The Study of Free Radical Polymerization of Acrylonitrile by Oxidation–Reduction System Using Potassium Persulfate–Thiourea in Aqueous Medium

G. K. Nagaraja, T. Demappa, Mahadevaiah

Department of Post-Graduate Studies and Research in Polymer Science, University of Mysore, Sir. M.V.PG Centre, Mandya 571402, Karnataka, India

ABSTRACT: The polymerization kinetics of acrylonitrile (AN) with the potassium persulfate $(K_2S_2O_8)$/thiourea redox system has been investigated volumetrically in an aqueous medium in the temperature range of 40–80°C. The rate of polymerization (R_p) and rate of $K_2S_2O_8$ disappearance have been measured. The effects of some water-miscible organic solvents, cationic, anionic, nonionic surfactants, and complexing agents on the R_p were investigated. The temperature dependence of the rate was studied, and the activation parameters were computed using the Arrhenius and Eyring plots. The effects of organic solvents on polymerization were also investigated. All of them depressed both the initial rate and limiting conversion. A mechanism consistent with the experimental data involving $K_2S_2O_8$–thiourea complex formation, which generates free radicals, is suggested. Molecular weight of the polymer was determined by viscometry. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 3395–3400, 2008

Key words: acrylonitrile; potassium persulfate–thiourea; redox system; activation energy

INTRODUCTION

Redox polymerization has the advantage of very short induction time, low activation energy (40–85 kJ/mol), production of high-molecular-weight polymers with high yields, easy control of the polymerization reaction at low temperature due to reduction of the side reactions, and the direct experimental proof of the transient radical intermediates.[1–5] In redox systems, oxidants form initially a complex by reacting with simple organic molecules, which then decompose unimolecularly to produce free radicals that initiate polymerization.[6] Numerous redox pairs containing organic and inorganic compounds as polymerization initiator have used successively. Commonly used oxidants include peroxides, persulfates, permanganates, etc., and the salts of transition metals. These oxidants form potential redox systems with various reducing agents like alcohols, aldehydes, amines, amides, ketones, acids, thiols, etc., for the aqueous polymerization of vinyl monomers.[7] Low-temperatures redox polymerization of vinyl monomers is of importance, especially for industrial viewpoints. Besides its economical benefits, suppression of side reactions such as branching is an additional advantage over common thermal initiation methods. In this way, various redox systems have used successfully for the polymerization of organic vinyl monomers in aqueous media.[8–21] A study of the kinetics of polymerization by thiourea and Ce(IV) have been studied.[22,23] Various redox systems have used potassium persulfate $(K_2S_2O_8)$ successfully for the polymerization of organic vinyl monomers in aqueous media.[24,25] In this article, the $K_2S_2O_8$/thiourea redox system was used to polymerize acrylonitrile (AN), and the kinetics of polymerization of the monomer with this redox pair has been studied.

EXPERIMENTAL

Acrylonitrile (S.D. Fine chem., India) was washed with 5% NaOH, followed by dilute orthophosphoric acid, and finally with distilled water. It was dried over anhydrous calcium chloride and distilled under reduced pressure of nitrogen atmosphere. The middle fraction was collected and stored at 5°C.[26] All other chemicals such as $K_2S_2O_8$, sulfuric acid, thiourea, methanol, ethanol, N,N-dimethylformamide (DMF), cetyltrimethylammonium bromide (CTABr), and Triton X-100 were of analytical grade. A solution of $K_2S_2O_8$ was prepared by triple distilled water and standardized with standard sodium thiosulfate

solution using starch as an indicator. Triple distilled water was used throughout the experiment, pure nitrogen, obtained by passing through a column of Fieser's solution and distilled water, was used for the deaeration condition of all experimental systems.

Kinetic measurements

Reactions were performed under nitrogen atmosphere in Pyrex glass vessels. In a typical kinetic measurements, a mixture of solutions containing requisite amounts of inhibitor-free AN ($0.607M$) monomer [M], thiourea [TU] (1.0×10^{-2} mol/dm^3), sulfuric acid (4.0×10^{-3} mol/dm^3), 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, K$_2$S$_2$O$_8$ solution (4.0×10^{-3} mol/dm^3) was added to the reaction vessel 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 at desired intervals of times by adding a known amount of ferrous sulfate solution or by cooling the reaction mixture to 0°C. The polyacrylonitrile (PAN) 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) was determined gravimetrically[27] and K$_2$S$_2$O$_8$ disappearance ($-R_m$) was measured iodometrically before and after the polymerization.

