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Graft Copolymerization of Methyl Methacrylate on Potato Starch Using Potassium Trioxalatomanganate, $K_3[Mn(C_2O_4)_3]$, as Initiator

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ABSTRACT

Graft copolymerization of methyl methacrylate on potato starch was carried out in methanol-water medium at 35 °C in the dark using potassium trioxalatomanganate, $K_3[Mn(C_2O_4)_3]$, as initiator. The effect of different methanol-water ratios (v/v), the temperature of polymerization, the initiator concentration, the monomer concentration, the starch content, and the time of polymerization were studied. Percent total conversion, % grafting, and grafting efficiency (%) under different conditions were evaluated and compared. High grafting efficiency (~80%), high % total conversion (~85%), and high % grafting (~95%) were readily obtained. The reaction mechanism for graft copolymer formation is discussed.

INTRODUCTION

Starch-based graft copolymers are drawing increasing attention because of their tremendous industrial importance. Since the work of Mino and Kaizerman [1] in 1958, a considerable amount of research on starch vinyl graft copolymer using ceric salt as the initiator has

been published [2-7]. Brockway [8-12] studied the graft copolymerization of vinyl monomers on starch using the $\text{Fe}^{3+}-\text{H}_2\text{O}_2$ redox system as initiator. Ranby [13-16] used manganic pyrophosphate as the initiator for the graft copolymerization of vinyl monomers on starch. Reports have also been published [17-20] on the radiation-induced (cobalt-60 and electron beam) graft copolymerization of vinyl monomers on starch. Up until now, major attention in the field of chemical modification of starch has been aimed at finding a better or more suitable condition for the graft copolymerization of vinyl monomers on starch. There is ample scope for further investigations in this area. The present work was undertaken with this in view, and we studied the graft copolymerization of methyl methacrylate (MMA) on potato starch (insoluble) in methanol-water medium in the dark at 35°C using potassium trioxalato-manganate as initiator.

EXPERIMENTAL

Materials

Potato starch (BDH, England) was used. Potassium trioxalato-manganate, $\text{K}_3[\text{Mn}(\text{C}_2\text{O}_4)_3]$, prepared in the laboratory following the procedure of Braner [21], and MMA from the local market and purified by a standard procedure [22] were used in the graft copolymerization experiments. The other reagents used were of analytical grade. Water, methanol, and acetone were distilled before use in all-glass distillation units.

Graft Copolymerization

A weighed amount of potato starch (1.7 g) was taken in a conical flask made of Corning-brand borosilicate glass containing 25.5 mL of a methanol-water mixture of known ratio (v/v) and the starch sample was allowed to get soaked for 30 min. A known volume of a freshly prepared aqueous $\text{K}_3[\text{Mn}(\text{C}_2\text{O}_4)_3]$ solution of known concentration was then added. The contents of the conical flask were flushed with purified nitrogen gas which was followed by the addition of a known volume of MMA. The flask was then stoppered, placed in a water bath fixed at 35°C , and polymerization was allowed to continue for a specific time period. The content of the flask was then filtered on a tared sintered bed crucible under suction, washed profusely with water, and then dried at 50°C under vacuum to constant weight. The dried polymer is called "gross polymer."

The gross polymer was extracted with acetone following the procedure of Brockway [19] to remove free polymethyl methacrylate (PMMA). The apparent graft copolymer in the residue containing true graft copolymer (starch/PMMA) and unreacted starch was treated with perchloric acid according to the procedure of Abbott [23] to hydrolyze out

the free and bound starch portions from the apparent graft copolymer and isolate the grafted PMMA portion. Percent grafting, % total conversion, and grafting efficiency (%) were calculated [24].

RESULTS AND DISCUSSIONS

The results are presented in Figs. 1-7. The effects of variation of the methanol-water ratio (v/v), the polymerization temperature, the initiator concentration, the monomer concentration, the starch content, and the time of polymerization on grafting parameters were studied.

