Kinetic Studies on Free Radical Polymerization of Acrylonitrile, Initiated by Chloramine-T/Hydrogen Peroxide Redox System

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ABSTRACT: The Kinetics of polymerization of Acrylonitrile initiated by chloramine-T/H_2O_2 Redox System was studied in aqueous medium in the temperature range of 35–50°C. The effects of variations such as [Monomer], [CAT], [H_2O_2], temperature, and chloramine-T disappearance ($-R_m$) were measured. The effect of some water- miscible organic solvents and surfactants on the rate of polymerization was investigated. The polymerization process is initiated by the free radical arising from oxidation of H_2O_2 by chloramine-T and terminated by the mutual combination of the growing polymer radicals. Based on the kinetic results, a suitable reaction scheme is proposed and discussed for the various rates of polymerization and thermodynamic parameters were evaluated. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 5877–5883, 2006

Key words: acrylonitrile; chloramine-T; H_2O_2; redox; kinetic study

INTRODUCTION

Free radical polymerization is one of the most important commercial processes because of the wide scope of suitable monomer and the simplicity of polymerization conditions.[1] However, it is always considered to be unable to afford polymers with well-defined structures and controlled molecular weights because of the unavoidable irreversible termination of propagating polymer chains such as radical recombination and disproportionation.[2] On the other hand, free radical polymerization would be minimized if a fast equilibrium between propagating radicals and some polymeric chains were established. This is similar to the equilibrium between propagating cations and non-propagating halogen terminated polymer in living carbocationic polymerization. In fact, many controlled radical polymerizations have been achieved based on this idea.[6–13]

H_2O_2 ion coupled with organic substrates, such as thiourea,[14] Fe^{2+},[15] etc, was used to initiate the graft copolymerization of vinyl monomers in aqueous medium. H_2O_2 was used as oxidant in all those, but H_2O_2 was having both oxidant and reductant properties. So, we used H_2O_2 as a reductant in this system.

Chloramine-T is a good oxidizing agent, hence we used it for the polymerization of vinyl monomers.

Thus chloramine-T, the prominent member of the aromatic sulfonyl halo amine series, is the sodium salt of N-chloro-p-toluene sulfonamide. Chloramine-T is a byproduct of saccharine manufacture. It was first prepared by Chattaway.[16] Chloramine-T is soluble in H_2O to an extent of 14 g/100 mL at 25°C. Chloramine-T (Loba-Chem, India) was purified by the method of Morris et al.[17] The purity of compound was checked by iodometric assay of the active halogen and its Fourier transform, ^{1}H and ^{13}C NMR spectra were recorded. An aqueous solution of the compound was standardized by iodometric method and preserved in brown bottles to prevent its photochemical deterioration. Aromatic sulfonyl halo amines have diverse properties and behave as oxidizing and halogenating agents. They are also used as disinfectants and antiseptics. The most important members of this class of compounds are chloramine-T and bromamine-T.

To elucidate these facts, a new system the chloramine-T/H_2O_2 ion redox system was used for the polymerization of acrylonitrile in aqueous medium under deaerated condition at the temperature range of 35–50°C.

EXPERIMENTAL

Preparation of materials

Acrylonitrile (S.D Fine-Chem, India) was washed with 5% NaOH followed by dilute orthophosphoric