Molecular weight determination

The molecular weight (M_v) of the purified sample of PAN 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) was determined and the M_v value was calculated by using the appropriate Mark-Houvink equation given by Stockmayer and Cleland[28]: $\eta = (3.335 \times 10^{-4}) \times M_v^{0.72}$ at 30°C for PAN in DMF. The M_v of the polymer product under standard conditions was found to be 5.81×10^4. It increases with monomer concentration and decreases with increase in [K$_2$S$_2$O$_8$], [thiourea], or temperature. This effect is attributed to the fact that increases in [K$_2$S$_2$O$_8$], [thiourea], or temperature provides more chances for premature termination of growing chain polymer radicals, thus reducing the degree of polymerization. Behari et al.,[29,30] have reported similar effects. Density and refractive index determined using the density bottle and Abbe's refractometer (1.261 and 1.433), respectively.

RESULTS AND DISCUSSION

Under the conditions of high temperature (40°C), it was found that there was no polymerization of the monomer even after 75 min with K$_2$S$_2$O$_8$ alone was used as an initiator. But with K$_2$S$_2$O$_8$–thiourea as redox initiator, it was noticed that the polymerization reaction proceeded without any induction period. The steady state was attained within 75 min. The polymerization of AN initiated by K$_2$S$_2$O$_8$–thiourea redox system takes place at a measurable rate in the temperature range 40–80°C. The rate of K$_2$S$_2$O$_8$ disappearance ($-R_m$) was found to be independent for K$_2$S$_2$O$_8$ at standard concentration. A plot of ($-R_m$) versus [K$_2$S$_2$O$_8$] was linear and passed through the origin. A plot of $-1/R_m$ versus $1/$[thiourea] was linear with an intercept on the rate axis, indicating Lineweaver-Burk kinetics for complex formation.

Rate of polymerization

The 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 log R_p versus log [M] was a straight line with zero intercept indicating that the order with respect to [monomer] was unity. R_p increases linearly with increase in the thiourea concentration up to [1.0–$5.0 \times 10^{-2}M$]. A plot of log R_p versus log [thiourea] was a straight line passing through the origin (Fig. 2). This showed that the order with respect to [thiourea] is 0.42. A regular increase in R_p was also noticed with the increase in [K$_2$S$_2$O$_8$] [4.0–$20.0 \times 10^{-3}M$]. A plot of log R_p versus log [K$_2$S$_2$O$_8$] was linear, having a slope of 0.45 with zero intercept (Fig. 3), indicating that the order with respect to [K$_2$S$_2$O$_8$] is fractional. These observations
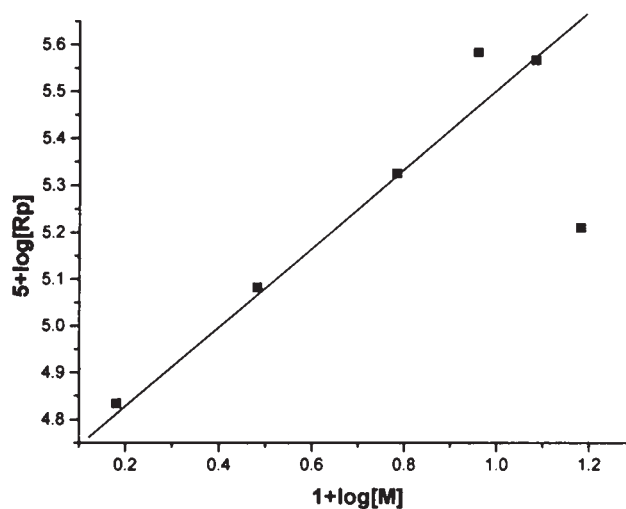

