Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Studies on Vinyl Polymerization: Polymerization of Acrylonitrile by Permanganate-Glucose Initiator System

S. S. Tripathy[a]; S. Jena[a]; N. P. Padhi[a]; B. C. Singh[a]
[a] Laboratory of Polymers and Fibres Department of Chemistry, Ravenshaw College, Cuttack, India

To cite this Article Tripathy, S. S. , Jena, S. , Padhi, N. P. and Singh, B. C.(1983) 'Studies on Vinyl Polymerization: Polymerization of Acrylonitrile by Permanganate-Glucose Initiator System', Journal of Macromolecular Science, Part A, 19: 6, 827 — 835

To link to this Article: DOI: 10.1080/00222338308060779

URL: http://dx.doi.org/10.1080/00222338308060779

J. MACROMOL. SCI.–CHEM., A19(6), pp. 827-835 (1983)

Studies on Vinyl Polymerization: Polymerization of Acrylonitrile by Permanganate-Glucose Initiator System

S. S. TRIPATHY, S. JENA, N. P. PADHI, and B. C. SINGH*

Laboratory of Polymers and Fibres
Department of Chemistry
Ravenshaw College
Cuttack 753003, India

ABSTRACT

Aqueous polymerization of acrylonitrile initiated by the permanganate-glucose system has been studied under atmospheric conditions at 35 to 45°C. The rate of polymerization (R_p) is maximum at an optimum concentration of activator, but directly proportional to the concentration of monomer. R_p increases with an increase of metal ion concentration to a certain value and then decreases with a further increase of metal ion concentration. The effects of various water-soluble salts and solvents have been investigated. The endgroup of the polymer has been characterized by IR spectra. A suitable kinetic scheme has been proposed, appropriate rate expressions have been derived, and they are explained in the light of the experimental findings.

---

*To whom all correspondence should be addressed.

0022-233X/83/1906-0827$3.50/0

INTRODUCTION

Detailed kinetic investigation of aqueous vinyl polymerization initiated by heavy metal ions in their higher valence states [cerium-(IV), vanadium(V), chromium(VI), permanganate, etc.] have provided valuable information regarding the mechanistic details of the individual steps [1-4]. In a series of interesting communications, a number of workers have shown that permanganate-organic substrate redox initiators effectively polymeriza vinyl monomers, e.g., acrylic acid, methacrylic acid, acrylonitrile, methyl acrylate, methyl methacrylate, acrylamide. Hussain and Gupta [5] have reported the effects of various foreign substances on acrylamide polymerization by the permanganate-oxalic acid redox system. Very recently Misra and Bajpai [6] studied the aqueous redox polymerization initiated by the permanganate-lactic acid system. No one seems, however, to have taken up polymerization studies involving carbohydrates as organic substrates. From this laboratory [7, 8] we have reported the aqueous polymerization of acrylonitrile by the use of cerium(IV) paired with glucose and sucrose redox systems with a view to utilizing these unique systems for the graft copolymerization of such natural macromolecules as wool and silk.

Permanganate has long been known as a versatile oxidizing agent. We have a program to carry out graft copolymerization using the permanganate-carbohydrate redox pair. As a part of this research program, this article presents the results of studies on vinyl polymerization of acrylonitrile initiated by permanganate-glucose redox systems.

EXPERIMENTAL

Acrylonitrile was washed with 5% NaOH solution, dilute orthophosphoric acid, and finally with distilled water dried over anhydrous calcium chloride. $KMnO_4$ was BDH AnalaR grade. All other reagents such as glucose, ferrous ammonium sulfate, and sulfuric acid were AnalaR grade. The conductivity water used for preparing all solutions was obtained by redistilling distilled water with a small quantity of alkaline permanganate. A stock solution of catalyst was prepared by dissolving an appropriate quantity of $KMnO_4$ in 1 $\underline{M}$ H_2SO_4. The polymerizations were carried out in Corning glass vessels fitted with ground joint beads carrying inlet and outlet tubes. Appropriate quantities of a reaction mixture containing monomer, H_2SO_4, and glucose were placed in the reaction vessel and kept in a thermostat at the desired temperature. Finally, the permanganate solution was added. The polymerization reaction was heterogeneous with the polymers precipitating continuously. After a specified time interval the reaction was arrested by the addition of a known excess of ferrous ammonium sulfate solution. The polymer was filtered off, washed with water, and dried to constant weight. The rate of polymerization was calculated from the slope of the plot of yield versus time.

