POLYMERIZATION OF ACRYLONITRILE INITIATED BY PEROXOMONOSULPHATE-THIOLS REDOX SYSTEMS

Gurusamy MANIVANNAN* and Pichai MARUTHAMUTHU

Department of Energy, University of Madras,
A. C. College Campus, Madras 600 025, India

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Aqueous thermal polymerization of acrylonitrile (AN) initiated by peroxomonosulphate (HSO_5^-, PMS)-thiolactic acid (TLA) and PMS-thiomalic acid (TMA) redox systems has been carried out in the temperature range 30—50°C. The effect of concentration of monomer, initiator, reducing agent, H^+, and ionic strength on rate of polymerization, R_p, has been investigated under deaerated conditions. The R_p has been found to depend on,

$$R_p \sim [AN]_0^{1.5}\,[PMS]^{0.5}\,[TLA]^{0.5} \quad \text{in PMS-TLA}$$

system and,

$$R_p \sim [AN]_0^{2.0}\,[PMS]^{1.0}\,[TMA]^{0} \quad \text{in PMS-TMA}$$

system. The degree of polymerization (X_n) values and thermodynamic parameters have been evaluated. Suitable reaction scheme has been proposed and expressions for R_p and X_n have been obtained.

The efficiency of peroxomonosulphate (HSO_5^-, PMS) as water soluble initiator in presence and absence of reducing agents[1-3] is reported by us. The thiol acids possessing both the thio and carboxylic groups are found to be efficient and tempting activators when coupled with oxidizing agents, owing to the presence of two different functional groups. The following thiols (RSH) have been used as the reducing agents of the redox pair coupled with peroxomonosulphate: 2-mercaptopropionic acid (thiolactic acid, TLA) and 2-mercaptosuccinic acid (thiomalic acid, TMA). The structural differences of the above compounds may be responsible for the variations in their behaviour as reducing agents of the redox initiators which lead to interesting results in the polymerization studies. This redox systems are employed for the first time to investigate the kintics and mechanism of polymerization of acrylonitrile.

Since the thiols have been found to be very sensitive towards oxygen[4], the latter probably sets up a co-redox system[5] with thiols. To avoid the mechanistic complexity of involving coredox system, the kinetic study was carried out under deaerated conditions.

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* Present address: Institut für Physikalische Chemie, Universitat Basel, CH-4054 Basel, Switzerland.

EXPERIMENTAL

Potassium peroxomonosulphate, supplied by E.I. du Pont de Nemours & Co., U.S.A., under the trade name "Oxone"; the sample was used as such as mentioned earlier[1-3]. All other chemicals were of analytical reagents (BDH) and were used without further purification. Doubly distilled water was always used for all the experiments.

The monomer purification and the experimental methods are essentially the same as described previously[1-3]. The stock solutions of thiols were prepared in nitrogen armosphere to avoid any serial oxidation before use in each experiment. All the polymerization reactions were carried out under deaerated conditions using purified nitrogen gas in aqueous solution at 30—50°C with the following starting concentration ranges of the reactants: $[\mathrm{AN}]_0 = (5{\cdot}32—9{\cdot}88)\,.\,10^{-1}$ mol dm^{-3}, $[\mathrm{PMS}] = (0{\cdot}69—4{\cdot}00)\,.\,10^{-2}$ mol dm^{-3}, $[\mathrm{RSH}] = (0{\cdot}50—3{\cdot}02)\,.\,10^{-2}$ mol dm^{-3}; the ionic strength, μ, was 1·00 mol dm^{-3} for PMS–TLA system and 0·75 mol dm^{-3} for PMS–TMA system (adjusted with sodium sulphate).

The molecular weight of the polymers were obtained with the formed poly(acrylonitrile) after purification by repeated precipitation from dimethylformamide–methanol system. The Mark–Houwink equation[6] employed for poly(acrylonitrile) to evaluate the molecular weight is $[\eta] = 3{\cdot}35\,.\,10^{-4}(M_\mathrm{v})^{0\cdot72}$. From the molecular weights of the polymerization values (X_n) were computed using the relation[7], $M_\mathrm{n} = MX_\mathrm{n}$ (assuming $M_\mathrm{v} \sim M_\mathrm{n}$), where M_v is molecular weight of the polymer from viscometry and M is molecular weight of the monomer.

RESULTS AND DISCUSSION

The observations made in the investigation of polymerization of acrylonitrile by PMS–TLA and PMS–TMA redox systems are given below: The percentage conversion of monomer (p, %) was found to increase with increase in time and temperature in both the systems (Fig. 1).

