerkinElmer (USA) RX I FTIR spectrometer in the spectral region from 4500 to 500 cm<sup>-1</sup>. Pellets of about 100 mg of KBr powder containing finely grained

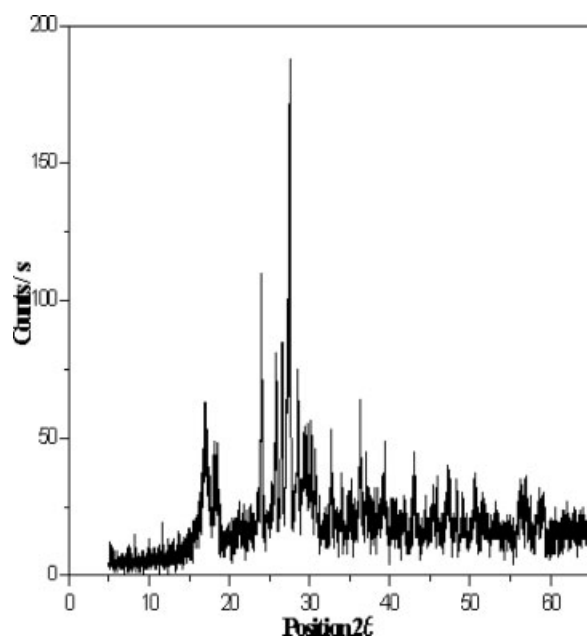


**Figure 7** FTIR spectral analysis of polyacrylonitrile.

powder of a polymer sample were made before the recording. FTIR spectroscopy confirmed a band at 2244 cm<sup>-1</sup> of the nitrile group of polyacrylonitrile (Fig. 7).

#### X-ray diffraction (XRD) analysis

Wide-angle XRD patterns were recorded on a PAN Analytical Xpert PRO instrument (Almelo, The Netherlands) operated at the Cu K $\alpha$  radiation wavelength



**Figure 8** XRD pattern of polyacrylonitrile.

of 1.54 Å at 45 mA and 40 kV. The measurement of the diffracted intensities was made over the angular range of 5–70° at the ambient temperature. The XRD pattern shows the crystalline nature of the polymer (Fig. 8).

### CONCLUSIONS

The free-radical polymerization of AN was successfully performed in the presence of DC-X as a PTC. The kinetic features, such as  $R_p$ , of the free-radical polymerization of AN increase with increasing concentrations of the monomer, initiator, and catalyst. The hydrogen-ion concentration and ionic strength of the medium do not show any appreciable effect on  $R_p$ . The reaction rate increases with increasing temperature. The phase-transfer-catalyzed polymerization of AN is first-order with respect to the monomer and half-order with respect to the initiator and catalyst. On the basis of the obtained results, a suitable mechanism has been proposed. The polymer obtained by the free-radical polymerization of AN was

confirmed by FTIR spectral analysis and XRD analysis.

### References

1. Starks, C. M.; Liotta, C. *Phase Transfer Catalysis: Principles and Techniques*; Academic: New York, 1994.
2. Dehmlow, E. V.; Dehmlow, S. S. *Phase Transfer Catalysis*, 3rd ed.; VCH: Weinheim, 1993.
3. Tagle, L. H. In *Hand Book of Phase Transfer Catalysis*; Sasson, Y.; Neumann, R., Eds.; Blackie: London, 1997.
4. Savitha, S.; Vajjiravel, M.; Umapathy, M. J. *Int J Polym Mater* 2006, 55, 537.
5. Balakrishnan, T.; Damodarkumar, S. *J Appl Polym Sci* 2000, 76, 1564.
6. Umapathy, M. J.; Mohan, D.; Hung, J. *Ind Chem* 1999, 27, 245.
7. Dharmendira Kumar, M.; Konguvel Thehazhnan, P.; Umapathy, M. J.; Rajendran, M. *Int J Polym Mater* 2004, 53, 95.
8. Umapathy, M. J.; Balakrishnan, T. *J Polym Mater* 1998, 15, 275.
9. Umapathy, M. J.; Mohan, D. *J Polym Mater* 1999, 16, 167.
10. Umapathy, M. J.; Mohan, D. *Ind J Chem Technol* 2001, 8, 510.
11. Umapathy, M. J.; Malaisamy, R.; Mohan, D. *J Macromol Sci Pure Appl Chem* 2000, 37, 1437.
12. Wang, M.-L.; Hsieh, Y.-M. *J Mol Catal A* 2004, 210, 59.
13. Brandrup, J.; Immergut, E. H. *Polymer Handbook*; Wiley-Interscience: New York, 1975.