RESULTS AND DISCUSSION

Mechanism

In the aqueous polymerization of acrylonitrile initiated by the $KMnO_4$-glucose system, the permanganate first reacts with the acrylonitrile to produce MnO_2, which then dissolves in the reaction mixture to produce highly reactive Mn^{3+} ions. These Mn^{3+} ions react with glucose to produce active free radicals which are capable of initiating the polymerization of acrylonitrile. The following mechanism may be put forward to explain the experimental facts:

(a) Radical formation:

$$Mn^{3+} + R \overset{K}{\rightleftharpoons} \text{complex} \xrightarrow{k} R^{\bullet} + Mn^{2+} + H^{+}$$

(b) Initiation and propagation:

$$R^{\bullet} + M \xrightarrow{k_i} R\text{-}M_1^{\bullet}$$

$$RM_1^{\bullet} + M \xrightarrow{k_p} R\text{-}M_2^{\bullet}$$

$$\vdots$$

$$RM_n^{\bullet} + M \xrightarrow{k_p} R\text{-}M_{n+1}^{\bullet}$$

(c) Termination:

$$R\text{-}M_{n+1}^{\bullet} + M_n^{3+} \xrightarrow{k_t} \text{polymer}$$

(d) Oxidation:

$$R^{\bullet} + M_n^{3+} \xrightarrow{k_0} \text{oxidation product} + Mn^{2+}$$

On applying the steady-state principle to the primary radical $R^{\bullet}$ as well as to the growing radical, and making the usual assumption that the radical reactivity is independent of radical size, we arrive at the following rate expression:

$$R_p = \frac{k_p[M]^2}{k_t}\left[\frac{kK[R]}{[M] + (k_0/k_i)[KMnO_4]}\right] \tag{1}$$

Equation (1) reduces to

$$\frac{[M]^2}{R_p} = \frac{k_i[M]}{k_p kK[R]} + \frac{k_0 k_t}{k_p k_i kK}\,\frac{[KMnO_4]}{[R]} \tag{2}$$

Relation between Conversion and Reaction Time

Acrylonitrile was polymerized in aqueous H_2SO_4 solution at 35 to 45°C in the presence of the $KMnO_4$-glucose redox system. A typical set of time conversion curves at 35°C and at various glucose concentrations (nil to 0.04 mL^{-1}) at constant concentration of permanganate ion (5×10^{-3} mL^{-1}) is shown at Fig. 1. A limiting conversion is attained within 60 min.

Acrylonitrile was also polymerized under identical conditions with $KMnO_4$ in the presence of sucrose, lactose, and fructose (Table 1).

Consideration of the values of R_p for the systems mentioned shows that under identical conditions the order of reactivities is as follows: glucose > control > lactose > sucrose > fructose.

A possible explanation for the above behavior is that glucose has a free aldehyde group which is highly oxidizable in comparison with fructose which possesses a keto group. Therefore, free radical formation is facilitated in the case of the $KMnO_4$-glucose system and hence the rate of polymerization increases. But polymerization is highly retarded in the case of fructose due to the keto group. Polymerization is also retarded to some extent in the $KMnO_4$-sucrose system due to the presence of the fructose unit along with a glucose unit joined through their glycosidic carbon atom. Hence, the rate comes down even below the control. Again in the case of the $KMnO_4$-lactose system, one free aldehyde group of glucose unit is equally as favorable for polymerization as a simple glucose, but because of higher probability of hydrogen abstraction in the case of lactose compared to glucose, the polymerization rate is depressed. Retardation by hydrogen abstraction is well recognized.