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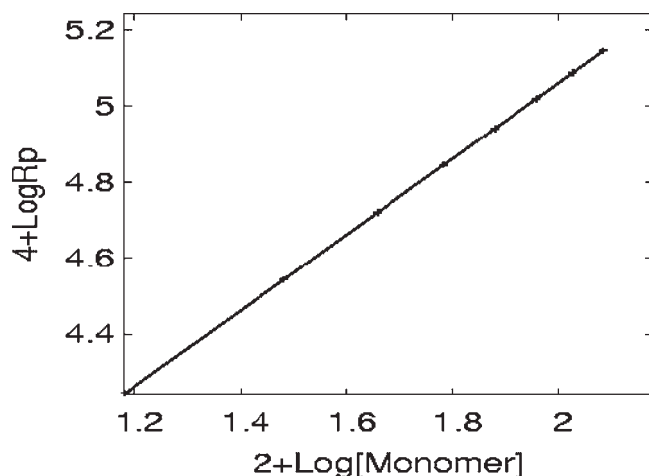
Figure 1 Effect of [Monomer] on the rate of polymerization; [CAT] = 4.0×10^{-2} mol/dm^3, [H$_2$O$_2$] = 12.0×10^{-3} mol/dm^3, [Monomer] = 1.519–15.18×10^{-1} mol/dm^3, Temperature = 323 K.

acid and finally with distilled H$_2$O. It was dried over unhydrous CaCl$_2$ and distilled under reduced pressure in a nitrogen atmosphere. The middle fraction was collected and stored at 5°C.[18] All other chemicals such as chloramine-T (Loba-Chem, India), H$_2$O$_2$ (Merck, India), methanol, ethanol, DMF, cetyltrimethyl ammonium bromide, and triton x-100 were of analytical grade.

A solution of chloramine-T was prepared by triple-distilled water and standardized with standard sodiumthiosulphate solution, using starch as an indicator. Triple-distilled H$_2$O was used throughout the experiment, pure nitrogen obtained by passing through a column of Fieser's solution and distilled H$_2$O was used for the deaeration condition of all experimental systems.

Kinetic measurements

Reactions were performed under the inert atmosphere of nitrogen in Pyrex glass vessels. In a typical kinetic measurement a mixture of solutions containing requisite amounts of inhibitor-free acrylonitrile (0.6075M) monomer, H$_2$O$_2$ (12 0 $\times$ 10^{-3}M), and H$_2$O (to keep the total volume constant) were taken in reaction vessels and thermostated at 50°C. The system was flushed with oxygen-free nitrogen for about 20–30 min to expel the dissolved oxygen. At the end of the duration, chloramine-T solution (about 4.0 $\times$ 10^2 M) was added to the reaction vessels and shaken well. The reaction vessel was then sealed with rubber gasket to ensure inert atmosphere. The polymerization starts without any induction period. After about 60 min the reaction was arrested by adding a known amount of ice-cold water or by cooling the reaction mixture to 0°C.

The polyacrylonitrile was filtered from the reaction mixture using funnels, washed several times with distilled H$_2$O, and dried at 70°C to a constant weight. Finally the rate of polymerization (R_p) and chloramine-T disappearance ($-R_m$) were determined[19] gravimetrically.

Molecular weight determination

The molecular weight M_v of the purified samples of polyacrylonitrile product was determined by viscometry method. A 0.1% solution of the polymer in DMF was filtered through fitted glass filter and placed in an Ubbelhode type suspended level dilution viscometer. The intrinsic viscosity (η) for the reaction mixture was determined and M_v values were calculated using the following Mark-Houvink equation given by Stock Mayer and Cleland[20]: $\eta = (3.335 \times 10^{-4}) \times M_v^{0.72}$ at 30°C for polyacrylonitrile in DMF. The molecular weight of the polymer product under standard conditions was found to be 6.5×10^4. It increases with increase in monomer concentration and decreases with increase in [Chloramine-T], [H$_2$O$_2$], or temperature. This effect is attributed to the fact that increase in [Chloramine-T], [H$_2$O$_2$], or temperature provides more chances for premature termination of growing chain polymer radicals, thus reducing the degree of polymerization. Similar effects have been reported by Behari et al.[21,22]