Figure 1 Effect of [monomer] on the rate of polymerization, [PS(II)] = 4.0×10^{-3} mol/dm^3, [TU] = 1.0×10^{-2} mol/dm^3, [monomer] = (0.1518–1.5188) $\times 10^{-2}$ mol/dm^3, temperature = 323 K.
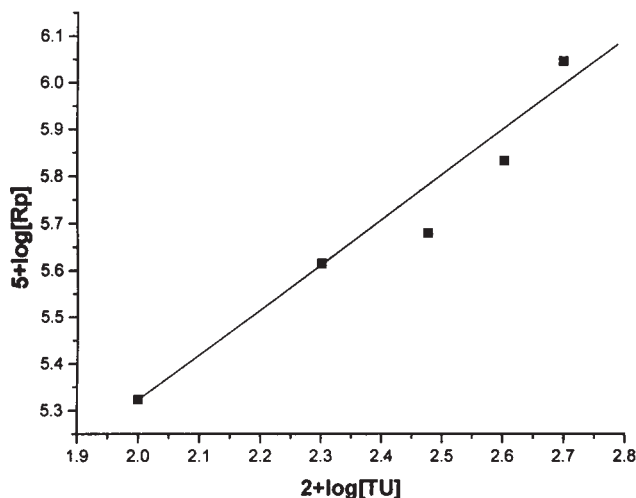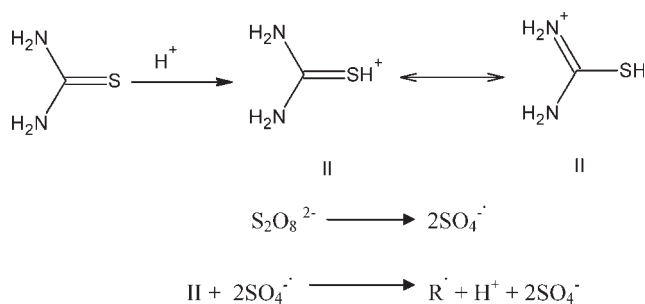
Figure 2 Effect of [thiourea] on the rate of polymerization, $[PS(II)] = 4.0 \times 10^{-3}$ mol/dm^3, $[TU] = 1.0\text{–}5.0 \times 10^{-2}$ mol/dm^3, [monomer] $= 0.6075 \times 10^{-2}$ mol/dm^3, temperature = 323 K.

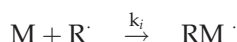suggest that the termination of polymerization may be caused by the mutual combination of growing polymer radicals.[31]

The rate of $K_2S_2O_8$ disappearance $(-R_m)$ was first order with respect to $K_2S_2O_8$ and is independent of AN concentration. It depends on $[K_2S_2O_8]$ and [thiourea]. A plot of $-1/R_m$ versus $1/[\text{thiourea}]$ is Linewear-Burk kinetics for complex formation.[32]
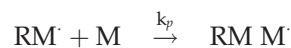
Reaction mechanism and rate law

The polymerization of AN in aqueous medium initiated by $K_2S_2O_8$–thiourea redox system shows characteristic features of heterogeneous polymerization. The reaction mixture becomes heterogeneous as soon as polymerization starts because of the insolubility of the polymer (PAN) in the aqueous media. From the kinetic results, a reaction has been proposed involving the initiation by organic free radicals generated by the interaction by the $K_2S_2O_8$ [PS (II)] with the NH_2
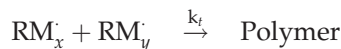

Initiation

$$M + R^{\cdot} \overset{k_i}{\to} RM^{\cdot}$$

Propagation

$$RM^{\cdot} + M \overset{k_p}{\to} RM\ M^{\cdot}$$

$$\dots\dots\dots\dots\dots\dots\dots\dots$$
$$\dots\dots\dots\dots\dots\dots\dots\dots$$
$$\dots\dots\dots\dots\dots\dots\dots\dots$$
$$RM_{x-1}^{\cdot} + M \to RM_x M^{\cdot}$$

