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Photograft Copolymerization of Methyl Methacrylate on Potato Starch Using Potassium Pervanadate as Initiator

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ABSTRACT

Graft copolymerization of methyl methacrylate on potato starch was carried out in methanol-water medium under visible light using potassium pervanadate as initiator. The effects of different methanol-water ratios (v/v), initiator concentrations, monomer concentrations, starch contents, and times of polymerization were studied. Percent grafting, % total conversion, and grafting efficiency (%) under different conditions were evaluated and compared. High grafting efficiency (~90%), 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 assuming increasing importance because of their tremendous industrial importance. Since the work of Mino and Kaizerman [1] in 1958, a considerable amount of research work on starch-vinyl graft copolymers using ceric salt as the initiator has been published [2-7]. Brockway [8-12] studied graft copolymerization of vinyl monomers on starch using Fe^{2+}-H_2O_2 as the

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initiator. Ranby [13-16] used manganic pyrophosphate as the initiator for the graft copolymerization of vinyl monomers on starch. Reports [17-20] were also published on radiation-induced (cobalt 60 and electron beam) graft copolymerization of vinyl monomers on starch. Much less has been published regarding graft copolymerization of vinyl monomers on starch under visible light. There is ample scope for further investigation in this area. The present work was undertaken with this in view, and we studied graft copolymerization of methyl methacrylate (MMA) on starch in a methanol-water medium under visible light using potassium pervanadate (KVO_4) as the initiator.

EXPERIMENTAL

Materials

Potato starch (BDH, England), KVO_4 prepared following the procedure of Henderson [21], and MMA purified by a standard procedure [22] were used in 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). The starch sample was allowed to soak for 30 min. A known volume of freshly prepared aqueous KVO_4 solution of known concentration was then added. Then the conical flask and the contents were flushed with purified nitrogen gas followed by addition of a known volume of MMA. The flask was then stoppered, placed between a pair of tube lamps (Philips India Ltd., 40 W), and polymerization was allowed to continue for a specific time period. The contents of the flask were 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 then extracted with acetone following the procedure of Brockway [9] 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 then calculated [24].

RESULTS AND DISCUSSIONS

The results are shown in Figs. 1-5. In order to establish the optimum reaction conditions for photograft copolymerization of MMA on starch in a methanol-water medium, the effects of variation of methanol-water ratios (v/v), initiator concentrations, monomer concentrations, starch contents, and polymerization times on the grafting parameters were examined. No polymerization was induced in the dark at 30-50°C within 3-4 h using aqueous KVO_4 solution in the absence of any added acid. However, acidic (H_2SO_4)KVO_4 can readily initiate polymerization or graft copolymerization of MMA on starch in the dark at 50°C. An aqueous solution of KVO_4 under photoactivated conditions can induce graft copolymerization of MMA on starch effectively. Studies on the graft copolymerization of MMA on starch were therefore made with aqueous solution of KVO_4 as the initiator under photoactivated condition.

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

Results showing the effects of variation of methanol-water ratio (v/v) on the grafting parameters are presented in Fig. 1. Grafting efficiency increases with an increase in the proportion of methanol in water and became 100% when the methanol-water ratio (v/v) was 50:1. Percent grafting and % total conversion increase with an increase in methanol content in water up to a methanol-water ratio (v/v) of 0.96:1. Beyond this ratio, both parameters fall sharply. When the methanol-water ratio (v/v) was 50:1 in the reaction medium, the % grafting and the % total conversion observed were rather low, i.e., 17.64 and 16.3%, respectively. The initial increase in % grafting and % total conversion with an increase in the proportion of methanol in water may be due to greater solubility (homogenization) of MMA in the methanol-water medium than in water alone, providing more readily available MMA to the free radical sites generated on starch (insoluble) macromolecule by the water-soluble photo initiator KVO_4. At a methanol-water ratio (v/v), of 0.96:1, the methanol tolerance of KVO_4 apparently becomes critical and beyond this point it starts to precipitate out because methanol is a precipitant for aqueous KVO_4, 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 polymerization (homo) of MMA becomes relatively more restricted, giving higher and higher grafting efficiencies with increasing methanol content. All subsequent experiments on the graft copolymerization on starch were carried out with a methanol-water ratio (v/v) of 0.96:1 as the polymerization medium.