RESULTS AND DISCUSSION

The polymerization of acrylonitrile initiated by chloromine-T-H$_2$O$_2$ redox system takes place at a measurable rate at 50°C. Although no induction period was observed under deaerated conditions, there exists an induction period if the solution was not deaerated.
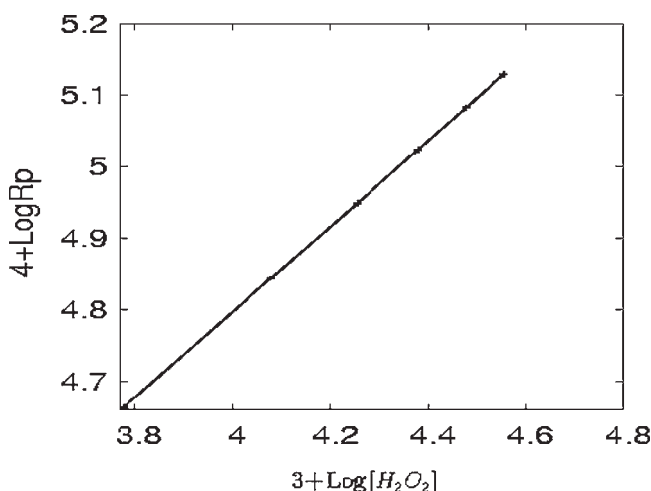

Figure 2 Effect of [H$_2$O$_2$] on the rate of polymerization; [CAT] = 4.0×10^{-2} mol/dm^3, [H$_2$O$_2$] = 6.0–48.0×10^{-3} mol/dm^3, [Monomer] = 6.075×10^{-1} mol/dm^3, Temperature = 323 K.

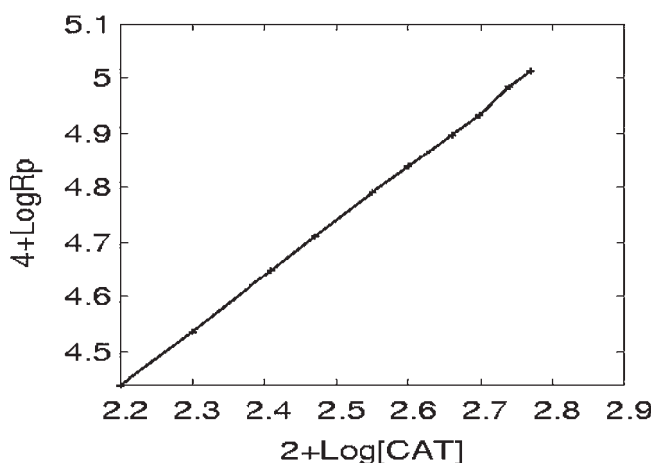**Figure 3** Effect of [Chloramine-T] on the rate of polymerization; [CAT] = 1.6–6.6×10^{-2} mol/dm^3, [H$_2$O$_2$] = 12.0×10^{-3} mol/dm^3, [Monomer] = 6.075×10^{-1} mol/dm^3, Temperature = 323 K.

Thus, it was evident that polymerization was initiated by free radicals formed *in situ* by the redox system. The steady state was attained within 60 min.[23]
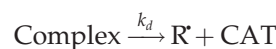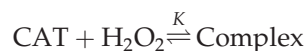
Rate of polymerization

The rate of polymerization (R_p) increases with the increase of monomer concentration (0.151–$1.518M$). A plot of log R_p versus log [M] was a straight line with a slope equal to one or unity.(Fig. 1), and a plot of R_p versus [M] was a straight line with zero intercept, indicating that the order with respect to monomer was unity. R_p increases linearly with the increase in the H$_2$O$_2$ concentration up to [6.0–$48.0 \times 10^3 M$]. A plot of log R_p versus log [H$_2$O$_2$] was a straight line passing through the origin (Fig. 2). This showed that the order with respect to [H$_2$O$_2$] is 0.59. A regular increase in R_p was also noticed with the increase in [Chloramine-T] [1.6–$6.6 \times 10^{-2}M$]. A plot of log R_p versus log [CAT] was linear, having a slope of 1.00 with zero intercept (Fig. 3), indicating that the order with respect to [CAT] is unity. These observations suggest that the termination of polymerization may be caused by the mutual combination of growing polymer radicals.[24]