Termination

$$RM_x^{\cdot} + RM_y^{\cdot} \overset{k_t}{\to} \text{Polymer}$$

Applying steady-state approximation

$$-d/dt[R^{\cdot}] = k_d[\text{complex}] - k_t[M][R^{\cdot}] = 0$$
$$k = [\text{complex}]/[TU][PS(II)]$$
$$[\text{complex}] = k[TU][PS(II)]$$
$$k_d k[TU][PS(II)] - k_i[M][R^{\cdot}] = 0$$
$$[R]^{\cdot} = k_d k[PS(II)][TU]/k_i[M]$$
$$k_i[R^{\cdot}][M] = -k_t[RM^{\cdot}n][RM^{\cdot}n] = k_t[RM^{\cdot}n]^2$$
$$[RM^{\cdot}n]^2 = (k_i/k_t)[R^{\cdot}][M]$$
$$[RM^{\cdot}n] = (k_i/k_t)^{1/2}[R^{\cdot}]^{1/2}[M]^{1/2}$$
$$k_p = [RM^{\cdot}n][M]$$
$$R_p = k_p(k_i/k_t)^{1/2}[R^{\cdot}]^{1/2}[M]^{1/2}[M]$$
$$R_p = k_p\ [RM^{\cdot}n][M]$$
$$R_p = k_p(k_i/k_t)^{1/2}k_p(k_d k/k_t)^{1/2}\{[PS(II)][TU]/[M]\}^{1/2}[M]^{3/2}$$
$$R_p = k_p(k_d k/k_t)^{1/2}[PS(II)]^{1/2}[TU]^{1/2}[M]^{1/2}[M]^{1/2}$$
$$R_p = k_p(k_d k/k_t)^{1/2}[PS(II)]^{1/2}[TU]^{1/2}[M]$$

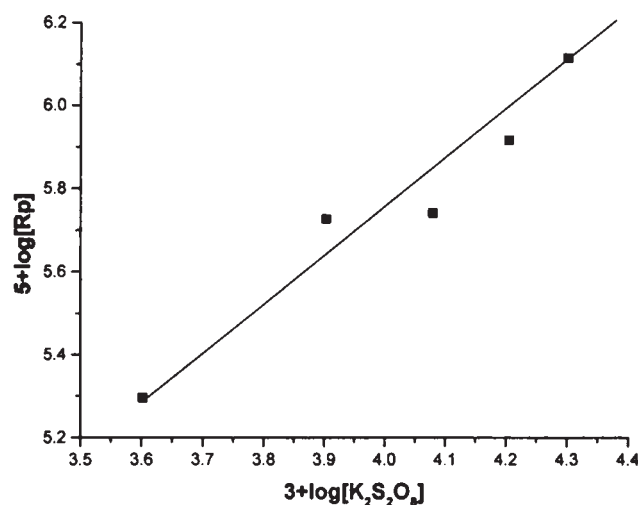**Figure 3** Effect of [PS(II)] on the rate of polymerization, $[PS(II)] = 4.0\text{–}20.0 \times 10^{-3}$ mol/dm^3, $[TU] = 1.0 \times 10^{-2}$ mol/dm^3, [monomer] $= 0.6075 \times 10^{-2}$ mol/dm^3, temperature = 323 K.

<div align="center">

TABLE I
Effect of Variations of [PS(II)], [TU], [Monomer], and Temperature on the Rate of Polymerization

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[PS(II)] (10^{-3}) (mol/dm^3)	[TU] (10^{-2}) (mol/dm^3)	[AN] (10^{-2}) (mol/dm^3)	H$_2$SO$_4$ (10^{-3}) (mol/dm^3)	Temperature (K)	R_p (10^{-5}) (s^{-1})
4.0	1.0	0.6075	4.0	323	1.97
8.0	1.0	0.6075	4.0	323	5.33
12.0	1.0	0.6075	4.0	323	5.51
16.0	1.0	0.6075	4.0	323	8.25
20.0	1.0	0.6075	4.0	323	13.01
4.0	1.0	0.6075	4.0	323	2.10
4.0	2.0	0.6075	4.0	323	4.21
4.0	3.0	0.6075	4.0	323	1.77
4.0	4.0	0.6075	4.0	323	0.21
4.0	5.0	0.6075	4.0	323	1.11
4.0	1.0	0.1518	4.0	323	0.68
4.0	1.0	0.3037	4.0	323	1.20
4.0	1.0	0.6075	4.0	323	2.11
4.0	1.0	0.9113	4.0	323	3.83
4.0	1.0	1.2151	4.0	323	36.98
4.0	1.0	1.5188	4.0	323	16.44
4.0	1.0	0.6075	2.0	323	3.103
4.0	1.0	0.6075	4.0	323	1.964
4.0	1.0	0.6075	6.0	323	1.535
4.0	1.0	0.6075	8.0	323	1.348
4.0	1.0	0.6075	10.0	323	1.347
4.0	1.0	0.6075	4.0	313	1.822
4.0	1.0	0.6075	4.0	323	2.10
4.0	1.0	0.6075	4.0	333	3.31
4.0	1.0	0.6075	4.0	343	5.15
4.0	1.0	0.6075	4.0	353	5.15