Effect of Variation of Methanol-Water Ratio (v/v)

Related results are shown in Fig. 1. Grafting efficiency increases with an increase in the proportion of methanol in water and becomes 100% when the methanol-water ratio (v/v) is 50:1. Percent grafting and % total conversion increase with an increase in the methanol content in water up to a methanol-water ratio (v/v) of 2.19:1, and both parameters fall sharply beyond this ratio. An initial increase in % grafting and % total conversion with an increase in the proportion of methanol in water may be due to more solubility (homogenization) of

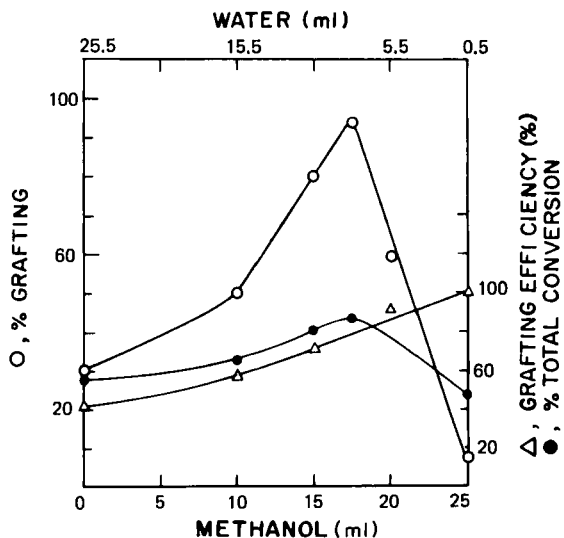


FIG. 1. Graft copolymerization of MMA on potato starch. Effect of variation of methanol-water ratio (v/v). Recipe: starch, 1.7 g; $[I] = 10.5 \times 10^{-4}$ mol/L; MMA, 2.5 mL; 35°C , time, 120 min. Initiator $(I) = K_3[Mn(C_2O_4)_3]$.

MMA in methanol-water medium than in water alone, providing more availability of MMA to the free radical sites generated on starch macromolecule by the water-soluble initiator, $K_3[Mn(C_2O_4)_3]$. For a methanol-water ratio (v/v) > 2.19:1 methanol tolerance of $K_3[Mn(C_2O_4)_3]$ apparently becomes critical and it starts to precipitate out because methanol is a precipitant for aqueous $K_3[Mn(C_2O_4)_3]$, thus lowering the effective initiator concentration in the polymerization medium. As a result, % grafting and % total conversion under high methanol proportions follow a decreasing trend and at the same time aqueous homopolymerization of MMA becomes relatively more restricted, giving higher and higher grafting efficiencies with increasing methanol content. All subsequent experiments on graft copolymerization of MMA on starch in the dark were carried out by using a methanol-water ratio (v/v) of 2.19:1 as the polymerization medium.

Effect of Variation of Polymerization Temperature

Related results are shown in Fig. 2. Percent grafting passes through a maximum around 35°C. Percent total conversion increases up to 40°C and then tends to level off. Grafting efficiency follows a decreasing trend over the temperature range (30-50°C) studied. All subsequent experiments on graft copolymerization of MMA on starch were carried out at 35°C.

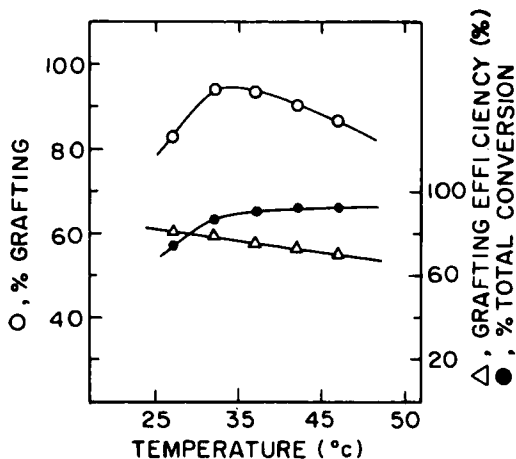


FIG. 2 Graft copolymerization of MMA on potato starch. Effect of variation of polymerization temperature. Recipe: starch, 1.7 g; water, 7.5 mL; methanol, 17.5 mL; $[I] = 10.5 \times 10^{-4}$ mol/L; MMA, 2.5 mL; time, 120 min. Initiator (I) = $K_3[Mn(C_2O_4)_3]$.

