

Persulphate-Co²⁺-Bisulphite Initiated Aqueous Polymerization of Acrylamide and Retardation by Organic Solvents

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The aqueous polymerization of acrylamide initiated by the persulphate metabisulphite redox couple and catalyzed by Co²⁺ ions has been iodometrically studied in atmospheric oxygen over the temperature range from 25° to 45 ± 0.2°C. The effect of varying concentration of monomer, persulphate, bisulphite and Co²⁺ ions on the course of polymerization has been investigated. The following rate dependence has been observed: $R_p \propto [\text{Monomer}]^{1.0} [\text{Co}^{2+}]^{1.0} [\text{HSO}_3^-]^0 [\text{PS}]^{1.0}$. Various inorganic salts and organic solvents were added to the reaction medium and the rate of polymerization was observed with a special emphasis on the retarding behaviour of organic solvents. The energy of activation was calculated to be 10.8 kcal/mol.

INTRODUCTION

Peroxydisulphate has been proved to be an effective initiator in redox polymerization of vinyl monomers, either alone¹ or in conjugation with a variety of reducing agents like malonic acid², aliphatic amines³, isoamyl alcohol⁴, mercaptoethanol⁵ etc. It has also been reported that the incorporation of metal ions to persulphates facilitates their decomposition to produce free radicals⁶. In the present paper the polymerization of acrylamide has been carried out by a three component redox system consisting of persulphate, Co²⁺ and metabisulphite. The monomer chosen for the polymerization is acrylamide as it finds a wide range of applications in various industrial and technological processes.

EXPERIMENTAL

Acrylamide (E. Merck, India) was crystallized twice from methanol (G.R.) and dried over silica gel for five days. Potassium persulphate (A.R.) was used without further purification. Cobaltous chloride (BDH, AnalaR) was used as received and its standard solution was prepared as reported by Vogel. Other reagents employed were of G.R. grade and all solutions were freshly prepared in conductivity water.

The polymerization procedure was similar to that as described in our other communications⁷⁻¹². For determining the viscosity average molecular weight the following relationship was used¹³:

$$[\eta] = 6.8 \times 10^{-4} M^{0.66}$$

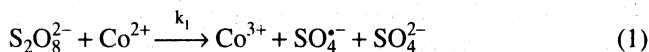
where $[\eta]$ is the intrinsic viscosity of the polymer solution.

RESULTS AND DISCUSSION

A plausible mechanism has been proposed for the polymerization of acrylamide (represented by M) as given below:

Formation of the Radicals

Persulphate reacts with Co^{2+} producing highly reactive Co^{3+} ions as follows:



The trivalent cobaltic ions react with metabisulphite ions to produce free radicals:

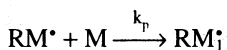


If free radicals $\text{SO}_4^{\cdot-}$ and $\text{HSO}_3^{\cdot-}$ are denoted by R^{\cdot} , then

(a) Initiation:



(b) Propagation:



(c) Termination: In presence of metal ions the most probable termination may be unimolecular in nature,



Based on steady state kinetic assumptions, the following rate expression has been derived:

$$R_p = \left(\frac{k_p k_i}{k_t} \right) [\text{M}]^{1.0} [\text{Co}^{2+}]^{1.0} [\text{HSO}_3^-]^0 [\text{PS}]^{1.0} \quad (6)$$

The resulting expression is in fair agreement with our experimental outcome.

Monomer Dependence: The rate of polymerization and percentage conversion were found to increase with increasing concentration of acrylamide in the range 5.0 to 2.5×10^{-2} mol/L as shown in Fig. 1. The increase observed is attributable to the fact that increased monomer concentration in the reaction medium brings about an increase in the availability of the monomer molecules in the propagation step which consequently results in the observed findings.