The rate of CAT disappearance ($-R_m$) was first order with respect to CAT and is independent of acrylonitrile concentration. It depends on [CAT] and [H$_2$O$_2$]. A plot of $-1/R_m$ versus $1/$[H$_2$O$_2$] is Line wear-Burk kinetics for complex formation[25] (Table I and Fig. 5).
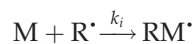
Reaction mechanism and rate law

The most likely reaction mechanism, which can satisfactorily explain the observed data is as shown in Scheme 1.[26–35]

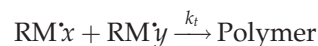Chloramine-T behaves like a strong electrolyte in aqueous solutions[36,37] and dissociates according to eq. (1)

$$ArSO_2NClNa \rightleftharpoons Ar\,SO_2NCl^- + Na^+ \qquad (1)$$

$$ArSO_2NCl^- + H_2O_2 \longrightarrow Ar\,SO_2NCl^- + OH^- + {}^\bullet OH$$

$$CAT + H_2O_2 \overset{K}{\rightleftharpoons} Complex$$

$$Complex \xrightarrow{k_d} R^\bullet + CAT$$

Initiation

$$M + R^\bullet \xrightarrow{k_i} RM^\bullet$$

Propagation

$$RM^\bullet + M \xrightarrow{k_p} RMM^\bullet$$

$$RM^\bullet_{x-1} + M \longrightarrow RM^\bullet x$$

Termination

$$RM^\bullet x + RM^\bullet y \xrightarrow{k_t} Polymer$$

Applying steady state approximation

$$-d/dt[R^\bullet] = k_d[Complex] - k_i[M][R^\bullet] = 0$$

$$K = [Complex]/[CAT][H_2O_2]$$

$$[Complex] = K[CAT][H_2O_2]$$

$$k_d\,K[CAT][H_2O_2] = k_i[M][R^\bullet] = 0$$

$$[R^\bullet] = k_d\,K[CAT][H_2O_2]/k_i[M]$$

$$k_i[R^\bullet][M] = k_i[RM^\bullet n][RM^\bullet n] = k_t[RM^\bullet n]^2$$

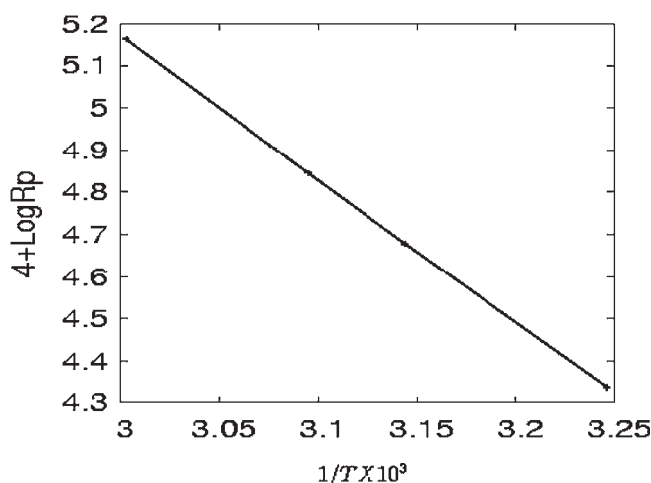**Figure 4** Effect of temperature on rate of polymerization; [CAT] = 4.0×10^{-2} mol/dm^3, [H$_2$O$_2$] = 12.0×10^{-3} mol/dm^3, [Monomer] = 1.519×10^{-1} mol/dm^3, Temperature = 298–323 K.