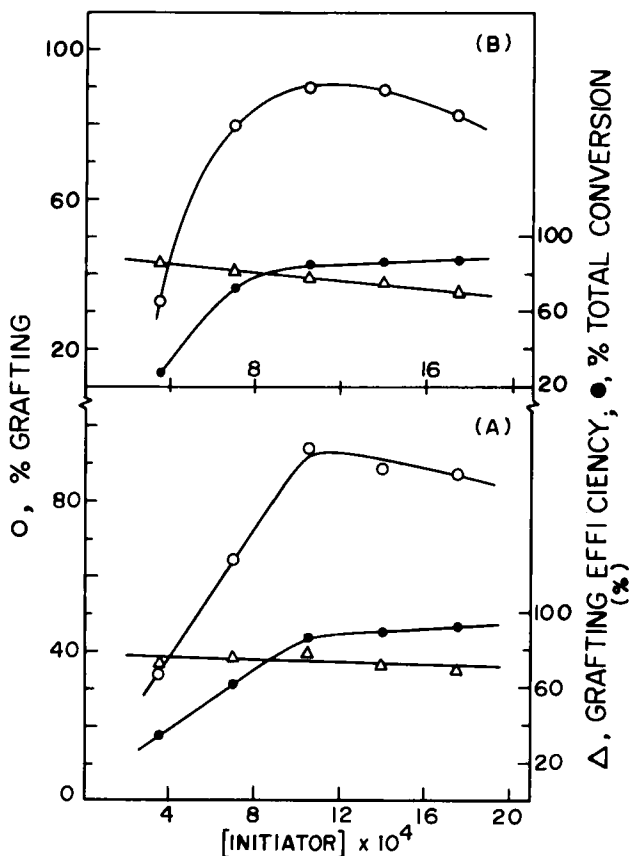


FIG. 3. Graft copolymerization of MMA on potato starch. (A) Effect of variation of [initiator], (dark). (B) Effect of variation of [initiator], (photo). Recipe: starch, 1.7 g; water, 7.5 mL; methanol, 17.5 mL; MMA, 2.5 mL; time, 120 min; 35°C. Initiator (I) = $K_3[Mn(C_2O_4)_3]$.

Effect of Variation of $K_3[Mn(C_2O_4)_3]$ Concentration

Related results are shown in Fig. 3(A). Percent grafting and % total conversion increase up to [initiator] = 10.5×10^{-4} mol/L. Beyond this point the % grafting tends to drop while the % total conversion tends to level off. Grafting efficiency follows a decreasing trend over the initiator concentration range studied.