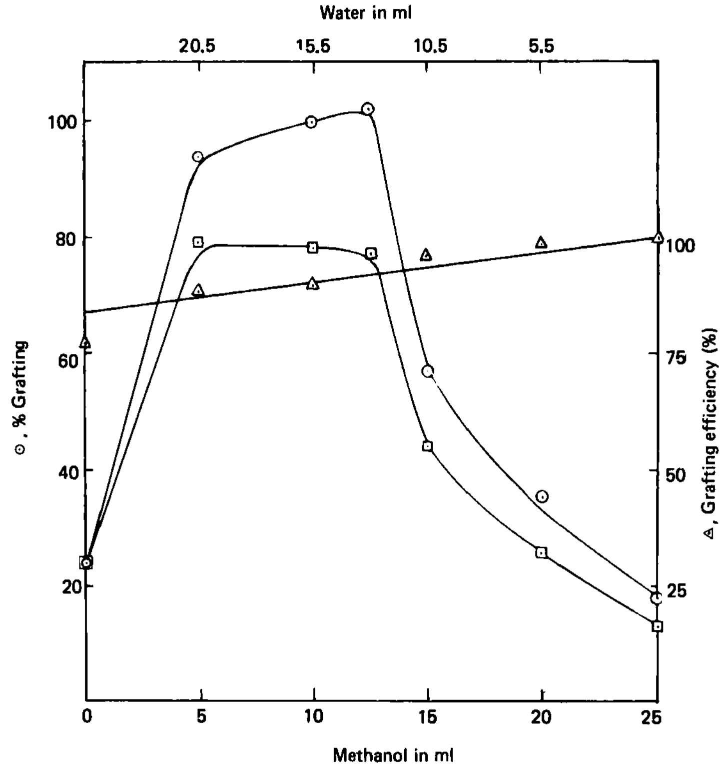

FIG. 1. Photograft copolymerization of MMA on potato starch at 32°C using KVO_4 as initiator. Effect of variation of methanol-water ratio (v/v) on grafting parameters. Starch, 1.7 g; $[KVO_4]$, 0.5×10^{-2} mol/L; MMA, 2 mL; time, 2 h; total volume (liquid), 27.5 mL.

Effect of Variation of Initiator (KVO_4) Concentration

Related results are shown in Fig. 2. Both % grafting and % total conversion pass through a maximum around $[KVO_4] = 0.5 \times 10^{-2}$ mol/L, but grafting efficiency follows a slightly decreasing trend over the full range $[KVO_4]$ studied.

Effect of Variation of Monomer (MMA) Content

Related results are shown in Fig. 3. Percent grafting increases expectedly with an increase in monomer content (1-3 mL) but % total

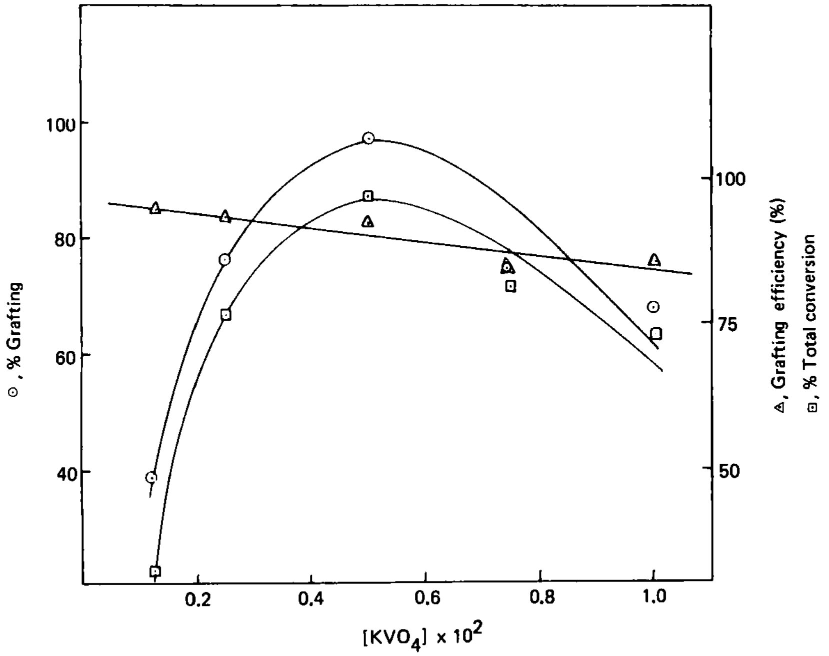

FIG. 2. Photograft copolymerization of MMA on potato starch at 32°C using KVO_4 as initiator. Effect of variation of $[KVO_4]$ on grafting parameters. Starch, 1.7 g; water, 13.0 mL; methanol, 12.5 mL; MMA, 2 mL; time, 120 min; total volume (liquid), 27.5 mL.

conversion passes through a maximum for 2 mL MMA in the given system. Grafting efficiency, however, tends to decrease marginally with an increase in the monomer content.