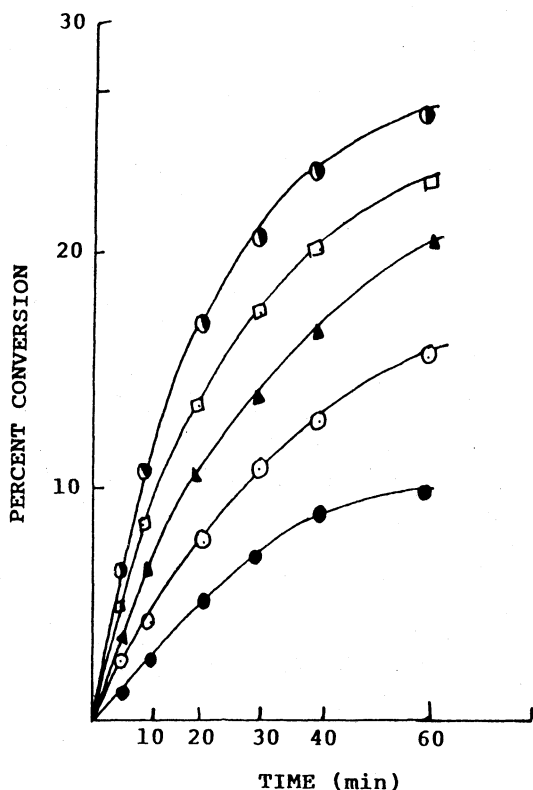


Fig. 1. Time Vs conversion curve for the polymerization of acrylamide with varying initial monomer concentration (mol/L) at fixed [persulphate] = 5.0×10^{-3} mol/L, [bisulphite] = 5×10^{-2} mol/L, $[Co^{2+}] = 1 \times 10^{-3}$ mol/L, at $30 \pm 0.2^\circ C$ (●) 5.0×10^{-2} , (○) 10.0×10^{-2} , (▲) 15.0×10^{-2} , (□) 20.0×10^{-2} , and (●) 15.0×10^{-2} .

The order with respect to the monomer has been found to be 0.95 as calculated from the double logarithmic plot shown in Fig. 2. The results obtained are identical to those reported by other workers¹⁴.

Redox Components Dependence: When the concentration of persulphate (initiator) varies from 2.0 to 10×10^{-3} mol/L, both the initial rate of polymerization and percentage conversion are found to increase. The observed increase is because of the fact that with enhancement in the concentration of persulphate, the rate of free radical generation (Eq. 1) becomes more and, therefore, the initial rate and percentage conversion increase. From the double logarithmic plot (Fig. 3) the dependence of rate on persulphate concentration has been found to be 1.01 and this first order dependence of initiator has richly been referenced in the literature¹⁵.

On the other hand, there is almost no change in the rate of polymerization when the concentration of bisulphite varies in the range 1.4 to 4.0×10^{-2} mol/L. This clearly shows that a zero order dependence on the bisulphite concentration exists there. The observed independence may be explained by the fact that there

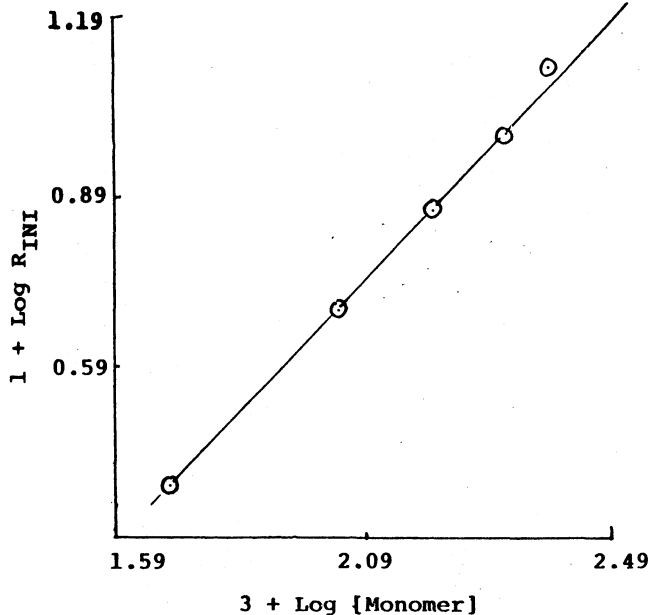


Fig. 2. Double logarithmic plot of the initial rate of polymerization (R_{INI} in % conversion per minute) vs the initial concentrations of monomer. slope = 0.95.

