

Graft Copolymerization onto Natural Rubber. XV. Graft Copolymerization of Methyl Methacrylate onto Natural Rubber Using a Potassium Permanganate-Ascorbic Acid Redox System

INTRODUCTION

The use of ascorbic acid in the presence of various oxidizing agents to yield free radicals capable of initiating vinyl polymerization is well known.^{1,2} Recently we have used a number of systems for the graft copolymerization of methyl methacrylate onto natural rubber.³⁻⁷ In the present investigation, ascorbic acid is used along with permanganate for the graft copolymerization of methyl methacrylate onto natural rubber.

EXPERIMENTAL

Crepe natural rubber with ash content 0.6% and acetone extract 2.2% was obtained as a gift sample from Dr. S. K. De (IIT, Kharagpur, India).

Potassium permanganate and ascorbic acid were pure-grade chemicals. The purification of monomers and graft copolymerization were carried out according to our previous communications.⁸

RESULTS AND DISCUSSION

Attempts were made to initiate graft copolymerization of methyl methacrylate (MMA) onto natural rubber using potassium permanganate ascorbic acid as the initiator. A graft yield of 91% was obtained at 55°C with a permanganate concentration of 0.5×10^{-2} mol/L.

EFFECT OF TEMPERATURE

The rate of grafting increases with an increase in temperature up to 55°C, and thereafter it decreases with a further increase in temperature.

At higher temperatures the formation of homopolymer increases; hence the percentage of grafting was depressed. From an Arrhenius plot of $\log R_p$ versus $1/T$ (Fig. 1), the overall activation energy was found to be 23 kcal/mol. Similar values were obtained by Nayak et al.^{3,9-11} in the case of grafting onto rubber using other redox systems.

EFFECT OF INITIATOR CONCENTRATION

The percentage of grafting increases with an increase in initiator concentration up to 0.5×10^{-2} mol/L and thereafter it decreases (Fig. 2). This is because, at higher initiator concentration, it facilitates the formation of homopolymer, decreasing the graft yield.

EFFECT OF MONOMER

The effect of monomer on the graft yield has been investigated by changing the monomer concentration from 2.347×10^{-1} to 11.735×10^{-1} mol/L. It has been shown that the graft yield significantly increases up to 0.9388 mol/L, and thereafter a decreasing trend was observed.

The increase of graft-on percentage with monomer concentration could be described in terms of gel effect. The plots of R_p versus [MMA] is found to be linear up to 0.9388 mol/L of the monomer concentration.

EFFECT OF ASCORBIC ACID ON GRAFT YIELD

The rate of grafting increased with an increase in ascorbic acid concentration up to 4.5×10^{-3} mol/L, and thereafter it decreased.

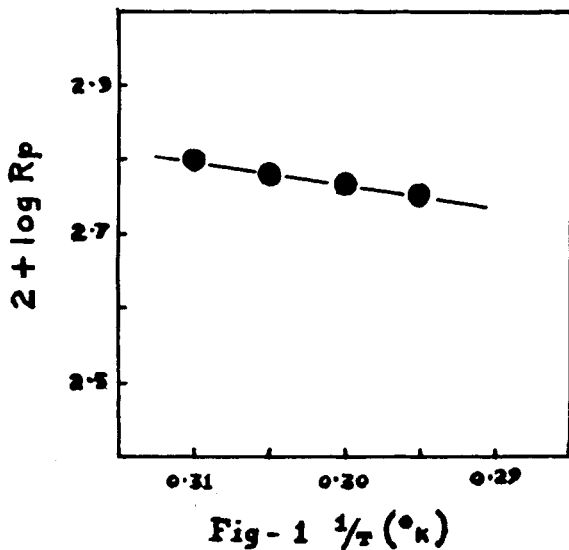


Fig. 1. Arrhenius plot of $\log R_p$ versus $1/T$.