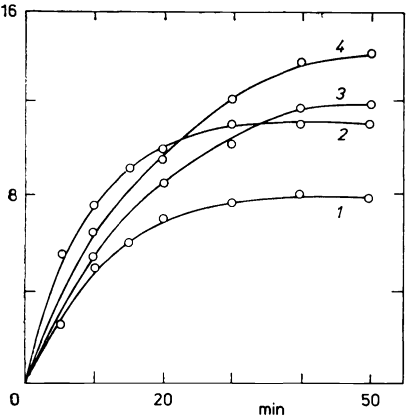

Fig. 1

Time course of the monomer conversion (p) on the polymerization of acrylonitrile (AN) in water ($[\mathrm{AN}]_0 = 0{\cdot}99$ mol dm^{-3}) initiated with peroxomonosulfate (PMS)-thiomalic acid (TMA) or PNS-thiolactic acid (TLA) redox systems. Concentrations (in 10^{-2} mol . . dm^{-3}): [PMS] 2·10, [TMA] 3·01, [TLA] 2·99. Temperature, °C (thiol): *1* 35 (TMA), *2* 45 (TMA), *3* 35 (TLA), *4* 45 (TLA)

Rate of Polymerization, R_p

To observe the effect of the monomer concentration on R_p, experiments were performed in the starting concentration range $(5{\cdot}32-9{\cdot}88) \,.\, 10^{-1}$ mol dm^{-3} of the monomer with varying [RSH] in the range $(1{\cdot}05-3{\cdot}02) \,.\, 10^{-2}$ mol dm^{-3}, at constant [PMS] in the range $(2{\cdot}03-4{\cdot}00) \,.\, 10^{-2}$ mol dm^{-3} keeping constant ionic strength at 40°C. The rate of formation of polymer was found to increase with increase in starting monomer concentration and the plot of log R_p vs log $[AN]_0$ was found to be linear with slope equal to 1·5 in the case of PMS–TLA and 2·0 in PMS–TMA system (Fig. 2*a*). Similarly the plot of R_p vs $[AN]_0^{1.5}$ and $[AN]_0^{2.0}$ with zero intercepts in the respective cases of PMS–TLA and PMS–TMA systems, clearly indicated the 1·5 and 2·0 order dependence on $[AN]_0$ of PMS–TLA and PMS–TMA systems, respectively.

By varying the concentration of PMS in the range $(0{\cdot}69-4{\cdot}00) \,.\, 10^{-2}$ mol dm^{-3} at constant $[AN]_0$ (0·99 mol dm^{-3}) and μ at 40°C with varying [RSH] in the range $(1{\cdot}05-3{\cdot}02) \,.\, 10^{-2}$ mol dm^{-3}, the effect of [PMS] on R_p was investigated. The R_p was found to increase with increase in [PMS] and the linear plot of log R_p vs log [PMS] (Fig. 2*b*) with slope equal to 0·5 and 1·0 for the PMS–TLA and PMS–TMA redox systems respectively pointed out the half-order and first order dependence of R_p on [PMS].

The effect of variation of [RSH] on R_p was investigated by performing experiments with varying thiol acid concentration in the range $(0{\cdot}50-3{\cdot}02) \,.\, 10^{-2}$ mol dm^{-3} at 40°C, $[AN]_0$ 0·99 mol . dm^{-3} and constant [PMS] in the range $(1{\cdot}05-3{\cdot}02) \,.\, 10^{-2}$ mol dm^{-3}. In the case of PMS–TLA system, R_p was found to increase with increase in [TLA], but in PMS–TMA system, variation of [TMA] was not found to exert any significant influence on R_p. The plot of R_p vs $[TLA]^{0.5}$ with straight lines passing through the origin and R_p vs [TMA] with linear line (Fig. 2*c*) clearly proved the half-order dependence of R_p on [TLA] and zero-order dependence on [TMA] in the investigated concentration range.

The R_p was found to increase with increase of temperature in both the systems and the overall activation energy computed from the plot of log R_p vs T^{-1} (Arrhenius plot) was 16·5 kJ mol^{-1} for the PMS–TLA system and 33·3 kJ mol^{-1} for the PMS–TMA system.

The ionic strength was varied from 0·40 to 1·00 mol dm^{-3} at constant $[AN]_0$, [PMS] and [RSH] at 40°C. The R_p was found to be little influenced in PMS–TLA system for the variation of ionic strength but showed a positive effect in PMS–TMA redox system. This may suggest the involvement of an ion and a neutral molecule in the primary radical producing reactions in former system and reactions involving ions of same charge in the latter system[8]. The R_p was found to show a decrease with increase in $[H^+]$ (0·10 – 0·35 mol dm^{-3}) in both the systems, which indicated the inverse dependence of $[H^+]$ on the primary radical producing reactions.