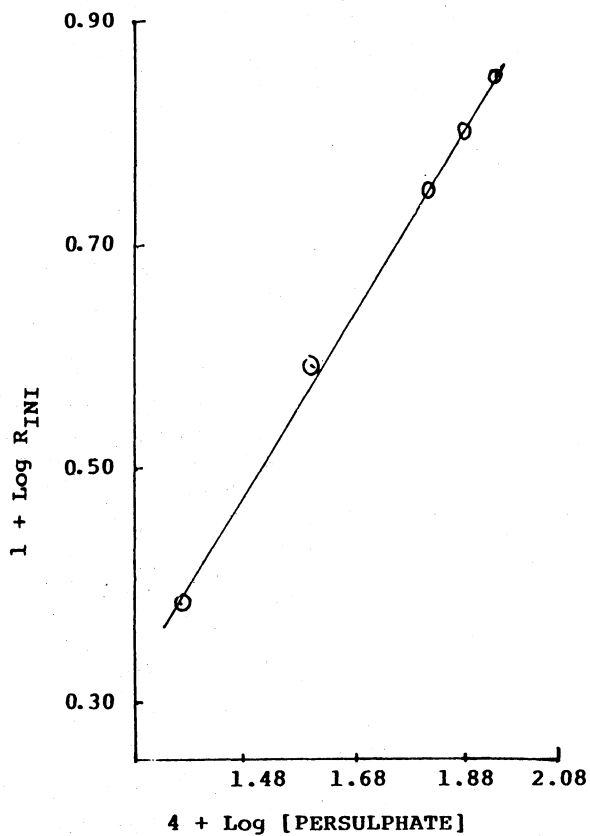


Fig. 3. Double logarithmic plot of the initial rate of polymerization (R_{INI} in % conversion per minute) vs the initial concentration of initiator. slope = 1.01.

automatically exists a balance between the bisulphite and persulphate concentrations if the concentration of the form is raised. When the concentration of bisulphite increases, the number of initiating free radicals (HSO_3^-) also increases and more persulphate is consumed in above process (Eq. 2). This obviously enhances the initial rate of polymerization and percentage conversion. But, at the same time, number of SO_4^- radicals decreases due to a fall in the concentration of persulphate ions (in Eq. 1). The two opposing reactions balance each other in the studied range of bisulphite concentration and, therefore, a zero order dependence is noticed. Similar type of results have also been reported by other workers¹⁶.

Effect of Co^{2+} ions: On increasing the concentration of Co^{2+} ions in the solution in the range 1.0 to 3.2×10^{-3} mol/L, both the initial rate and percentage conversion increase. The increase observed is quite obvious as on raising the concentration of Co^{2+} ions, the rate of generation of initiating radicals (SO_4^- and HSO_3^-) will increase which, therefore, results in a greater initial rate and percentage conversion. The dependence of the initial rate of polymerization on Co^{2+} ions concentration has been found to be 0.98 as shown in double logarithmic plot (Fig. 4).