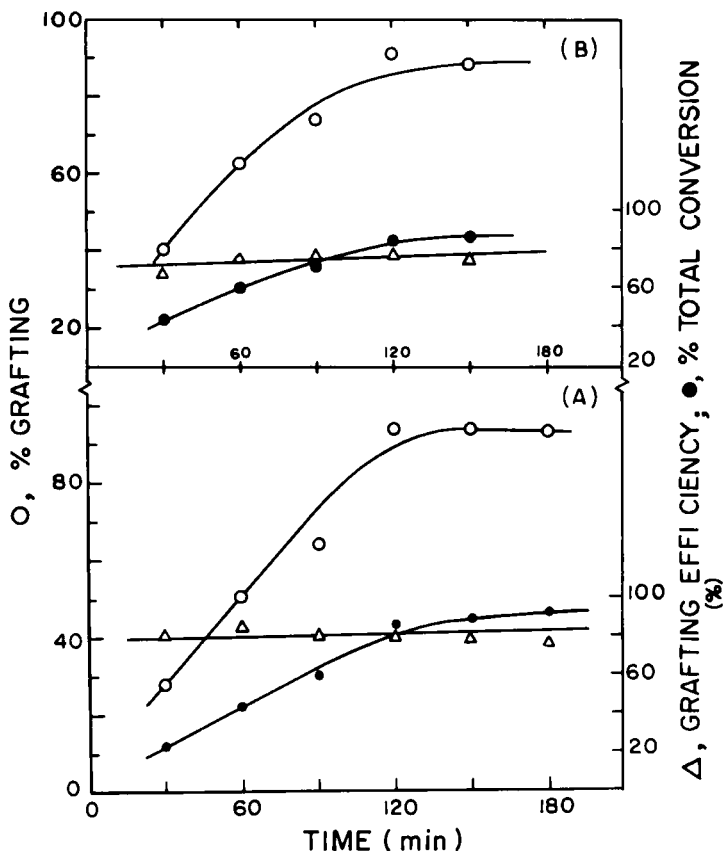


FIG. 4. Graft copolymerization of MMA on potato starch. (A) Effect of variation of polymerization time (dark). (B) Effect of variation of polymerization time (photo). Recipe: starch, 1.7 g; water, 7.5 mL; methanol, 17.5 mL; $[I] = 10.5 \times 10^{-4}$ mol/L; MMA, 2.5 mL; 35°C. Initiator (I) = $K_3[Mn(C_2O_4)_3]$.

Effect of Variation of Polymerization Time

Related results are shown in Fig. 4(A). Both % grafting and % total conversion increase with an increase in polymerization time up to 120 min and then both parameters tend to level off. Grafting efficiency tends to remain more or less steady around 80% with some scatter in the plot as shown in Fig. 4(A).

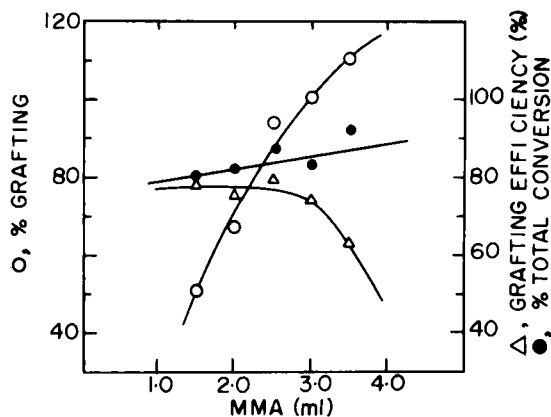


FIG. 5. Graft copolymerization of MMA on potato starch. Effect of variation of monomer concentration. Recipe: starch, 1.7 g; water, 7.5 mL; methanol, 17.5 mL; $[I] = 10.5 \times 10^{-4}$ mol/L; 35°C , time, 120 min. Initiator (I) = $\text{K}_3[\text{Mn}(\text{C}_2\text{O}_4)_3]$.

Effect of Variation of Monomer Concentration

Related results are shown in Fig. 5. Percent grafting conversion increase expectedly with an increase in monomer concentration (1.5-3.5 mL). Grafting efficiency remains steady up to 2.5 mL MMA and then falls sharply.

Effect of Variation of Starch Content

Related results are shown in Fig. 6. Percent grafting decreases quite expectedly with an increase in the amount of starch, the effect being just the reverse of what was observed for an increase in monomer concentration (Fig. 5). Percent total conversion passes through a maximum around 1.7 g starch but grafting efficiency increases slowly over the full range of starch content studied.

