Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Permanganate-Pyruvic Acid Initiated Polymerization of Methacrylamide

U. D. N. Bajpai[a]

[a] Department of Post-Graduate Studies and Research in Chemistry, University of Jabalpur, Jabalpur, India

To cite this Article Bajpai, U. D. N.(1981) 'Permanganate-Pyruvic Acid Initiated Polymerization of Methacrylamide', Journal of Macromolecular Science, Part A, 16: 3, 629 — 636

To link to this Article: DOI: 10.1080/00222338108056810

URL: http://dx.doi.org/10.1080/00222338108056810

J. MACROMOL. SCI.–CHEM., A16(3), pp. 629-636 (1981)

Permanganate-Pyruvic Acid Initiated Polymerization of Methacrylamide

U. D. N. BAJPAI

Department of Post-Graduate Studies and Research in Chemistry
University of Jabalpur
Jabalpur 482001, India

ABSTRACT

A combined system of potassium permanganate and pyruvic acid was found to initiate radical polymerization of vinyl monomers, especially acrylamides. From kinetic investigations of the polymerization of methacrylamide, it was found that this initiator induced a radical polymerization which proceeded with an overall activation energy of 15.7 kcal/mol. The rate is given by

$$R_p = K[\text{methacrylamide}]^1[\text{pyruvic acid}]^0[KMnO_4]^1$$

in aqueous and water-DMF mediums. In the presence of DMF the initial rate was found to decrease but the kinetic equation remained the same. The investigations were done at 35 ± 0.2°C in nitrogen.

Besides the clinical importance of pyruvic acid found in blood, urine, muscles, etc., it is a good initiator in conjunction with $KMnO_4$ for vinyl polymerization. It is therefore interesting to study the polymerization of methacrylamide using the $KMnO_4$-pyruvic acid redox couple in aqueous systems in order to find whether this system follows the same kinetic features of vinyl polymerization by a radical mechanism.

EXPERIMENTAL

Reagents

Methacrylamide was recrystallized thrice from methanol and dried in vacuum. The pyruvic acid used was made by Reidel (Germany). All reagents were of AR or equivalent grade. The solvent, conductivity water, used in all experiments was prepared by redistilling distilled water to which a small quantity of alkaline permanganate had been added.

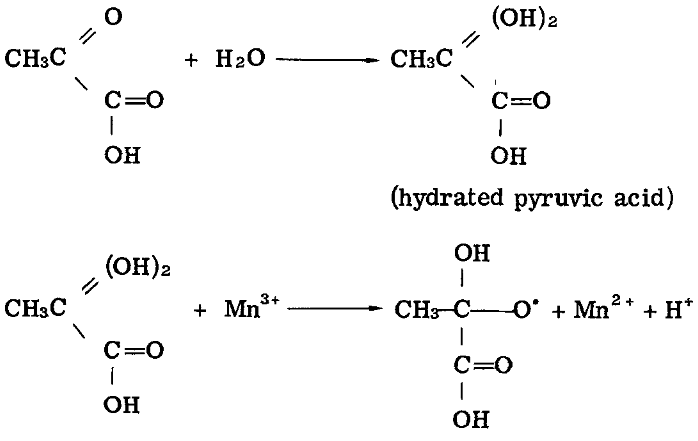
Polymerization Procedure

The polymerization was followed by a quantitative estimation of the double bonds in methacrylamide as described by Wallace et al. [1]. The experimental procedure was essentially of Misra et al. [2]. The conversion was calculated using the formula given by Misra et al. [3].

RESULTS AND DISCUSSION

Mechanism

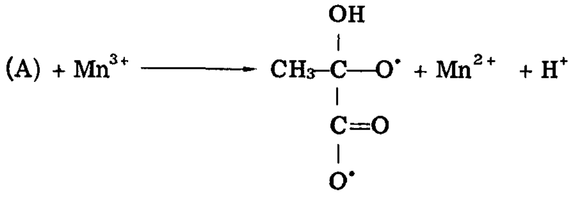
α-Keto acids are known to be partially hydrated in aqueous solution [4]. The hydrated form of pyruvic acid possibly reacts with Mn^{3+} ions produced in the system, generating free radicals responsible for the polymerization. A plausible mechanism is



$$CH_3C(=O)-C(=O)-OH + H_2O \longrightarrow CH_3C(=(OH)_2)-C(=O)-OH$$

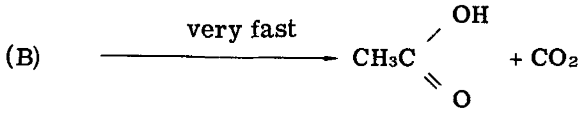
$$CH_3C(=(OH)_2)-C(=O)-OH + Mn^{3+} \longrightarrow CH_3-C(OH)(-O^{\bullet})-C(=O)-OH + Mn^{2+} + H^{+}$$

(A)



$$(A) + Mn^{3+} \longrightarrow CH_3\text{-}\overset{OH}{\underset{C=O-O^{\bullet}}{C}}\text{-}O^{\bullet} + Mn^{2+} + H^+$$

(B)



$$(B) \xrightarrow{\text{very fast}} CH_3C(=O)OH + CO_2$$

In this system the initiating species are only free radicals (A) because another free radical (B) produced in the system would degrade to acetic acid as it is being formed. The formation of an oxygen-free radical was also checked by the negative mercuric chloride test.