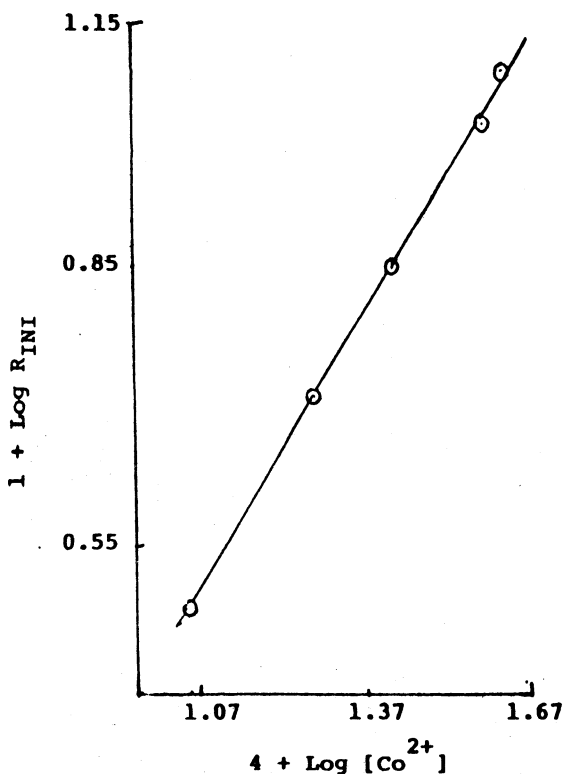


Fig. 4. Double logarithmic plot of the initial rate of polymerization (R_{INI} in % conversion per minute) vs the initial concentration of Co^{2+} ions. slope = 0.98 .

Temperature Effect: The effect of temperature on the kinetics of polymerization has been investigated by varying the temperature of the medium in the range 25 to 45°C. It has been found that a rise in the temperature of the solution causes polymerization rate and percentage conversion to increase because of the fact that at higher temperature the rate of active centre formation also increases which as a consequence increases the rate of polymerization. The energy of activation has been found to be 10.8 kcal/mol as calculated from Arrhenius plot (Fig. 5).

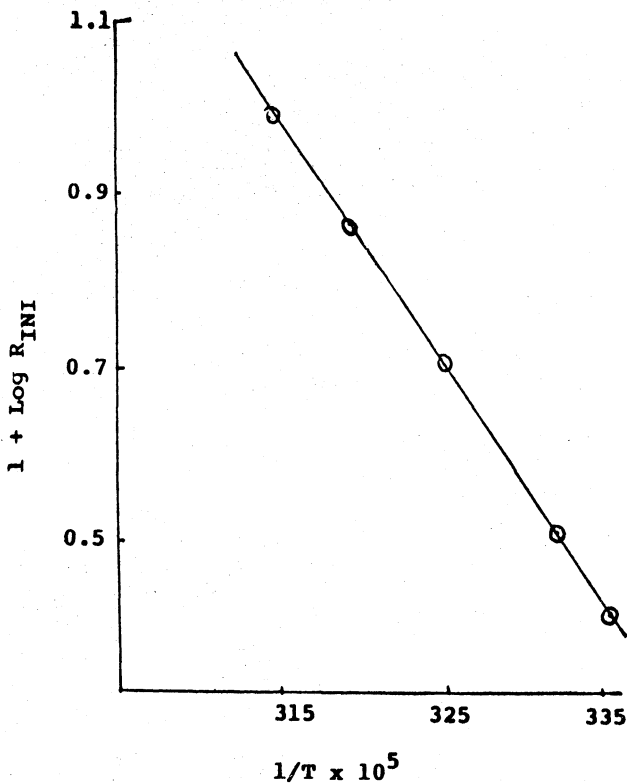


Fig. 5. Arrhenius plot of the initial rate of polymerization vs reciprocal of absolute temperature (T) of polymerization, $E_a = 10.8$ kcal/mol.

Effect of Inorganic Salts: Addition of equimolar amounts of neutral salts to the reaction medium causes a fall in the polymerization rate and percentage conversion as well. The results have been shown in Fig. 6 and Fig. 7 which clearly describe the effect of anions and cations addition on the course of polymerization. It is also reveal from the figures that the following order of increasing depression is found in both the cases, $Cl^- < Br^- < I^- < SO_4^{2-}$ and $Li^+ < Na^+ < K^+$.