TABLE I
Plots of $1/(-R_m)$ versus $1/[H_2O_2]$

$1/[H_2O_2]$	$1/(-R_m)$
166.66	4985.05
83.33	3294.89
55.55	2590.67
41.66	2179.72
33.33	1906.00
27.77	1711.95
23.80	1694.91

$$[RM^{\bullet}n]^2 = [k_i/k_t]\,[R^{\bullet}][M]$$

$$[RM^{\bullet}n]^2 = [k_i/k_t]^{1/2}\,[R^{\bullet}]^{1/2}[M]^{1/2}$$

$$k_p = [RM^{\bullet}n][M]$$

$$R_p = k_p[k_i/k_t]^{1/2}[R^{\bullet}]^{1/2}[M]^{1/2}[M]$$

$$R_p = k_p[RM^{\bullet}n][M]$$

$$R_p = k_p[k_i/k_t]^{1/2}[k_dK/k_t]^{1/2}\left\{\frac{[CAT][H_2O_2]^{1/2}}{[M]}\right\}[M]$$

$$R_p = k_p[k_dK/k_t]^{1/2}\frac{[CAT][H_2O_2]^{1/2}[M]}{[M]}$$

$$R_p = k_p[k_dK/k_t]^{1/2}[CAT][H_2O_2]^{1/2}[M]$$

Thus, the observed dependence of R_p on [M], [CAT], and [H$_2$O$_2$] are all consistent with the experimental results (Table II). The low energy of activation is an indication of the high reactivity of the initiator and provides direct experimental evidence of the existence of transient radical intermediates generated in redox reactions. It also enables the identification of these radicals as end groups of the polymer. Further work on the kinetics of polymerization of various vinyl monomers initiated by the reaction of cerium(IV) and other transition metal ions with suitable reductant is in progress in our laboratory.

Effect of monomer concentration on the rate

The rate of polymerization increases with the increase of monomer concentration. The availability of monomer molecules in the propagation step increases, which obviously increases the rate of polymerization. The order of the reaction with respect to monomer concentration is calculated from the plot of log R_p versus log [M] (Fig. 1). The order with respect to monomer concentration was found to be unity in the range of 0.1519–1.518 mol/dm^3 At higher monomer

concentration, the rate decreases because of increase in viscosity of the medium, due to the solubility of the polymer in the monomer, rendering the diffusion of the ions difficult through the medium. An order of the reaction higher than unity is indicative of the occurrence of cage effect.[38]

Effect of [Chloramine-T] on the rate

The rate of polymerization increases with the increase of concentration of chloramine-T. That is due to increase in the concentration of active species. The order of the reaction with respect to [Chloramine-T] was found to be first order in the concentration range 1.6×10^{-2}–6.6×10^{-2} mol/dm^3 This also clearly indicates that termination occurs through unimolecular interaction of growing polymer chain radicals. The molecular weight of polyacrylonitrile decreases with increase of chloramine-T (Fig. 3). This can be explained by the fact that increasing the [CAT] provides more chance for premature termination of growing chain radicals, which reduces the degree of polymerization.[39]