Some graft copolymerization experiments were also carried out under visible light (tube lamp, 40 W, Philips India Ltd.) at 35°C with all other conditions fixed. Data shown in Figs. 3 and 4 give a comparative account of the results obtained in the dark (A) and under photo conditions (B). There are small to marginal differences between the

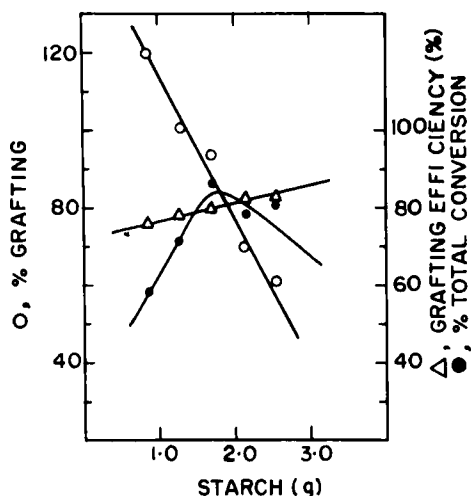
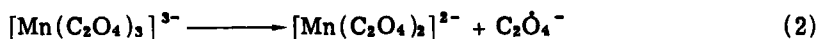
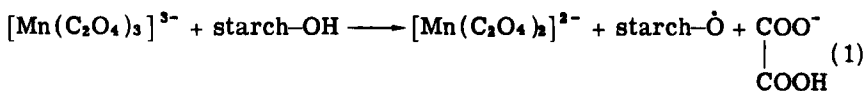


FIG. 6. Graft copolymerization of MMA on potato starch. Effect of variation of starch concentration (dark). Recipe: water, 7.5 mL; methanol, 17.5 mL; MMA, 2.5 mL; $K_3[Mn(C_2O_4)_3]$, $[I] = 10.5 \times 10^{-4}$ mol/L; time, 120 min, $35^\circ C$.

two sets (dark and photo) of results. There are no specific trends in the differences over the range of variables studied (time and initiator concentration).

Mechanism

The cherry-red color of the polymerization medium produced by the addition of $K_3[Mn(C_2O_4)_3]$ disappeared over the course of graft copolymerization, and the medium became colorless, indicating reduction of trivalent manganese, Mn(III), to the divalent state, Mn(II). Generation of radical species in the present systems may be considered to take place as follows:



Reaction (1), which generates radical sites on starch molecules, leads to graft copolymerization. Oxalate ion radical ($C_2\dot{O}_4^-$), generated according to Eq. (2), would normally produce free vinyl polymer (PMMA) and may also lead to graft copolymerization of MMA on starch by a

chain transfer mechanism. Endgroup [25] analysis of the free PMMA isolated from the gross polymers gave a positive test for anionic (carboxyl) endgroups.

The above mechanism for graft copolymerization and free PMMA formation may also be applicable to the photo system.

Effect of Addition of Oxalic Acid

Some experiments were also carried out at 35°C in the dark in the presence of oxalic acid (different concentrations) with all other conditions fixed. Related results are shown in Fig. 7. With an increase in oxalic acid content $(0.0-16.0) \times 10^{-3}$ mol/L, both % grafting and % total conversion pass through a maximum around [oxalic acid] = 2×10^{-3} mol/L. The grafting efficiency tends to level off from this point after an initial increase. The initial uptake in % conversion and grafting parameters in the presence of oxalic acid may be understood on the basis of the reported formation of H_2O_2 in the Mn(III)-oxalic acid system under conditions of low acidity [26] through association of intermediate radicals ($C_2O_4^-$ or HC_2O_4) and subsequent hydrolysis of the percompound intermediates (peroxalic acid or performic acid). The sharp fall in % conversion and % grafting at a relatively high oxalic acid concentration may be interpreted on the basis of lower initiation efficiency (fast annihilation of primary radical) due to a greatly enhanced primary radical concentration in the higher concentration range of the reducing acid (oxalic acid).