The observed fact may be attributed to the following reasons:

(a) Added electrolytes cause an increase in the ionic strength of the medium which interferes with the normal polymerization procedure thus depressing the initial rate and percentage conversion.

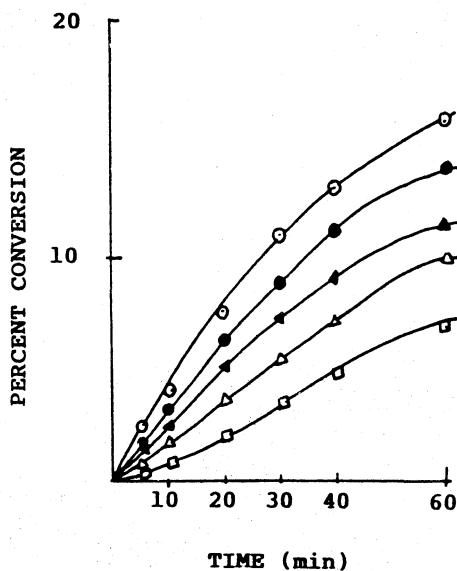


Fig. 6. Effect of addition of anions on the polymerization rate of acrylamide at fixed [monomer] = 10.0×10^{-2} mol/L, [persulphate] = 5.0×10^{-3} mol/L, [bisulphite] = 5.0×10^{-2} mol/L, $[\text{Co}^{2+}] = 1.0 \times 10^{-3}$ mol/L, at $30 \pm 0.2^\circ\text{C}$ (○) control, (●) = 0.01 (mol/L KCl, (▲) 0.01 mol/L KBr, (△) 0.01 mol/L KI and (◻) 0.01 mol/L K_2SO_4 .

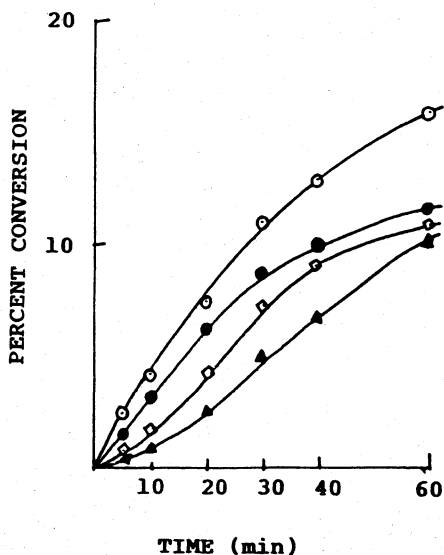


Fig. 7. Effect of addition of cations on the polymerization rates of acrylamide, at fixed [monomer] = 10.0×10^{-2} mol/L, [persulphate] = 5.0×10^{-3} mol/L, [bisulphite] = 5.0×10^{-2} mol/L, $[\text{Co}^{2+}] = 1 \times 10^{-3}$ mol/L, at $30 \pm 0.2^\circ\text{C}$, (●) 0.01 mol/L Li_2SO_4 , (◻) 0.01 mol/L Na_2SO_4 , (▲) 0.01 mol/L K_2SO_4 , (○) no salt.

(b) It is also probable that the increased number of ions in the reaction medium results in a higher termination rate which also leads to the observed results.

(c) The possibility of ion pair formation between the added and already existing ions may not be ruled out which will also cause the initial rate and percentage conversion to decrease.

Similar type of results have also been reported by many workers¹⁷.