Rate Dependence on Initiator Concentration

In this investigation $KMnO_4$ in conjugation with glucose constitutes the initiator. $KMnO_4$ alone can initiate polymerization of vinyl monomers, but the presence of glucose enhances polymerization. It is the quantity of reactive species produced by the reaction between $KMnO_4$ and glucose which affects the rate of polymerization (R_p).

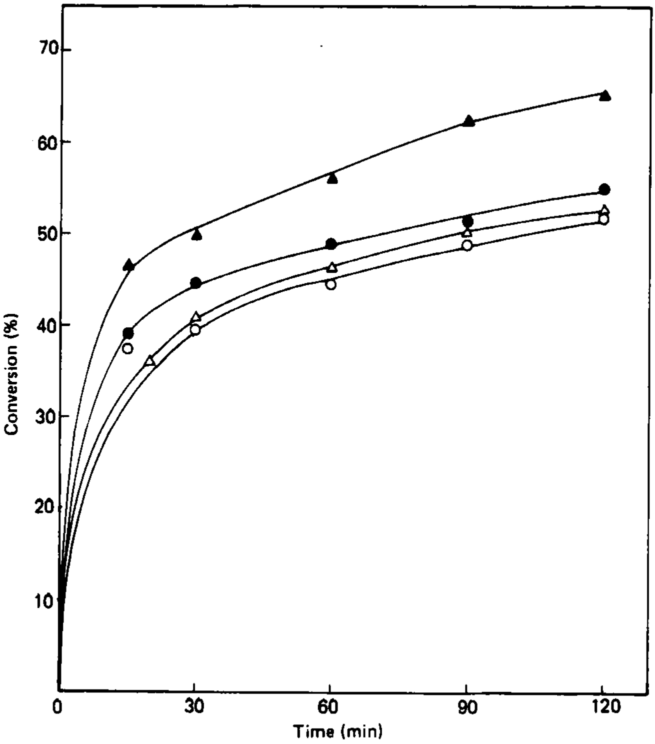

FIG. 1. Time conversion curves. [$KMnO_4$] = 0.005 M, [AN] = 0.753 M, [H_2SO_4] = 0.2 M, temperature = 35°C. (○) [GLU] = 0.04 M. (△) [Glu] = 0.02 M. (●) [Glu] = nil. (▲) [Glu] = 0.01 M.

TABLE 1. [M] = 0.753 mL^{-1}, [H_2SO_4] = 0.2 mL^{-1} [$KMnO_4$] = 0.005 mL^{-1}

Sugar	Concentration of the substrate	$R_p \times 10^5$ $mL^{-1}s^{-1}$
Glucose	0.01	19.35
Sucrose	0.01	13.65
Lactose	0.01	18.50
Fructose	0.01	7.20
Control	Nil	18.59

