Matrix-Induced Variation in Kinetics and Control of Molecular Weight of Methacrylic Acid Polymers During Graft Copolymerization with Starch

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ABSTRACT: Polymerization of synthetic monomers is known to be influenced by the solvent, initiator system, dilution, temperature, etc. Substrates like starch granules, when used for graft copolymerization, can be expected to provide a drastically different environment for the monomers (as compared to the bulk of the solvent medium), and therefore we predicted this to influence the kinetics of polymerization and stereoregularity of the synthetic polymer. This was investigated with respect to polymerization of methacrylic acid with starch. The rate of methacrylic acid polymerization was found to be significantly higher in grafting with starch as compared to homopolymerization in the absence of starch. Control of molecular weight of the grafted chains was achieved by use of chain transfer agents, and the chain transfer constants for graft copolymerization were determined for two chain transfer agents. The polydispersity of the grafted chains was also found to be dependent on the chain transfer agents. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 397–403, 1997

Key words: graft copolymerization; redox initiation; polymethacrylic acid; kinetics of polymerization; chain transfer agents

INTRODUCTION

Graft copolymerizations of synthetic monomers onto starch have been of great interest to researchers. Graft copolymers are prepared by first generating free radicals on starch and then allowing these macroradicals to serve as initiators for vinyl or acrylic monomers. A number of free radical initiating systems, like ceric ammonium nitrate and Fenton's reagent, have been used to prepare graft copolymers.[1–6] We have earlier reported[7,8] an efficient method for the preparation of polymethacrylic acid and polymethyl methacrylate-grafted starches. Use of a hydrotrope-like urea was found in these cases to improve the reaction efficiency, possibly due to the improved diffusion of monomer into the starch granules, as urea is known to disrupt the intermolecular hydrogen bonding between amylose and amylopectin molecules in starch. Graft copolymerization was carried out using a redox initiator system comprised of ferrous ammonium sulfate, ascorbic acid, and hydrogen peroxide. The conversion was $> 85\%$ for both monomers. Graft copolymerization is usually carried out on a slurry of starch granules in water, and there is indirect evidence[9] to indicate that grafting takes place within the starch granules. The granules are comprised of crystalline and amorphous networks of amylopectin and amylose molecules associated through H-bonding. Polymerization of synthetic monomers in this environment could be controlled by rate of diffusion of the monomer inside the granules and the orientation of the molecules within the granule (due to interaction of the functional groups with the hydroxyls of amylose and amylopectin molecules).

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This was expected to influence the kinetics of polymerization, molecular weight, polydispersity, and stereoregularity of the grafted chains.

We have now carried out extensive comparative investigations on kinetics of homopolymerization and graft copolymerization of starch with methacrylic acid. Control of molecular weight and polydispersity of the grafted chains to some extent was achieved by use of chain transfer agents such as triethylamine and mercaptosuccinic acid.

EXPERIMENTAL

Materials

Tapioca starch (with 13% moisture) was commercial grade, from Lakshmi Starch, Mumbai. Methacrylic acid (MAA) (Fluka), ferrous ammonium sulfate (FAS), hydrogen peroxide (H_2O_2), urea, and triethylamine were all laboratory grade chemicals and were used as such. Ascorbic acid was I.P. grade, perchloric acid and mercaptosuccinic acid were A.R. grade reagents, and were used without further purification.

Methods

Preparation of Starch Graft Poly(methacrylic acid) (SPMAA)

Tapioca starch (100 g containing 13% moisture) was slurried in urea solution (3 g urea in 100 mL distilled water) and was treated with MAA (10 g) as per the procedure reported elsewhere.[7,8] The redox initiator used was FAS (0.1 g), ascorbic acid (0.5 g), and H_2O_2 (1 mL of 30% solution). Homopolymer (PMAA) was removed from grafted starch by repeated water washing (experimental conditions of Figure 2).

Preparation of SPMAA in Dilute Starch Slurry

Effect of Dilution. Tapioca starch (100 g) was slurried in 1000 mL water instead of 100 mL water. The amounts of other reagents were kept the same (experimental conditions of Fig. 4).