Effect of Organic Solvents: Retarding behaviour of water miscible organic solvents in vinyl polymerization is a well known phenomenon and has been largely studied in many polymerization experiments¹⁸. The reason for using organic solvents as retarders is due to their manifold actions that not only result in a decrease in the initial rate and percentage conversion but also does in a fall in the molecular weight of the resulting polymers which also have specific applications. In the present work different aliphatic alcohols have been chosen as retarders for the polymerization reaction. The effect of these solvents on polymerization rate has been studied both qualitatively and quantitatively. It is clear from Fig. 8 that a decrease in the polymerization rate and percentage

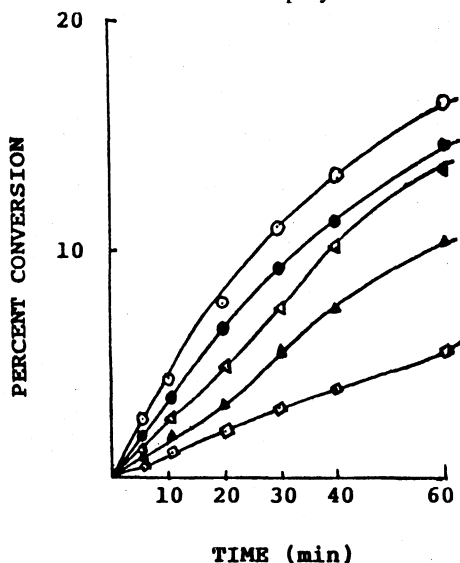
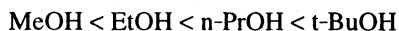


Fig. 8. Effect of addition of water miscible organic solvents 5% (v.v) on the polymerization rate of acrylamide at fixed $[\text{Monomer}] = 10.0 \times 10^{-2} \text{ mol/L}$, $[\text{Persulphate}] = 5.0 \times 10^{-3} \text{ mol/L}$, $[\text{bisulphite}] = 5.0 \times 10^{-2} \text{ mol/L}$, $[\text{Co}^{2+}] = 1 \times 10^{-3} \text{ mol/L}$ at $30 \pm 0.2^\circ\text{C}$. (●) methanol, (△) ethanol, (▲) iso-propanol and (◻) n-butanol, (○) water.

conversion is observed when these alcohols are added (5% v/v) to the reaction medium. The following order of increasing depression has been observed:



The observed results may be attributed to the following reasons:

(i) The added organic solvents may also be oxidized to some extent by the

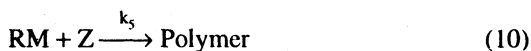
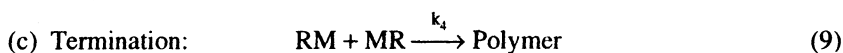
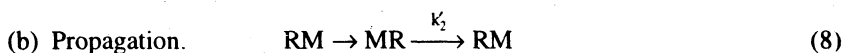
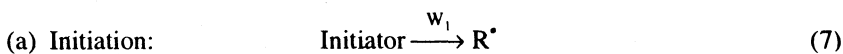
initiator (persulphate) producing less reactive alcoxy radicals which have much lower tendency to reinitiate the polymerization.

(ii) The growing macroradicals may transfer their activity to the solvent molecules (chain transfer) thus resulting in a lower rate of polymerization.

(iii) Since some of the initiator gets consumed in the oxidation of alcohols, its reduced concentration will result in a fall in the initial rate of polymerization and percentage conversion as well.

Retarding Effect of Solvents: The concept of retardation in vinyl polymerization has largely been employed in producing antioxidants and stabilizers for various uses^{19, 20}. In the present communication we are quantitatively evaluating the retarding behaviour of organic solvents in terms of Tudos' parameter (β)²¹ and retardation constants.

Scheme Proposed by Tudos



where M, R' and Z are monomer, chain carrier and retarder respectively. If rate of initiation is assumed to be constant then the Tudos' parameter β may be given as:

$$\beta = uk_5 X^{1/2} / 2 (w_1 k_4)^{1/2} = \phi X^{1/2} Z \quad (11)$$

Here u = stoichiometry of the hydrogen abstraction reaction.

$$\text{Now } \phi = \frac{1}{2} \left(\frac{W_{ST}}{W} - \frac{W}{W_{ST}} \right) \quad (12)$$

Here W = rate of retarded polymerization

W_{ST} = rate of unretarded polymerization

X = initial concentration of retarder

thus with the help of Eqs. (11) and (12), ϕ may be calculated.