Activator and Catalyst Dependence

The initial rate of polymerization and the limiting conversion were found to remain practically constant over a wide range of pyruvic acid concentration at a fixed concentration of methacrylamide (10.0×10^{-2} mol/dm^3) and $KMnO_4$ (2.25×10^{-3} mol/dm^3). Usually in a redox system an increase in the activator concentration results in an increase in the rate of generation of the primary free radicals which initiate the polymerization. An enhancement in the rate of polymerization would therefore be expected at higher concentrations of pyruvic acid. However, it has been found in this system that the rate is independent of the concentration of the activator. Such a behavior has also been reported by Palit et al. [5, 6], Misra et al. [7-9], and Shukla et al. [10-12]. It may be due to the balance existing between the rates of the radical generation step and the side reaction occurring in the system.

An insight into the effect of varying the pH of the polymerization medium on the rate can be made by consideration of the pyruvic acid dependence. The pH decreases with increasing concentration of activator. The rate and limiting conversion remain unaffected by a decrease of pH in the range 3.8 to 3.52.

In the absence of $KMnO_4$, pyruvic acid alone is incapable of initiating polymerization of methacrylamide in the dark. The initial rate and limiting conversion are found to increase with an increase in the concentration of the catalyst ($KMnO_4$) and at a fixed concentration of activator and monomer. The increase in the amount of the catalyst in the system causes an increase in the number of free radicals, thereby increasing both the rate and conversion.

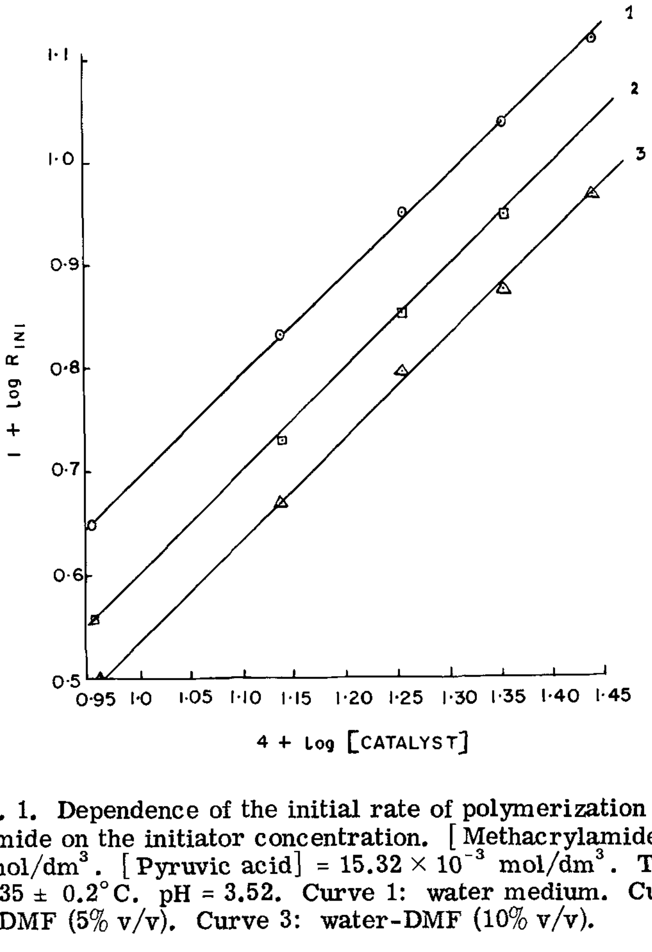


FIG. 1. Dependence of the initial rate of polymerization of methacrylamide on the initiator concentration. [Methacrylamide] = 10.0×10^{-2} mol/dm^3. [Pyruvic acid] = 15.32×10^{-3} mol/dm^3. Temperature = 35 ± 0.2°C. pH = 3.52. Curve 1: water medium. Curve 2: water-DMF (5% v/v). Curve 3: water-DMF (10% v/v).