Degree of Polymerization, X_n

By the viscometric studies, the molecular weights of the polymers were computed and using these data, values of degree of polymerization, X_n, were obtained. The X_n was

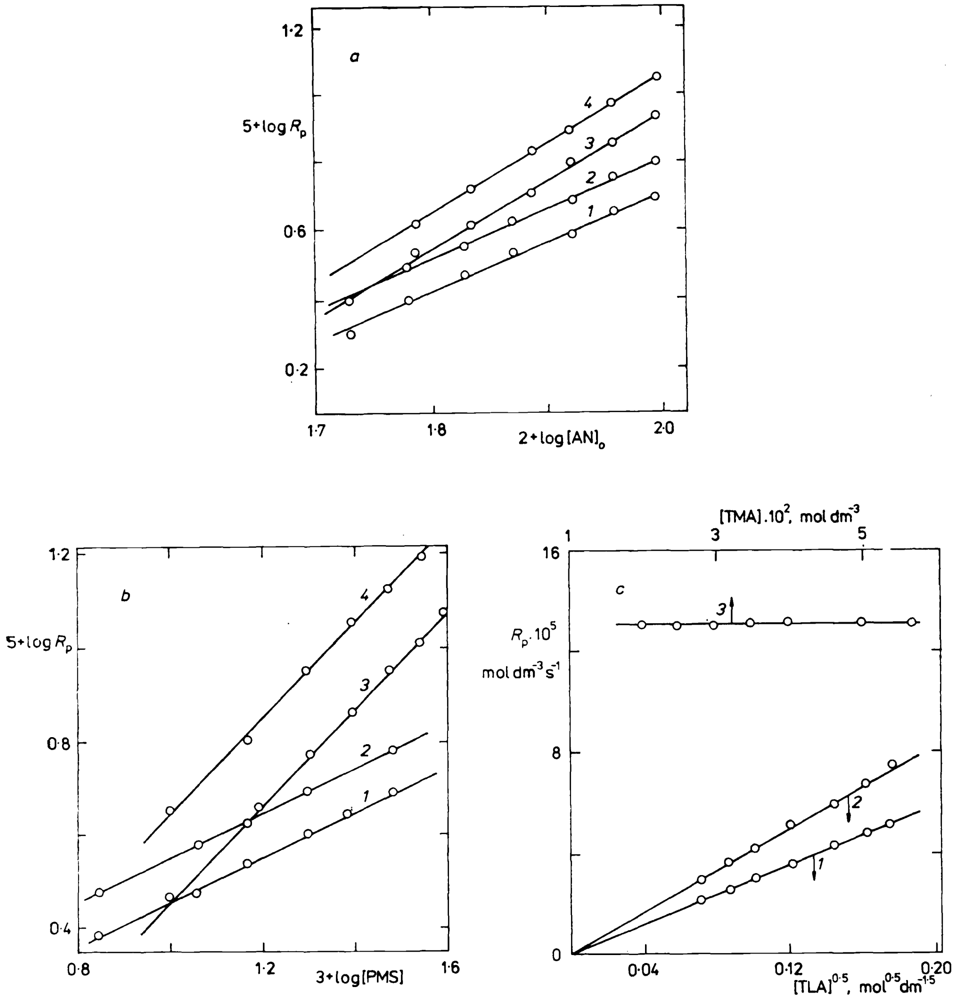

FIG. 2

Effect of the starting concentration of monomer, PMS, or thiol on the rate of polymerization (R_p) in the polymerization of acrylonitrile at 40°C and fixed ionic stregnth (1·00 or 0·75 mol dm^{-3} for TLA or TMA, respectively). The concentrations are expressed in 10^{-2} mol dm^{-3}. *a* [PMS]/ /[TLA]: *1* 2·04/1·51, *2* 2·04/2·16; [PMS]/[TMA]: *3* 2·03/3·02, *4* 3·02/3·02. *b* [AN]$_0$/[TLA]: *1* 99/1·05, *2* 99/1·51; [AN]$_0$/[TMA]: *3* 84/3·02, *4* 99/3·02. *c* [AN]$_0$/[PMS]: *1* 99/1·05, *2* 99/2·02, *3* 99/3·02 found to increase steadily with increase in $[AN]_0$ but showed a uniform decrease with increase in [PMS] and [TLA] (Fig. 3*a*). But in PMS–TMA system, the X_n was found to show a small increase with increase in $[AN]_0$, but decreased with increase in [PMS]. The [TMA] variation did not influence X_n (Fig. 3*b*).

Reaction Scheme

The observed dependences of R_p are:

$$R_p \sim [AN]_0^{1.5} [PMS]^{0.5} [TLA]^{0.5} , \qquad (1)$$

$$R_p \sim [AN]_0^{2.0} [PMS]^{1.0} [TMA]^{0} . \qquad (2)$$

All the experiments have been carried out under natural pH (3·0 – 3·2) and so peroxomonosulphate exists in the form of HSO_5^- as the active species[9]. Similarly, the active species of TLA (ref.[10]) and TMA (ref.[11]) are, undissociated form of TLA and the monoanion of TMA. The observation of decrease of R_p with increase in H^+ and increase of rate with increase in ionic strength also supports the active species of TLA and TMA. To explain the observed dependence of R_p, following reaction scheme is proposed, representing the TLA and TMA as RSH.