Effect of Variation of Starch Content

Related results are shown in Fig. 4. Percent grafting decreases quite expectedly with an increase in the amount of starch, the effect being the reverse of what was observed for an increase in monomer content (Fig. 3). Percent total conversion passes through a maximum with an increase in the amount of starch (around 1.7 g starch), but grafting efficiency increases slowly over the full range of starch content studied.

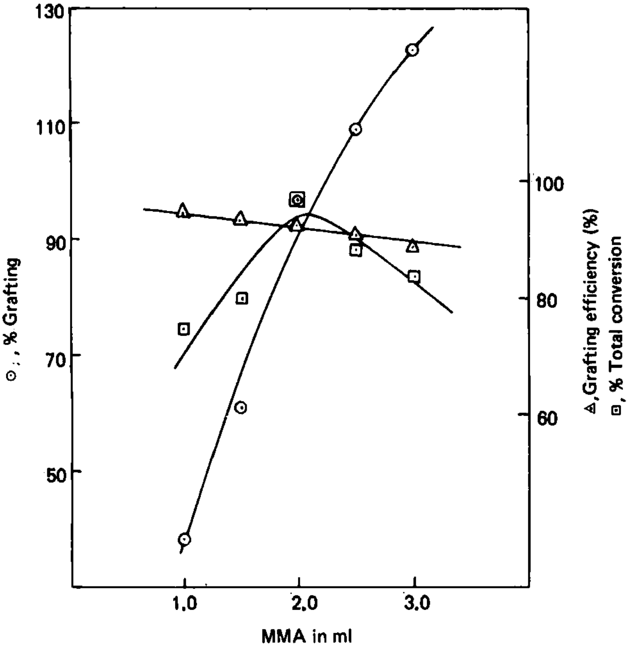

FIG. 3. Photograft copolymerization of MMA on potato starch at 32°C using KVO_4 as initiator. Effect of variation of [MMA] on grafting parameters. Starch, 1.7 g; water, 13.0 mL; methanol, 12.5 mL; [KVO_4], 0.5×10^{-2} mol/L; time, 120 min; total volume (liquid), 27.5 mL.

Effect of Variation of Polymerization Time

Related results are shown in Fig. 5. Percent grafting and % total conversion increase expectedly with an increase in time of graft copolymerization, but grafting efficiency remains more or less steady around 93% over the time period studied.

Mechanism

KVO_4 is a reasonably stable yellow compound, particularly in the absence of moisture. In a dilute aqueous solution, KVO_4 is reported [25] to remain as a complex represented by the formula $KVO_3.H_2O_2$, which is yellow in color. An aqueous solution of KVO_4 is incapable of inducing vinyl polymerization or graft copolymerization of vinyl monomers such as MMA on starch in the dark but can do so in the

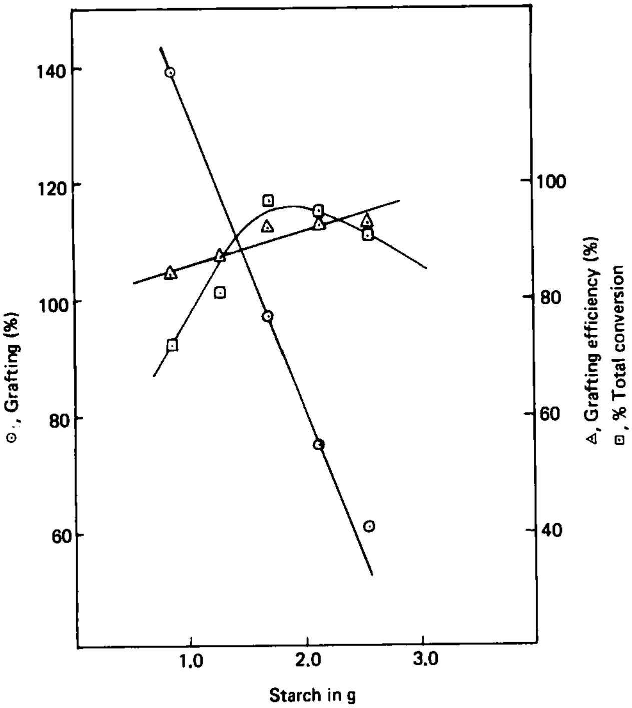

FIG. 4. Photograft copolymerization of MMA on potato starch at 32°C using KVO_4 as initiator. Effect of variation of starch content on grafting parameters. Water, 13.0 mL; methanol, 12.5 mL; $[KVO_4]$, 0.5×10^{-2} mol/L; MMA, 2 mL; time, 120 min; total volume (liquid), 27.5 mL.

presence of visible or near ultraviolet light. However, aqueous KVO_4 acidified with H_2SO_4 can readily initiate polymerization or copolymerization of MMA on starch, even in the dark.