To determine the order of reaction with respect to catalyst the logarithm of the initial rate (R_{ini}) was plotted against the logarithm of the $KMnO_4$ concentration in the range studied (0.90 to 2.70×10^{-3} mol/dm^3). The catalyst exponent (slope of the curves in Fig. 1) is found to be one which indicates a first-order dependence of the polymerization rate on the catalyst concentration and an unimolecular mechanism of termination.

Rate Dependence on Monomer Concentration

The effect of variation in the monomer concentration on the kinetic parameters of a polymerization system is shown in Fig. 2. It is clear

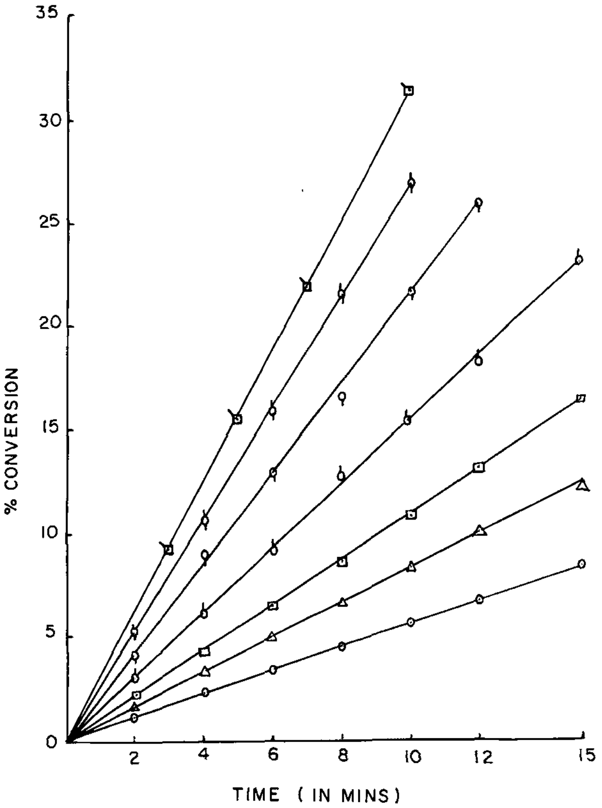


FIG. 2. Kinetic curves for the polymerization of methacrylamide (MA) in aqueous medium at 35 ± 0.2°C. [Pyruvic acid] = 15.32×10^{-3} mol/dm^3, pH = 3.52. [$KMnO_4$] = 2.25×10^{-3} mol/dm^3. [MA] values in mol/dm^3 are (○) 5.0×10^{-2}, (△) 7.5×10^{-2}, (□) 10.0×10^{-2}, (ό) 15.0×10^{-2}, (♀) 20.0×10^{-2}, (ϕ) 25.0×10^{-2}, and (⧠) 30.0×10^{-2}.

from Fig. 2 that the initial rate and the percent conversion are found to increase with an increasing concentration of monomer. The order of the reaction with respect to monomer concentration was found to be 1 (slope of Curve 1 in Fig. 3). Burfield et al. [13] also found a normal first-order dependence on monomer concentration in the persulfate-initiated polymerization of methacrylamide.

Temperature Dependence

The effect of temperature was studied over the range 25 to 50°C. The initial rate and limiting conversion increase up to 35°C, but a

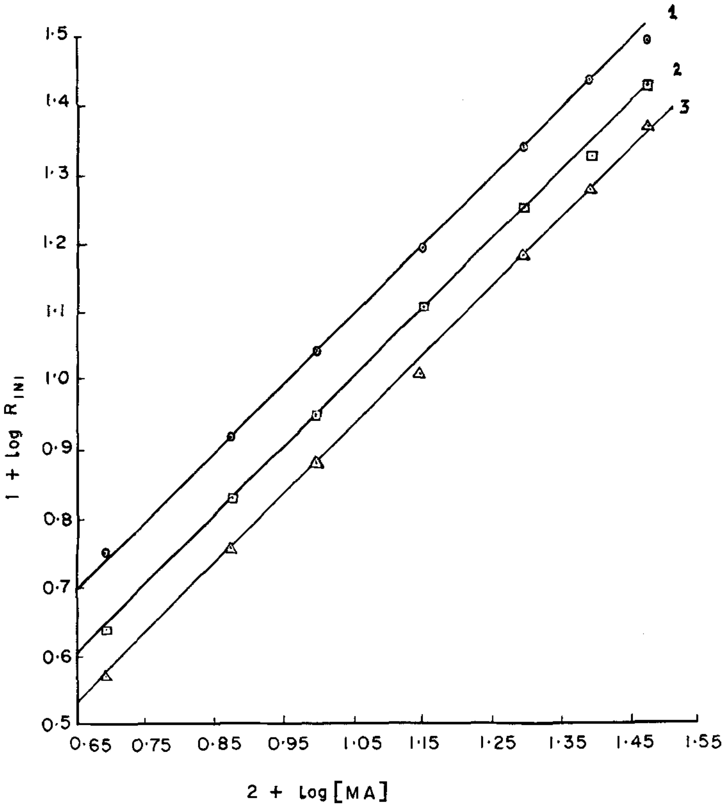


FIG. 3. Dependence of the initial rate of polymerization of methacrylamide on the monomer concentration at 35 ± 0.2°C. [Pyruvic acid] = 15.32×10^{-3} mol/dm^3. [$KMnO_4$] = 2.25×10^{-3} mol/dm^3. Curve 1: water medium. Curve 2: water-DMF (5% v/v). Curve 3: water-DMF (10% v/v).