Thus, the dependence of R_p on [M] [PS (II)] and [TU] all of which are observed are consistent with the experimental results. The low energy of activation (E_a) 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, various vinyl monomers initiated by the reaction of PS (II), and other transition metals ions with suitable reductants is in progress in our laboratory.

Dependence on monomer concentration

The R_p increases with increasing monomer concentration. The order of the reaction with respect of monomer concentration is calculated from the plot of log R_p versus log [M] (Fig. 1 and Table I). The order with respect to AN concentration is found to be unity in the range of 0.1518–1.5188 mol/dm^3. At higher [AN] 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.[33]

Rate dependence on thiourea concentration

The increase of thiourea concentration, increase the R_p and reaches optimum level and then it is decreasing gradually. The exponent (slope) of the thiourea was found to be fractional order (0.42) from the plot of log R_p versus log [thiourea] in the concentration range of 1.0×10^{-2}– 5.0×10^{-2} mol/dm^3 (Fig. 2 and Table I). At higher concentration of thiourea, the rate decreases due to the chain transfer or mutual interaction of the growing polymer chain radicals.

Rate dependence on [K$_2$S$_2$O$_8$]

R_p increases with increase in the concentration of K$_2$S$_2$O$_8$, which is due to increases in the concentration of active species. The order of the reaction with respect to K$_2$S$_2$O$_8$ is found to be fractional order in the concentration range 4.0×10^{-3} – 20.0×10^{-3} mol/dm^3. This is also clearly indicates that the termination occurs through unimolecular interaction of growing polymer chain radical. The M_v of PAN decreases with increases in [K$_2$S$_2$O$_8$] (Fig. 3 and
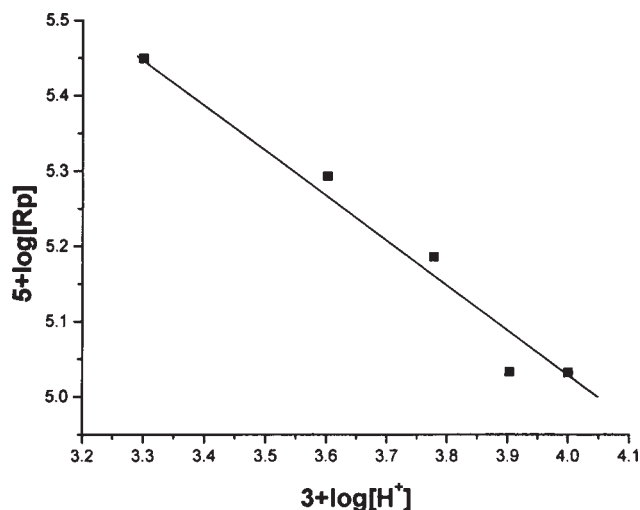
Figure 4 Effect of H_2SO_4 on the rate of polymerization, [PS(II)] = 4.0–20.0 × 10^{-3} mol/dm^3, [TU] = 1.0 × 10^{-2} mol/dm^3, [monomer] = 0.6075 × 10^{-2} mol/dm^3, [H$_2$S0$_4$] = (2.0–10.0) × 10^{-3} mol/dm^3, temperature = 323 K.

Table I). This can be explained by the fact that increasing in [K$_2$S$_2$O$_8$] provides more chances for premature termination growing chain radicals, which reduce the degree of polymerization.[34]

Rate dependence on H_2SO_4 concentration

The kinetic measurements were performed in H_2SO_4 aqueous solution of different H$^+$ ion concentration. The R_p decreases with an increase in [H$^+$]ion, indicates that the hydrolyzed species of K$_2$S$_2$O$_8$ is more reactive than the unhydrolysed species and also that the unprotonated form of thiourea is more reactive than the protonated form. The order with respect to H$^+$ ion concentration was found to be inverse fractional order from the plots of log R_p versus log [H$^+$]. (Fig. 4 and Table I).

