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Grafting onto Starch. IV.
Graft Copolymerization of Methyl Methacrylate by Use of AIBN as Radical Initiator

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ABSTRACT

Grafting of poly(methyl methacrylate) onto starch has been investigated in aqueous medium by using AIBN as radical initiator. Starch-g-PMMA has been characterized by determination of starch in the graft copolymer. Percentage of grafting has been determined as functions of concentration of monomer, concentration of initiator, reaction time, and temperature. From scanning electron microscopic studies, evidence for grafting of PMMA onto starch has been presented.

INTRODUCTION

Modification of cellulose [1, 2] and natural rubbers [3] by a graft copolymerization method involving chain transfer has been extensively studied. Recently attempts have been made to study graft copolymerization of fibrous protein (wool) by using a variety of initiation methods [4-7]. Very little information is available on grafting onto starch. Starch graft copolymer is assuming increasing importance because of its tremendous potential application in industry. In order to prepare starch graft copolymer of commercial importance, a comprehensive research program has been initiated in our laboratory. Russell et al. [8, 9] have reported that vinyl monomers can be successfully grafted to starch by using ceric ion and various other redox system. Grafting onto starch by using radical initiator has not received much attention. The present authors have studied grafting of PVAc [10] onto starch by using azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) as radical initiators and observed that both AIBN and BPO are capable of effecting grafting of vinyl monomers. Misra et al. [11] have reported that in BPO-initiated grafting, acrylonitrile (AN) was more reactive than methyl acrylate (MA). The greater reactivity of AN was attributed to the greater polarity of AN. Recently Misra and co-workers [10], in an attempt to compare the reactivities of BPO and AIBN in grafting of PVAc onto starch, observed that BPO was more reactive than AIBN in graft copolymerization. No attempt has been made to study grafting of MMA to starch by using radical initiator. In the present communication, we report studies on grafting of methyl methacrylate (MMA) onto starch in presence of AIBN as radical initiator. The percentage and efficiency of grafting have been reported as functions of various reaction variables.

EXPERIMENTAL

Materials

Unmodified, dried, soluble potato starch (BDH) was used in all experiments. Methyl methacrylate was washed with 5% NaOH solution, followed by washing with water, and dried over anhydrous sodium sulfate. MMA was then distilled, and the middle fraction was collected and used. AIBN was recrystallized from MeOH, and the recrystallized AIBN was dissolved in minimum amount of acetone. Nitrogen gas was purified by passage through freshly prepared alkaline pyrrogallol solution.

Graft Copolymerization

Pure dry starch (2.0 g) was dispersed in 100 ml of hot deaerated water (60°C) in a three-necked flask. The starch dispersion was purged with purified nitrogen for 30 min, and the temperature of the mixture was brought to the water bath temperature. A weighed amount of catalyst (AIBN) dissolved in 1 ml of acetone was added to the flask. The flask was again purged with nitrogen for another 5 min. Measured amounts of MMA was added to the reaction mixture dropwise and the graft copolymerization was carried out under constant stirring by a magnetic stirrer. A continuous supply of nitrogen was maintained throughout the reaction period. Graft copolymerization was carried out for 60, 90, 120, 150, and 210 min at 40, 50, and 60°C.

After completion of the reaction, the mixture was immediately filtered and the residue was first extracted with water for 24 hr, followed by extraction with acetone for 48 hr. After complete removal of homopolymer, the residue was dried at 50°C until constant weight was obtained.

Evidence of Grafting

The infrared spectrum of grafted starch showed a carbonyl absorption at 1730 cm^{-1} due to poly(methyl methacrylate); no such band was present in the infrared spectrum of starch.

An intimate mixture of starch (1.0 g) and PMMA (0.5 g) was prepared by dispersing starch in acetone solution of PMMA. The physical mixture was stirred for 24 hr at room temperature, and the solvent was evaporated. The residue was extracted with acetone for 24 hr when all the PMMA was quantitatively removed, leaving behind 0.99 g of starch. This indicated that homopolymer (PMMA) is completely removed by extraction with acetone. The grafted starch, on the other hand, when hydrolyzed with 1 N HCl at 110°C for 2 hr left a resinous mass which was identified as PMMA. Isolation of PMMA from the grafted sample after acid hydrolysis constituted further evidence for grafting.

Comparison of scanning electron micrograph of starch (Fig. 1) and grafted starch (Fig. 2) showed that a considerable amount of PMMA was deposited onto the starch surface.