The exact mechanism of KVO_4 initiation for photograft copolymerization of MMA on starch appears to be somewhat complex. Assuming that the main and consequential oxidizing species in aqueous potassium pervanadate solution is KVO_4, i.e., V^{7+}, and having knowledge that V^{7+} is reduced to the pentavalent state, i.e., V^{5+}, the primary reaction in the graft copolymerization system, activated only in the presence of visible light, is

$$V^{7+} + 2\ \text{starch–OH} \xrightarrow{h\nu} V^{5+} + 2\ \text{starch–}\dot{\text{O}} + 2H^{+} \qquad (1)$$

Endgroup analysis [26] of the free PMMA extracted from the gross polymer gave a positive test for hydroxyl endgroups. Photopolymeri-

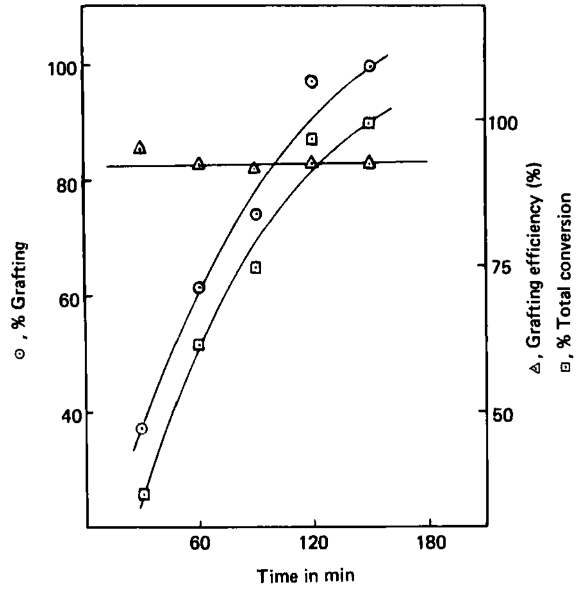

FIG. 5. Photograft copolymerization of MMA on potato starch at 32°C using KVO_4 as initiator. Effect of variation of polymerization time on grafting parameters. Starch, 1.7 g; water, 13.0 mL; methanol, 12.5 mL; $[KVO_4]$, 0.5×10^{-2} mol/L; MMA, 2 ml; total volume (liquid), 27.5 mL.

zation by aqueous KVO_4 thus appears to be initiated by $\dot{O}H$ radicals which may be formed in the following way:

$$V^{7+} + 2\,H_2O \xrightarrow{h\nu} V^{5+} + 2\dot{O}H + 2H^+ \qquad (2)$$

The pH of the polymerization medium was found to decrease from an initial value of 6.5 (for $[KVO_4] = 0.5 \times 10^{-2}$ mol/L) to about 5.35 after about 3 h of graft copolymerization, which is strong support of the above mechanisms of chain initiation.

Graft copolymerization with KVO_4 (V^{7+}) initiator is unique in the sense that grafting is effected strictly under photoconditions, with high grafting efficiencies (≥ 90%) readily obtained.

REFERENCES

[1] G. Mino and S. Kaizerman, *J. Polym. Sci.*, 31, 242 (1958).
[2] G. F. Fanta, 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., Prod. 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. F. 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, J. Polym. Sci., Part C, 24, 139 (1968).

[12] C. E. Brockway and P. A. Seaberg, J. Polym. Sci., 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, New York, 1973, Chap. 1.

[20] Z. Reyes, C. F. Clark, M. Comas, C. R. Russell and C. E. Rist, Nucl. Appl., 6, 509 (1969).

[21] W. E. Henderson and W. C. Fernelius, A Course in Inorganic Chemistry (International Chemical Series), McGraw-Hill, New York, 1935.

[22] P. Ghosh, A. R. Mukherjee, and S. R. Palit, J. Polym. Sci., A2, 2807 (1964).

[23] I. P. Abbott, J. Polym. Sci., Polym. Lett. Ed., 14, 693 (1976).

[24] P. Ghosh and T. K. Ghosh, J. Macromol. Sci.–Chem., 17, 847 (1982).

[25] J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. IX, Longmans Green, 1947, p. 795.

[26] P. Ghosh, S. C. Chanda, A. R. Mukherjee, and S. R. Palit, J. Polym. Sci., A2, 4433 (1964).

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