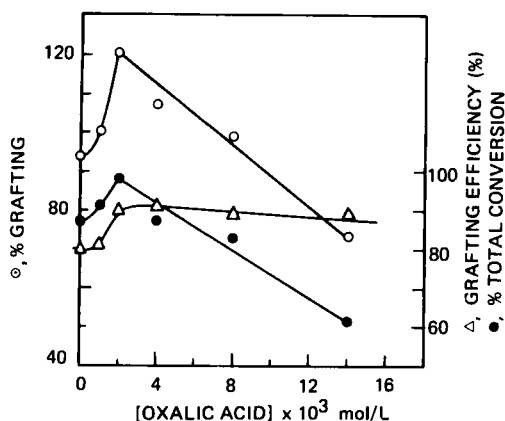


FIG. 7. Graft copolymerization of MMA on potato starch. Effect of [oxalic acid] variation. Recipe: starch, 1.7 g; water, 7.5 mL; methanol, 17.5 mL; $[I] = 10.5 \times 10^{-4}$ mol/L; MMA, 2.5 mL; 35°C; time, 120 min. Initiator (I) = $K_3[Mn(C_2O_4)_3]$.

REFERENCES

- [1] G. Mino and S. Kaizerman, J. Polym. Sci., **31**, 242 (1958).
- [2] G. F. Fants, R. C. Burr, C. R. Russell, and C. E. Rist, J. Appl. Polym. Sci., **13**, 133 (1969).
- [3] Z. Reyes and C. R. Russell, U.S. Patent 2,518,176 (1970).
- [4] L. A. Gugliemelli, W. M. Doane, C. R. Russell, and C. L. Swanson, J. Polym. Sci., Polym. Lett. Ed., **10**, 415 (1972).
- [5] Z. Reyes, C. F. Clark, F. Dreier, R. C. Phillips, C. R. Russell, and C. E. Rist, Ind. Eng. Chem., Proc. Res. Dev., **12**, 62 (1973).
- [6] Z. Reyes, C. E. Rist, and C. R. Russell, J. Polym. Sci., Part A-1, **4**, 1031 (1966).
- [7] G. F. Fanta, R. C. Burr, C. R. Russell, and C. E. Rist, J. Macromol. Sci.-Chem., **4**, 331 (1970).
- [8] C. E. Brockway and K. B. Moser, J. Polym. Sci., **A1**, 1025 (1963).
- [9] C. E. Brockway, Ibid., **A2**, 3733 (1964).
- [10] C. E. Brockway, Ibid., **A2**, 3721 (1964).
- [11] C. E. Brockway, Ibid., **Part C**, **24**, 139 (1968).
- [12] C. E. Brockway and P. A. Seaberg, Ibid., **Part A-1**, **5**, 1313 (1967).
- [13] B. Ranby and R. Mehrotra, J. Appl. Polym. Sci., **21**, 1647 (1977).
- [14] B. Ranby and R. Mehrotra, Ibid., **21**, 3407 (1977).
- [15] B. Ranby and R. Mehrotra, Ibid., **22**, 2991 (1978).
- [16] B. Ranby and R. Mehrotra, Ibid., **22**, 3003 (1978).
- [17] R. L. Walrath, Z. Reyes, and C. R. Russell, Adv. Chem. Ser., **34**, 87 (1962).
- [18] Z. Reyes, M. G. Syz, M. L. Huggins, and C. R. Russell, J. Polym. Sci., Part C, **23**, 401 (1968).
- [19] R. J. Ceresa, Block and Graft Copolymerization, Vol. 1, Wiley-Interscience, 1973, Chap. 1.
- [20] Z. Reyes, C. F. Clark, M. Comar, C. R. Russell, and C. E. Rist, Nucl. Appl., **6**, 509 (1969).
- [21] G. Braner (ed.), Handbook of Preparative Inorganic Chemistry, Academic, New York, 1962.
- [22] P. Ghosh, A. R. Mukherjee, and S. R. Palit, J. Polym. Sci., **A2**, 2807 (1964).
- [23] T. P. Abbott, J. Polym. Sci., Polym. Lett. Ed., **14**, 693 (1976).
- [24] P. Ghosh and T. K. Ghosh, J. Macromol. Sci.-Chem., **A17**, 847 (1982).
- [25] P. Ghosh, S. C. Chanda, A. R. Mukherjee, and S. R. Palit, J. Polym. Sci., **A2**, 4433 (1964).
- [26] S. Taube, J. Am. Chem. Soc., **70**, 1216 (1948).

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