Effect of [H$_2$O$_2$] on the rate

The increase of H$_2$O$_2$ concentration increases the rate of polymerization and reaches optimum level, later it decreases gradually. Then the order of the reaction with respect to H$_2$O$_2$ concentration was found to be of fractional order (0.59) from the plot of log R_p versus log [H$_2$O$_2$] in the concentration range of 6.0×10^{-3}–48.0×10^{-3} mol/dm^3 (Fig. 2)
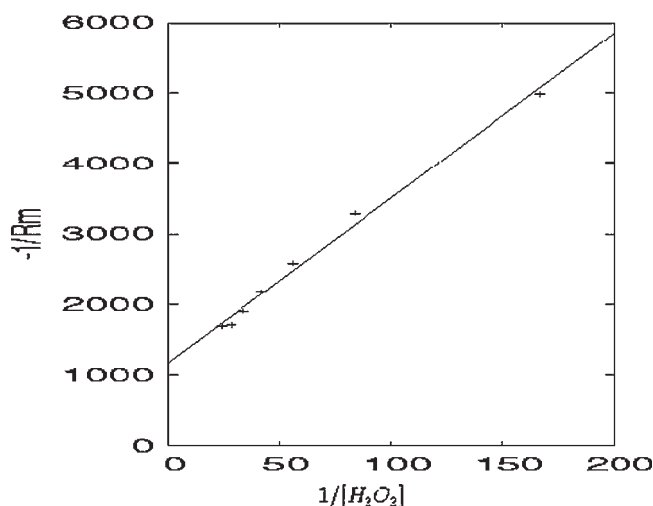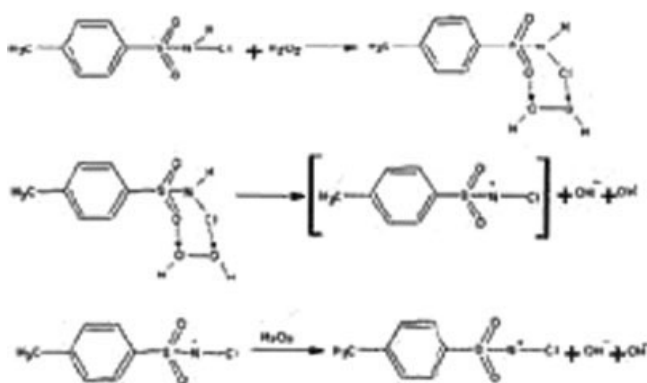

Figure 5 Inverse plot of [Chloramine-T] disappearance versus [H$_2$O$_2$]. [CAT] = 4.0×10^{-2} mol/dm^3, [H$_2$O$_2$] = 12.0×10^{-3} mol/dm^3, [Monomer] = 6.075×10^{-1} mol/dm^3, Temperature = 323 K.

Scheme 1 Organic reaction mechanism.

Effect of temperature on the rate

The rate of polymerization and the percentage conversion increases steadily with rising temperature. At a higher temperature (Fig. 4), the maximum conversion decreases. The activation energy (E_a = 64.57 kJ/mol) is calculated from the Arrhenius plot of log R_p versus $1/T$ in the temperature range of 35–50°C.

The other thermodynamic parameters calculated from the Eyring plots are:

$$\Delta H^{\neq} = 6.86 \text{ kJ/mol}, \quad \Delta G^{\neq} = 98.88 \text{ kJ/mol}, \quad \text{and}$$

$$\Delta S^{\neq} = -114 \text{ J K}^{-1} \text{ mol}^{-1}.$$

The over all activation energy for this system was 64.57 kJ/mol.

Effect of organic solvents on the rate

Addition of water-miscible organic solvents (5% w/v) such as methanol, ethanol, and DMF to the reaction mixture, depressed initial rate as well as the maximum conversion. This is due to the decrease in the area of shielding of a strong hydration layer in the aqueous medium, resulting in the termination of the radical end of the growing chain or due to the increase in the regulated rate of production of primary radicals caused by the solvent, which renders the termination rate to the relatively fast as com-

TABLE II
Effect of Variations of [H₂O₂], [Chloramine-T], [Monomer], and Temperature on the rate of Polymerization