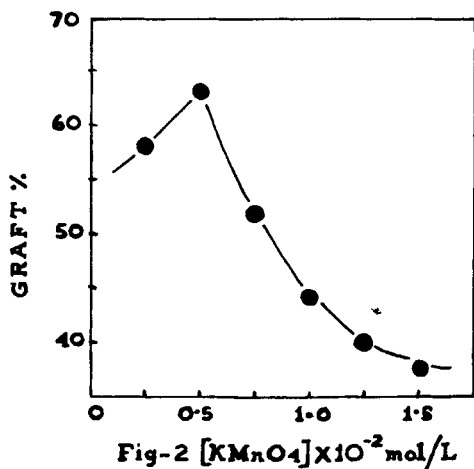
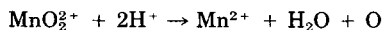


Fig. 2. Effect of $[KMnO_4]$: $[MMA] = 4.694 \times 10^{-1}$ mol/L; $[AA] = 3.5 \times 10^{-3}$ mol/L; $[H^+] = 0.2$ mol/L; M/L = 1:100; time = 5 h; temperature = $55^{\circ}C$.

At higher ascorbic acid concentrations, a large amount of $KMnO_4$ is required to break ascorbic acid to threonic and oxalic acids. The proportion of $KMnO_4$ is decreased to break oxalic acid to free radicals. Also at high activator concentration, a considerable amount of MnO_2 is used up in the side reaction



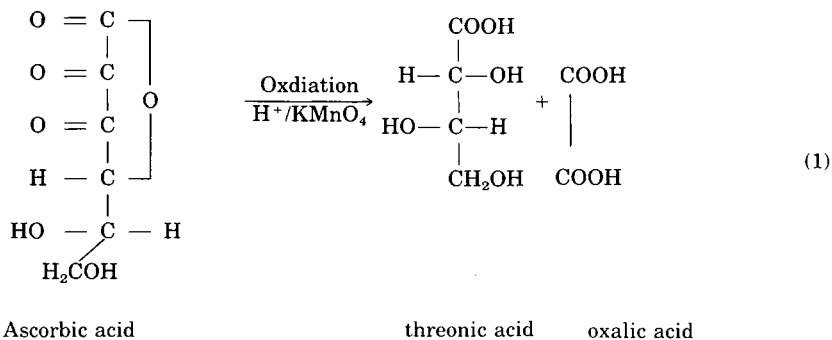
Where Mn^{4+} is reduced directly to Mn^{2+} and the intermediate step producing carboxyl free radical from Mn^{3+} and $C_2O_4^{2-}$ is suppressed.

The pH of the medium is also found to affect the rate of grafting, and an acid concentration

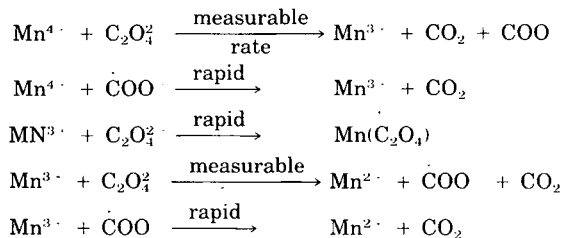
of 0.2 mol/L was found to be most suitable for the present system. The presence of a small amount of solvent was also found to affect the rate of grafting by favoring (1) the swelling capability of the rubber, (2) miscibility with the monomer, (3) the formation of a solvent radical from the primary radical species of the initiating system, and (4) the contribution of the solvent radical in activating the radical.