further rise in temperature showed a fall in limiting conversion. The overall energy of activation as calculated from the Arrhenius plot was found to be 15.7 kcal/mol which is in good agreement with those reported earlier for similar redox systems [2, 3, 14].

Effect of Organic Solvents

It has been found that the use of water-organic solvents and water-salt mixtures reveal the influence of the medium on the polymerization and the properties of the resulting polymers [15-17]. Keeping this in mind, the effect of water-DMF mixtures has been studied in the present investigations.

The influence of initiator concentration on the rate of polymerization was investigated for fixed monomer and pyruvic acid concentration in water-DMF mixtures. The rate of polymerization in every case was found to be first order with respect to catalyst concentration as in the case of aqueous medium (Fig. 1, Curves 2 and 3).

Curves 2 and 3 in Fig. 3 represents the relationship between the rate and the initial monomer concentration in various water-DMF mixtures. From Fig. 3 it is very clear that the polymerization rate is accurately proportional to the monomer concentration in the range studied.

Other water-soluble organic solvents like alcohols also have a diminishing effect on both the rate and limiting conversion. The decrease in polymerization rate and percentage conversion may be explained as follows. The addition of water-miscible organic solvents:

1. Decreases the area of shielding of a strong hydration layer in an aqueous medium, resulting in the termination of the radical end of the growing chains.
2. Increases the regulated rate of production of primary radicals, which under the existing experimental conditions means that the rate of termination is faster as compared to the rate of propagation, as pointed out by Kern et al. [18].
3. Makes the interchain hydrogen bonding which interlocks the polymethacrylamide chain not rigid (perfect), whereby the tendency of mutual termination of the polymer chain increases.

A similar type of tendency was found by Palit et al. [6] even for the homogeneous polymerization in nonaqueous media in the presence of traces of water.

REFERENCES

[1] R. A. Wallace and D. C. Young, J. Polym. Sci., 4, 1179 (1966).
[2] G. S. Misra, J. S. Shukla, and H. Narain, Makromol. Chem., 119, 74 (1968).
[3] G. S. Misra and H. Narain, Ibid., 113, 85 (1968).
[4] S. Yuguchi, H. Kiuchi, and M. Watanbe, Kobunshi Kagaku, 15, 829 (1966).
[5] S. R. Palit and R. S. Konar, J. Polym. Sci., Part A-2(4), 1731 (1964).
[6] U. S. Nandi, P. Ghosh, and S. R. Palit, Nature, 195, 1197 (1962).
[7] G. S. Misra and C. V. Gupta, Makromol. Chem., 156, 195 (1972).
[8] U. D. N. Bajpai and G. S. Misra, Vysokomol. Soedin., 21, 1720 (1979).

[9] U. D. N. Bajpai and G. S. Misra, Paper Presented at the International Symposium on Macromolecular Chemistry, Macro-78, Tashkent, USSR, October 17-21, 1978.

[10] J. S. Shukla and D. C. Misra, Makromol. Chem., 158, 9 (1972).

[11] J. S. Shukla and D. C. Misra, Ibid., 173, 91 (1973).

[12] J. S. Shukla and D. C. Misra, J. Polym. Sci., Polym. Chem. Ed., 11, 751 (1973).

[13] D. R. Burfield and S. C. Ng, Eur. Polym. J., 12, 873 (1976).

[14] G. S. Misra and J. J. Rebello, Makromol. Chem., 177, 21 (1976).

[15] V. F. Kurenkov, E. V. Kuznetsov, S. Ya. Frenkel, and V. A. Myangohenkov, Eur. Polym. J., 6, 1643 (1965).

[16] S. Ya. Frenkel, Vvedeniye v Statisticheskiy Theoiy Polymerizatsii, Nauka, Moscow, 1965.

[17] E. A. Bekturev, Troynie Polymerniye sistemi v rastvoroh, Nauka, Alma-Ata, 1975.

[18] A. Sohulz, G. Renner, A. Hunglein, and W. Kern, Makromol. Chem., 12, 50 (1954).

Accepted by editor March 25, 1980
Received for publication April 22, 1980