Retardation Constant I

For calculating retardation constants, following equation would be helpful.

$$[M]_0 = I \cdot \frac{[W]_0}{\left(\frac{1}{DP} - \frac{R_p}{(DP)'R'_p} \right)} \quad (13)$$

Here different terms have their usual significance as described elsewhere¹⁵.

The quantitative effect of above parameter has been summarized in Table-1. It is quite clear from Table that both Tudos' parameter β and retardation constant I provide a numerical basis to the retardation phenomena.

TABLE-I
TUDOS' PARAMETERS AND RETARDATION CONSTANTS FOR VARIOUS
ORGANIC SOLVENTS IN POLYMERIZATION OF ACRYLAMIDE

Solvent	Tudos' parameter (β) ^a $\times 10^3$	Retardation constant ^b $\times 10^5$
Methanol	9.9	9.3
Ethanol	22.0	26.4
iso-Propanol	48.9	67.5
n-Butanol	57.2	78.4

^acalculated from Eq. (11).

^bcalculated from Eq. (13).

REFERENCES

1. Sukumar Guchhait, Monoranjan Banerjee and Ranjit Sinha Konar, *Indian J. Chem.*, **30A**, 130 (1991).
2. K.C. Gupta and K. Behari, *Polymer Bulletin*, **16**, 10 (1986).
3. X. Guo, K. Qiu and X. Fenz, *Sci. Sin., Ser. B*, **30**, 897 (1987) (Eng.).
4. L.P. Tolstukhova, Gromov and E.N. Teleshov, *Plast MARRY*, **3**, 6 (1988).
5. K.C. Gupta, M. Lal and K. Behari, *Acta Polym.*, **37**, 722 (1986).
6. U.D.N. Bajpai, Alka Jain and A.K. Bajpai, *Revue Roum. Chim.*, **33**, 629 (1988).
7. U.D.N. Bajpai and A.K. Bajpai, *J. Makromol. Sci. Chem.*, **19A**, 487 (1983).
8. _____, *Macromolecules*, **18**, 2113 (1985).
9. _____, *J. Polym. Sci., Polym. Chem. Edn.*, **22**, 1803 (1984).
10. U.D.N. Bajpai, A.K. Bajpai and J. Bajpai, *J. Appl. Polym. Sci.*, **42**, 2005 (1991).
11. U.D.N. Bajpai, A.K. Bajpai and A. Soni, *Iranian J. Chem.*, **31**, 31 (1993).
12. U.D.N. Bajpai, A.K. Bajpai and J. Bajpai, *J. Indian Chem. Soc.*, **69**, 841 (1992).
13. T.J. Suen, Y. Jen and J. Lockwood, *J. Polymer Sci.*, **31**, 481 (1958).
14. A.K. Bajpai and S.K. Bajpai, *Iranian J. Pol. Sci. Tech.*, **4**, 10 (1995).
15. U.D.N. Bajpai, A.K. Bajpai and A. Jain, *Polymer Int.*, **32**, 137 (1993).
16. U.D.N. Bajpai, *J. Macromol. Sci. Chem. (A)*, **16**, 629 (1981).
17. G.S. Misra and U.D.N. Bajpai, *Prog. Polym. Sci.*, **8**, 61 (1982).
18. Mikiharu Kamachi, *Adv. in Polymer Sci.*, **38**, 55 (1981).
19. R.A. Bird and K.E. Russell, *Canad. J. Chem.*, **43**, 2123 (1965).
20. J. Pospisil, L. Kotulak and B.V. Malaska, *Eur. Polymer J.*, **7**, 33 (1971).
21. M. Simonyl, F. Fudos and J. Pospisil, *Eur. Polymer J.*, **3**, 101 (1967).

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