Characterization of Starch-g-PMMA

The starch graft copolymer was characterized by determination of starch in a definite amount of graft copolymer by determination of starch by the method developed in our laboratory [10]. In this method a weighed amount of grafted material (10-15% of total reaction mass) was hydrolyzed with 1 N HCl at 110°C for 2 hr when all the starch went into solution as glucose. The liberated glucose was estimated by titration against standard Fehling's solution in presence of methylene blue as indicator. From the amount of starch in the graft copolymer, percentage P and efficiency E of grafting were calculated:

$$\%\ G = (W_2/W_1)100$$

$$\%\ E = (W_2/W_3)100$$

where W_1, W_2, and W_3 denote, respectively, the weights of starch

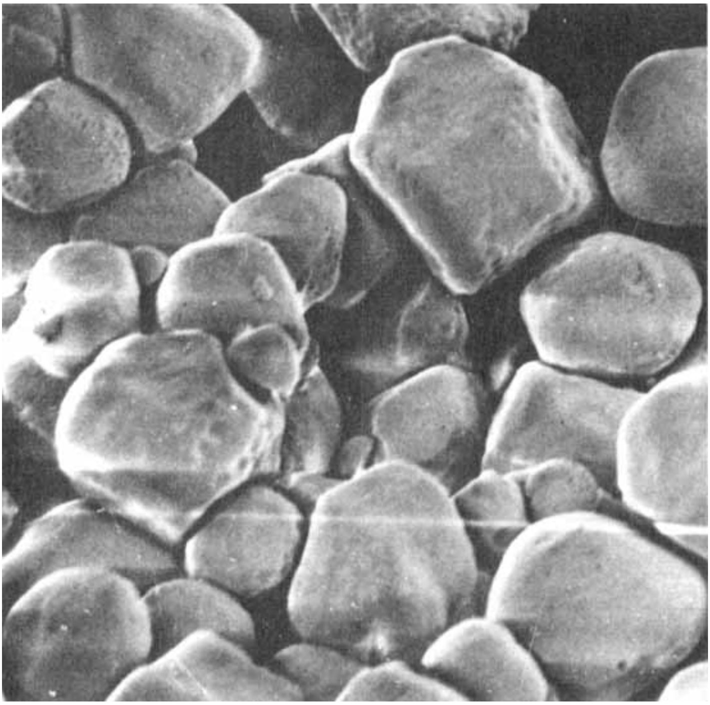

FIG. 1. Scanning electron micrograph of pure starch. Magnification 2500×.

graft copolymer, of polymer grafted, and of monomer used. The results are reported in Table 1.

RESULTS AND DISCUSSION

It is well known that in a chain-transfer process, a free-radical species such as growing chain or radical fragments arising from decomposition of initiator can abstract a labile atom or hydrogen to generate active sites onto polymeric backbone where grafting of appropriate vinyl monomer can occur. The success of chain transfer process in producing graft is directly dependent upon the structure of monomer, the nature of initiator used, and the nature of polymer backbone employed. A plausible mechanism [Eqs. (1)-(8)] is suggested for grafting of MMA to starch in presence of AIBN as radical initiator.

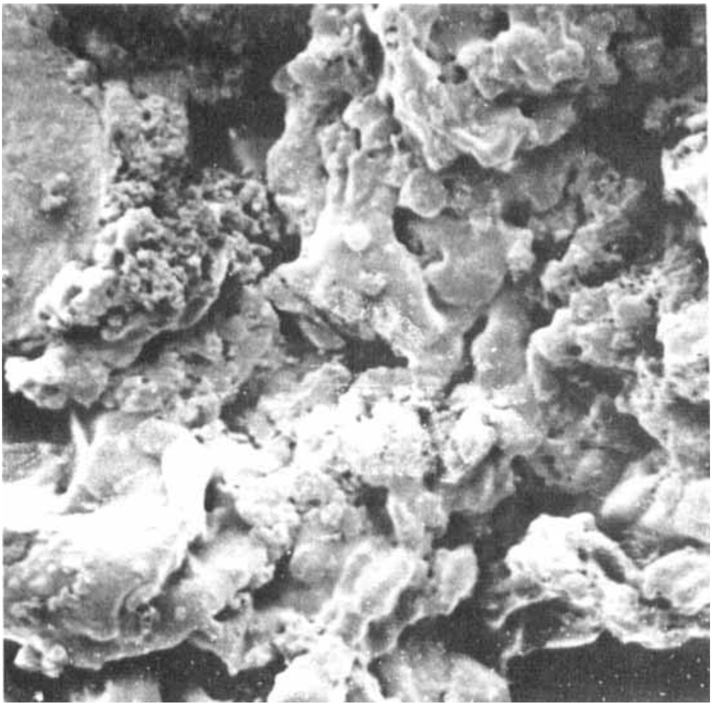

FIG. 2. Scanning electron micrograph of grafted starch (sample 6 of Table 1). Magnification 2500×.