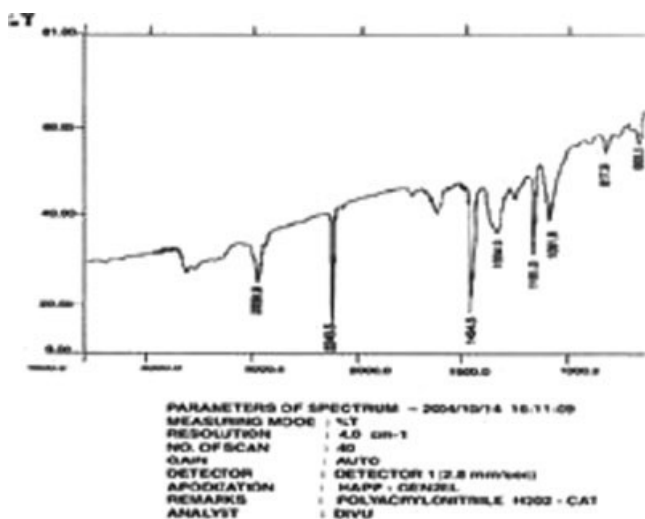| [CAT] (10^2) (mol/dm^3)	[H$_2$O$_2$] (mol/dm^3)	[AN] (mol/dm^3)	Temperature (K)	R_p (10^4) (S^{-1})
1.6	12.0	0.6075	323	2.75
2.0	12.0	0.6075	323	3.44
2.6	12.0	0.6075	323	4.66
3.0	12.0	0.6075	323	5.15
3.6	12.0	0.6075	323	6.19
4.0	12.0	0.6075	323	6.90
4.6	12.0	0.6075	323	7.90
5.0	12.0	0.6075	323	8.59
5.6	12.0	0.6075	323	9.64
6.0	12.0	0.6075	323	10.32
6.6	12.0	0.6075	323	10.46
4.0	6.0	0.6075	323	4.62
4.0	12.0	0.6075	323	6.99
4.0	18.0	0.6075	323	8.89
4.0	24.0	0.6075	323	10.57
4.0	30.0	0.6075	323	12.08
4.0	36.0	0.6075	323	13.46
4.0	42.0	0.6075	323	13.59
4.0	48.0	0.6075	323	12.99
4.0	12.0	0.1519	323	1.75
4.0	12.0	0.3037	323	3.49
4.0	12.0	0.4556	323	5.24
4.0	12.0	0.6075	323	6.99
4.0	12.0	0.7594	323	8.73
4.0	12.0	0.9113	323	10.47
4.0	12.0	1.0630	323	12.21
4.0	12.0	1.2150	323	13.96
4.0	12.0	1.5180	323	13.77
4.0	12.0	0.6075	308	2.18
4.0	12.0	0.6075	313	3.45
4.0	12.0	0.6075	318	4.77
4.0	12.0	0.6075	323	7.00
4.0	12.0	0.6075	333	14.53

Figure 6 IR spectra of poly(acrylonitrile), with CAT/H_2O_2 redox system.

pared to the growth of the polymer chains as shown by Schulz et al.[40]

Konar and Palit[41] have made similar observations with a homogeneous medium in which water is the additive. The interchain hydrogen bonding interlocking the polymer chain is not rigid, causing premature mutual combination of the polymer chains or it may be due to a change in the termination rate arising from a change in the degree of occlusion of the radicals.

Effect of surfactants on the rate

Addition of anionic surfactant like sodium lauryl sulfate increases the R_p above and below the CMC value. The cationic surfactants like cetyltrimethyl ammonium bromide decreases the rate above and below the CMC value. In contrast, nonionic surfactants like Triton x-100 have no effect on the rate, and especially arrested the polymerization of this chloramine-T-H_2O_2 redox system. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization.[42]

Spectroscopic analysis of the prepared polymer

The formation of PAN in the system was endorsed by spectroscopic analyses.

FTIR

The FTIR scan in Figure 6 of the prepared polymer revealed the manifestation of peaks at 2243.50 cm^{-1} (C—H stretching), 2939.9 cm^{-1} (C≡N stretching), and 1454.5 cm^{-1} (C—H bending), which matched with the reported FTIR spectra for polyacrylonitrile.[43]

CONCLUSIONS

Acrylonitrile is polymerized in a nitrogen atmosphere by the redox system of chloramine-T/hydrogen peroxide via a free radical mechanism. The polymerization reaction with respect to monomer concentration is 1.0, and the reaction order related to the chloramine-T and hydrogen peroxide concentrations are 1.0 and 0.59 respectively, which indicates that bimolecular mechanism is suggested and the following rate equation is derived:

$$V_p = k[M]^{1.0}[CAT]^{1.0}[H_2O_2]^{0.59}$$

From the Arrhenius plot, the overall energy of activation (E_a) has been calculated as 64.57 kJ/mol in the investigated range of temperatures.

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