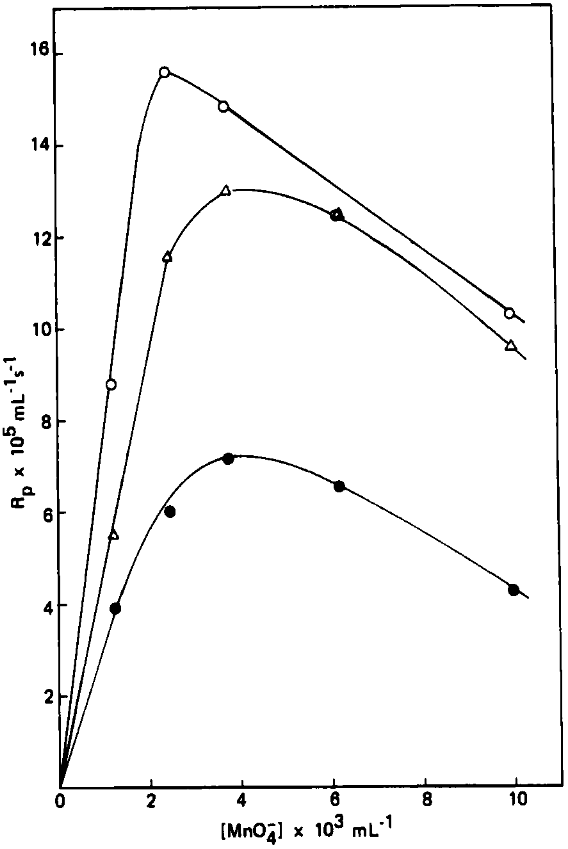

FIG. 2. Effect of KMnO$_4$. [AN] = 0.753 M, [Glu] = 0.01 M, [H_2SO_4] = 0.2 M. (○) = 35°C. (△) = 40°C. (●) = 45°C.

The initial rate of polymerization and the percentage conversion have been found to increase with increasing concentration of glucose up to a limiting concentration of 0.01 mL^{-1}. Beyond this concentration there is a consistent decrease in the rate even below the control, possibly because of transfer of radical with the reductant.

The relation between R_p and KMnO$_4$ is shown in Fig. 2. The rate increased up to 3 × 10^{-3} mL^{-1}, and thereafter consistently decreased. This indicates that mutual termination predominates over linear termination at lower concentration, and at higher concentration (the conditions under which the present investigation was carried out) linear termination predominates over mutual termination.

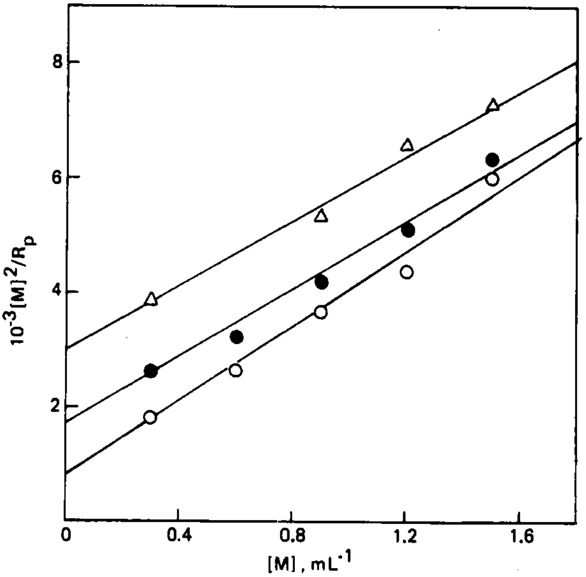

FIG. 3. Plot of $[M]^2/R_p$ vs $[M]$. $[KMnO_4]$ = 0.005 M, $[H_2SO_4]$ = 0.2 M, [Glu] = 0.01 M. (○) = 35°C. (●) = 40°C. (△) = 45°C.

Rate Dependence on Monomer Concentration

The initial polymerization rate and the percentage conversion are found to increase with increasing monomer concentration. A slight deviation from this behavior is observed at higher concentration of monomer (1.206 mL^{-1}) which may be due to the higher viscosity of the medium, preventing the conversion of monomer into polymer. According to rate Eq. (2), which is obtained by rearrangement of the equation based on the suggested mechanism, values of $[M]^2/R_p$ have been plotted against [M] for various temperatures (Fig. 3). Reasonable straight lines are obtained, the slopes and intercepts of which can throw light on the composite rate constants involved in the polymerization steps.

Effect of Temperature

The effect of temperature on this sytem is very interesting. A marked decrease in the initial rate and the maximum conversion are noticed when the temperature is increased from 35 to 45°C. This may be explained in terms of some side reaction undergone by the primary