MECHANISM

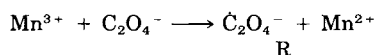
The following reaction mechanism is suggested for the graft copolymerization of MMA onto natural rubber (NR) using the permanganate-ascorbic acid system:



The formation of oxalic acid from ascorbic acid indicates that the free radical $\dot{\text{C}}\text{OO}$ is obtained by the oxidation of $\text{H}_2\text{C}_2\text{O}_4$ by KMnO_4 :

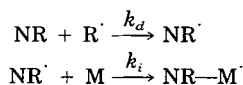


This mechanism was suggested by Launer and Yost¹² and supported by Palit and Kona.¹³ According to Weiss,¹⁴ the production of active oxalic acid ion radical ($\text{C}_2\text{O}_4^{\cdot -}$) is as follows:



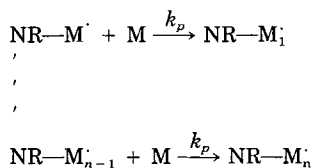
According to Weiss, the production of this free radical (R^{\cdot}) is continuous, which initiates the graft copolymerization:

Initiation:

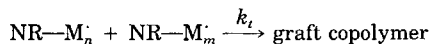


where NR is natural rubber and M is the monomer.

Propagation:



Termination:



Applying the steady-state principle to the growing radical, the rate of graft copolymerization R_p was found to be

$$R_p = k_p \left(\frac{k_i}{k_t} \right)^{1/2} [\text{AA}]^{1/2} [\text{NR}]^{1/2} [\text{MMA}]$$

The plots of R_p versus $[\text{MMA}]$ and R_p versus $[\text{AA}]^{1/2}$ are found to be linear, passing through the origin as in Fig. 3.

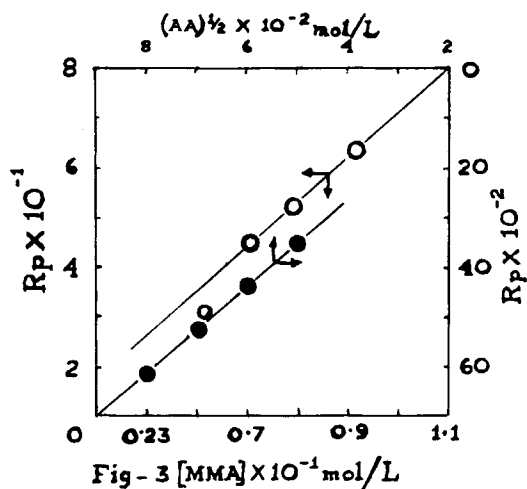


Fig. 3. Plot of R_p versus $[\text{M}]$ and R_p versus $[\text{AA}]^{1/2}$.

References

1. Z. C. Suros, M. Gava, and I. Cyurkovics, *Acta Chim. Acad. Sci. Hung.*, **29**, 207 (1961).
2. J. S. Shukla and D. C. Mishra, *J. Polym. Sci.*, **11**, 751 (1973).
3. S. Lenka, P. L. Nayak, A. P. Das, and I. B. Mohanty, *Angew Macromol. Chem.*, **126**, 107 (1984).
4. P. L. Nayak, S. Lenka, and N. C. Pati, *Angew. Macromol. Chem.*, **84**, 183 (1980).
5. S. Lenka and P. L. Nayak, *J. Macromol. Sci.*, **A18**(5), 695 (1982).
6. S. Lenka, P. L. Nayak, S. B. Dash, and S. Roy, *Colloid Polym. Sci.*, **261**, 40 (1983).
7. P. L. Nayak, S. Lenka, and A. Basak, *J. Polym. Sci.* (Accepted).
8. B. C. Singh, T. R. Mohanty, and P. L. Nayak, *Eur. Polym. J.*, **12**, 371 (1976).
9. S. Lenka, P. L. Nayak, and I. B. Mohanty, *J. Appl. Polym. Sci.*, (In Press).

10. S. Lenka, P. L. Nayak, and I. B. Mohanty, *Angew. Macromol. Chem.* (In Press).
11. S. Lenka, P. L. Nayak, and A. P. Das, *J. Polym. Sci.*, (In Press).
12. H. F. Launer and D. M. Yost, *J. Amer. Chem. Soc.*, **56**, 2571 (1934).
13. S. R. Palit and R. S. Konar, *J. Polym. Sci.*, **58**, 85 (1962).
14. J. Weiss, *Discussion Faraday Soc.*, **2**, 188 (1947).

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