Rate dependence on temperature

When temperature of reaction mixture is increased from 40 to 80°C, the initial R_p and % conversion was increases and beyond 80°C fall in the initial rate and limiting conversion is observed. The observed increase is due to the fact that, with increase in temperature, the rate of active center formation increases, which consequently increases the initial rate and conversion with temperature. Further, beyond 80°C, the initial rate and limiting conversion decreases. The overall E_a has been calculated from the Arrhenius plot of log R_p versus $1/T$ (Fig. 5 and Table I) in the temperature range of 40–80°C. Activation energy (E_a) = 18.64 kJ/mol. The other activation

parameters calculated from the Eyring plot are as follows:

$$\Delta H^{\neq} = 16.03 \text{ kJ/mol}, \quad \Delta S^{\neq} = -192 \text{ JK}^{-1}/\text{mol}, \quad \text{and}$$
$$\Delta G^{\neq} = 80.66 \text{ kJ/mol},$$

Rate dependence on organic solvents

Because the properties of a polymer mostly depend on the nature of the medium, various water-miscible organic solvents such as methanol, DMF, and ethanol have been observed their effect on the R_p. When added to the reaction mixture in equal volume (5% v/v), a depression in the initial R_p and the limiting conversion has been observed. The increasing order of depression by these solvents is methanol < ethanol < DMF.

The cause of depression in the R_p and % conversion by the added organic solvents may be explained.

1. When the organic solvents are added to the reaction mixture, they cause a decrease in the area of shielding of a strong hydration layer in aqueous medium, which results in the termination of radical end of the growing chain.
2. Some amount of catalyst may be consumed in the oxidation of these organic solvents due to which the concentration of catalyst decreases and a depression in rate is observed. The sluggish radicals thus produced may not be equally capable of initiating the polymerization.
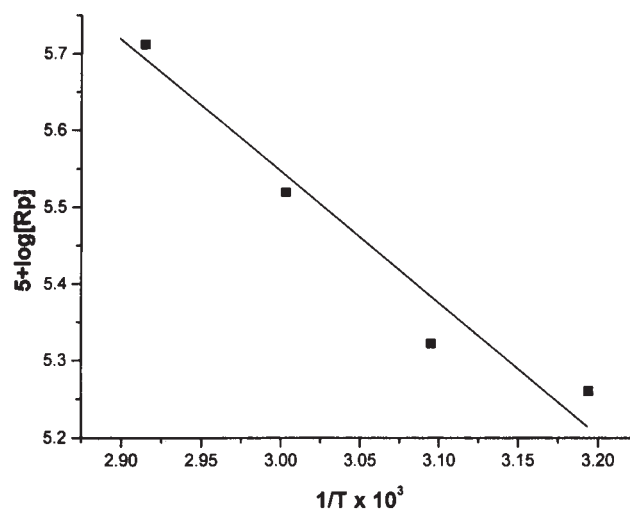

Figure 5 Effect of temperature on the rate of polymerization, [PS(II)] = 4.0–20.0 × 10^{-3} mol/dm^3, [TU] = 1.0 × 10^{-2} mol/dm^3, [monomer] = 0.6075 × 10^{-2} mol/dm^3, temperature = 313–353 K.

Rate dependence on surfactants

Addition of anionic surfactant sodium lauryl sulfate (SLS) increases the R_p above and below the CMC value. The cationic surfactant CTABr is increasing the rate above and below CMC value. In contract, nonionic surfactants like Triton X-100 have no effect on the R_p. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the R_p.[35]

CONCLUSIONS

AN is polymerized in a nitrogen atmosphere by the redox system of $K_2S_2O_8$/thiourea via a free radical mechanism. The polymerization reaction with respect to monomer concentration is 1.0. And, the reaction order related to the $K_2S_2O_8$ and thiourea concentrations are 0.45 and 0.42, respectively, which indicates that bimolecular mechanism is suggested and the following rate equation is derived:

$$V_p = k[M]^{1.0}[\text{Potassium Persulphate}]^{0.45}[\text{thiourea}]^{0.42}$$

From the Arrhenius plot, the overall E_a has been calculated as 18.64 kJ/mol in the investigated range of temperatures.

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