$$I_2 \longrightarrow 2I^{\cdot} \tag{1}$$

$$I^{\cdot} + M \longrightarrow IM^{\cdot} \xrightarrow{M} IMM^{\cdot} \tag{2}$$

$$I^{\cdot} + \text{starch} \longrightarrow \text{starch}^{\cdot} + IH \tag{3}$$

$$IMM^{\cdot} + \text{starch} \longrightarrow \text{starch}^{\cdot} + IMMH \tag{4}$$

$$\text{starch}^{\cdot} + M \longrightarrow \text{starch} - M^{\cdot} \longrightarrow \text{starch}\ (M)_n^{\cdot} \tag{5}$$

$$IMM^{\cdot} + M \longrightarrow IM - (M)_n H \tag{6}$$

$$\text{starch} - (M)_n^{\cdot} + I^{\cdot} \longrightarrow \text{starch} - (M)_n - I \tag{7}$$

TABLE 1. Effect of Concentration of Catalyst and Monomer (MMA), Time, and Temperature upon AIBN-Initiated Grafting[a]

No.	AIBN concn (mole/liter) $\times 10^4$	Monomer concn (mole/liter)	Temp (°C)	Time (min)	Grafting (%)	Efficiency (%)
1	59.0	0.474	40	120	14.6	1.5
2	59.0	0.474	50	120	20.8	2.2
3	59.0	0.474	60	120	42.1	4.4
4	59.0	0.474	60	60	36.1	3.8
5	59.0	0.474	60	90	53.9	5.7
6	59.0	0.474	60	150	72.6	7.7
7	59.0	0.474	60	210	70.2	7.5
8	28.6	0.474	60	150	39.0	4.2
9	120.7	0.474	60	150	49.4	5.2
10	181.7	0.474	60	150	54.6	5.8
11	59.0	0.0948	60	150	0	0
12	59.0	0.284	60	150	12.1	2.3
13	59.0	0.663	60	150	69.8	5.3

[a] Reaction conditions: water = 100 cm^3, starch = 2 g.

$$\text{starch} - (M)_n^{\bullet} + {}^{\bullet}\text{MMI} \longrightarrow \text{starch} - (M)_{n+2} - I \qquad (8)$$

Thus in the postulated mechanism, generation of active sites onto polymeric backbone (-P-) can occur in two ways: the primary radical (I·) arising from the decomposition of initiator may abstract a hydrogen atom from (-P-) by process (3) or the growing polymeric radical may abstract a hydrogen atom from (-P-) to give free-radical sites by process (4). Since the concentration of initiator (I_2) is usually extremely low, generation of active sites by process (3) is possible only when I· is extremely reactive. With AIBN, it seems that I· from AIBN due to resonance stabilization will not be reactive enough to come out of the solvent cage to abstract a hydrogen atom from (-P-). However, I· from AIBN is reactive enough to initiate vinyl polymerization of MMA which is present in larger concentration. Hence, generation of active sites on (-P-) in presence of AIBN occurs through the agency of growing chain by process (4).

In accordance with the above postulated mechanism, percentage of grafting should increase with increase in monomer concentration. It is apparent from Table 1 that, as the monomer concentration increases, the percentage of grafting increases and reaches a maximum value at a monomer concentration of 0.474 mole/liter. Beyond this concentration, percent grafting remains essentially constant. At lower concentration, the graft yield is low, and at a monomer concentration of 0.0948 mole/liter, the percent grafting under optimum conditions is reduced to zero. The dependence of percent grafting on monomer concentration indicates that in AIBN-initiated reaction, active sites on starch are generated by growing grafted chains.

Table 1 shows that percent grafting increases with increase in initiator concentration; similar behavior was shown by BPO in grafting PVAc onto starch [10]. However, in the case of BPO, percent grafting was tremendously affected by the change in initiator concentration. When the BPO concentration exceeded the optimum concentration, percent grafting decreased considerably. With AIBN it is observed that maximum grafting occurred at an initiator concentration of 59.0×10^{-4} mole/liter. At higher initiator concentration, a slight decrease in percent grafting occurred, indicating that at higher initiator concentration homopolymerization occurs preferentially, and termination of growing grafted chains by $I^{\bullet}$ is negligible.

The effect of temperature on percent grafting was studied, and it was observed that maximum grafting occurs at 60°C; below this temperature, decomposition of AIBN into free radicals slows down. Table 1 shows that with increase in reaction period, grafting increases and then levels off. Maximum grafting occurred within 150 min.

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