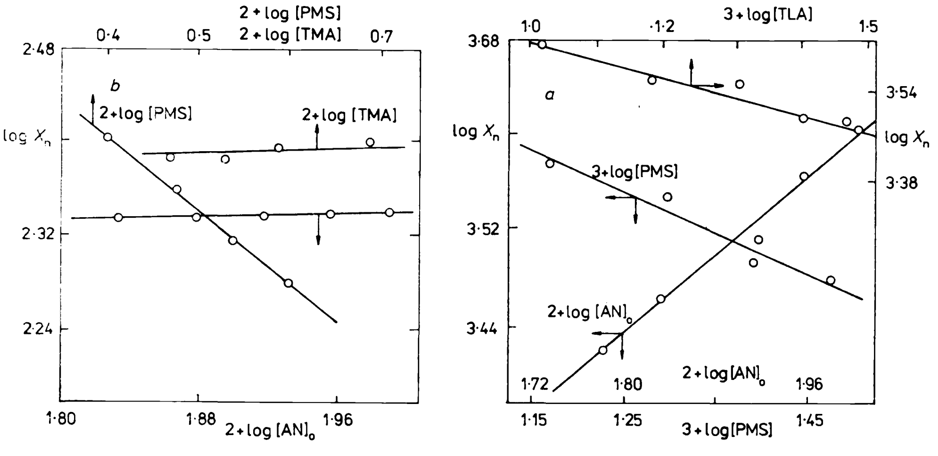

FIG. 3

Dependence of the degree of polymerization (X_n) upon the starting concentration of monomer, PMS, or thiol at the polymerization of acrylonitrile in water initiated with PMS–thiol redox system. Initiation: *a* PMS–TLA, *b* PMS–TMA

Initiation:

$$HSO_5^- + RSH \underset{}{\overset{K_1}{\rightleftharpoons}} \text{adduct}\,(C_1) \qquad (A)$$

$$C_1 + M \xrightarrow{k_1} M_1^{\bullet} + RS^{\bullet} + HSO_4^-(M^{\bullet}\!-\!OH) \qquad (B)$$

$$M + RS^{\bullet} \xrightarrow{k_2} M_1^{\bullet}(M^{\bullet}\!-\!SR) \qquad (C)$$

Termination:

$$M_n^{\bullet} + M_n^{\bullet} \xrightarrow{k_{t1}} \text{polymer} \qquad (D)$$

$$M_n^{\bullet} + RSH \xrightarrow{k_{tr}} \text{polymer} + R^{\bullet}\,(\text{where } R^{\bullet} = (RSH)^{\bullet +}) \qquad (E)$$

$$R^{\bullet} + L \xrightarrow{k_{t2}} \text{product (where L stands for solvent)} \qquad (F)$$

By applying steady state approximation for all the involved radicals in the reaction scheme, expressions for rate of polymerization could be obtained. Mutual termination (k_{t1}) is found to be effective termination for PMS–TLA system whereas termination involving RSH ($k_{tr} + k_{t2}$) is effective in PMS–TMA system. The derived expressions are

$$R_p = k_p(k_1K_1/k_{t1})^{0.5}\,[AN]_o^{1.5}\,[PMS]^{0.5}\,[RSH]^{0.5} \qquad (3)$$

$$X_n = k_p(k_1k_{t1}K_1[PMS]\,[RSH])^{-0.5}\,[AN]^{0.5} \qquad (4)$$

for PMS–TLA system,

$$R_p = k_p(2k_1K_1/k_{tr})\,[AN]_o^{2.0}\,[PMS]^{1.0} \qquad (5)$$

$$X_n = k_{tr}k_p/2k_{t2}k_1K_1[PMS] \qquad (6)$$

for PMS–TMA system. The observed effects of $[AN]_o$, $[PMS]$ and $[RSH]$ on X_n (Fig. 3*a* and Fig. 3*b*) are in good agreement with the derived expressions. The evaluated thermodynamic parameters (in kJ mol^{-1}) are: for PMS–TLA system $\Delta H^{\neq} = 13{\cdot}89$, $\Delta G^{\neq} = 83{\cdot}72$; for PMS–TMA system $\Delta H^{\neq} = 30{\cdot}72$, $\Delta G^{\neq} = 99{\cdot}63$.

The present work of the thermal, aqueous vinyl polymerization reactions by the new redox initiators, peroxomonosulphate–thiols, lead to perform more efficient redox initiations with a wide scope of using peroxomonosulphate in presence of reducing agents to polymerize different vinyl monomers.

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