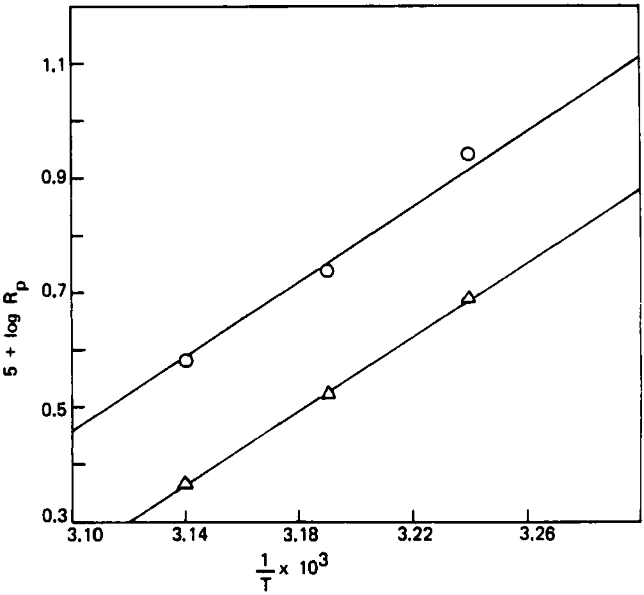

FIG. 4. Arrhenius Plot of log R_p vs 1/T. [Glu] = 0.01 M, [H_2SO_4] = 0.2 M. (○) [$KMnO_4$] = 1.25 × 10^{-3} M, [AN] = 0.753 M. (△) [$KMnO_4$] = 5 × 10^{-3} M, [AN] = 0.3012 M.

radicals responsible for the polymerization process. Similar observations have been reported by many workers [10-12] in certain redox polymerization systems. The overall energy of activation as calculated from the Arrhenius plot (Fig. 4) is found to be -15.82 kcal/mol.

Rate Dependence on Additives

The use of water-soluble solvents and inorganic salts gives information about the influence of the medium on polymerization. Some solvents enhance the rates of polymerization and some suppress it. The effect of organic solvents when added in the same proportions (5% v/v) is in the order DMF > methanol > control > ethanol > dioxane. The effect of neutral salts such as $MnSO_4$, K_2SO_4, NaCl, and $CuSO_4$ on polymerization was investigated. All the neutral salts except $MnSO_4$ depress polymerization. This can be attributed to the ionic dissociation of the added electrolyte which interferes with the normal polymerization process and results in premature termination of the growing polymer chains. The increase of rate by the addition of $MnSO_4$ can be explained by the disproportionation reaction occurring between Mn^{2+} and Mn^{4+} to generate Mn^{3+} ions. $Mn^{4+} + Mn^{2+} \rightarrow 2Mn^{3+}$. Mn^{3+} ion is responsible for the enhancement of the rate of polymerization. This type of observation has been made by Misra et al. [6].

IR Spectra

The IR spectra of the isolated polymer shows aliphatic –OH absorption along with peaks characteristic of the homopolymer. This shows that the polymer contains glucose residue as an endgroup, thus confirming the proposed mechanism.

REFERENCES

[1] E. A. S. Cavell and A. C. Meeks, Polymer, 8, 79 (1967).
[2] V. S. Ananthanarayan and M. Santappa, J. Appl. Polym. Sci., 9, 2437 (1965).
[3] S. Saccubai and M. Santappa, J. Polym. Sci., A-1, 7, 643 (1969).
[4] N. G. Devi and V. Mahadevan, Makromol. Chem., 152, 177 (1972).
[5] M. Hussain and A. Gupta, Ibid., 178, 29-36 (1977).
[6] G. S. Misra and U. D. N. Bajpai, Colloid Polym. Sci., 258, 102-105 (1977).
[7] N. P. Padhi and B. C. Singh, J. Polym. Sci., In Press.
[8] N. P. Padhi and B. C. Singh, Colloid Polym. Sci., Submitted.
[9] R. K. Satapathy, S. N. Patnaik, B. K. Misra, S. P. Rout, and M. K. Rout, J. Macromol. Sci.–Chem., A13(2), 273-283 (1979).
[10] S. R. Palit and R. S. Konar, J. Polym. Sci., 58, 85 (1962).
[11] G. S. Misra and C. V. Gupta, Makromol. Chem., 156, 195 (1973).
[12] M. M. Hussain, S. N. Misra, and A. Gupta, Ibid., 177, 2919 (1976).

Accepted by editor August 14, 1982
Received for publication September 14, 1982