Effect of Concentration of Starch. Varying amounts of tapioca starch (10, 20, 30, 40, 60, 80, and 100 g) were slurried in 1000 mL water. The grafting was carried out with 100 g MMA, 0.1 g FAS, 0.5 g ascorbic acid, and 1 mL 30% solution of H_2O_2 (experimental conditions of Fig. 5).

Preparation of SPMAA Using Gelatinized Starch

Tapioca starch (100 g) was slurried in 1000 mL water and was heated in a boiling water bath for 30 min. The cooked starch dispersion was cooled to 30°C. Graft copolymerization was carried out using 10 g methacrylic acid, 0.1 g FAS, 0.5 g ascorbic acid, and 1 mL 30% H_2O_2 solution. The grafted starch was separated by precipitating in ethyl alcohol (experimental conditions of Fig. 6).

Preparation of Grafted Starches in Presence of Chain Transfer Agents

Tapioca starch (100 g) was slurried in urea (3 g in 100 mL) solution. Methacrylic acid 10 g, FAS 0.5 g, ascorbic acid 0.5 g, and H_2O_2 (1 mL of 30% solution) were used for graft copolymerization. SPMAA samples were prepared in presence of varying amounts (0.1 to 1.5% based on dry weight of starch) of triethylamine and mercaptosuccinic acid.

Preparation of PMAA

Poly(methacrylic acid) was prepared using an identical procedure used for SPMAA synthesis, except that no starch was employed in the reaction and the reaction time was extended to 24 h. Methacrylic acid 10 g, urea 3 g, FAS 0.1 g, ascorbic acid 0.5 g, and H_2O_2 1 mL of 30% solution were used. The PMAA formed was precipitated in acetone, redissolved in water, reprecipitated in acetone, and dried at 60°C for 16 h (experimental conditions of Fig. 1).

Isolation of Grafted Side Chains of PMAA from SPMAA Samples

The grafted side chains of PMAA were separated from the starch backbone by perchloric acid cleavage of the starch backbone in acetic acid.[5] Approximately 2 g of starch-graft copolymer was weighed accurately and added to 100 mL of glacial acetic acid. The mixture was stirred for 1 h at 90–100°C. Perchloric acid (2 mL, 70%) was then added dropwise, and within 2 min the mixture became a clear solution. The product was immediately poured into acetone to precipitate the PMAA side chain. The precipitate was thoroughly washed to neutral pH and dried until constant weight was obtained.

Estimation of Percent Monomer Conversion to Grafted Starch

The grafted starch (2 g, which was washed free of homopolymer) was slurried in 100 mL distilled

water and cooked in a boiling water bath for 30 min. The cooked dispersion was cooled to 30°C and 20 mL of 1*N* standard sodium hydroxide solution was added and kept for 30 min with occasional stirring. Excess sodium hydroxide was back-titrated using standard hydrochloric acid solution. A blank titration was carried out using tapioca starch. The percent monomer conversion to grafted starch was calculated as follows

$$\text{Percent monomer conversion to grafted starch} = \frac{(T_1 - T_2)N \times 86 \times 100}{W_1 M}$$

Where T_2 is the titer value of mL of HCl consumed for grafted starch, T_1 is the titer value for tapioca starch, N is the normality of standard HCl solution, W_1 is the dry weight of grafted starch, and M is the weight of monomer used for grafting 100 g of tapioca starch.

Gravimetric Estimation of Homopolymer Formed During Graft Copolymerization

Starch slurry ($\sim$ 25 g) was removed and filtered after specific time durations of graft copolymerization reaction. The filtrate was added to a large excess of acetone and the precipitate was filtered and dried to constant weight at 100°C. From the weight of the precipitate the amount of homopolymer formed during grafting was estimated.

Gravimetric Estimation of PMAA Formed During Homopolymerization

Poly(methacrylic acid) formed at various reaction times was determined by precipitating in acetone. For this purpose 10 mL of the reaction mixture was drawn at 0, 0.16, 0.5, 1, 2, 24, and 168 h. The precipitate was dissolved in water and reprecipitated in acetone and dried at 60° for 16 h. From the weights of the precipitates the percent conversion was estimated.

Molecular Weight Determination of PMAA

The PMAA side chains recovered by perchloric acid treatment of graft copolymer were dissolved in 1*M* sodium chloride solution, and the number average molecular weight (M_n) and the polydispersity (M_w/M_n) were determined from GPC. A column combination of PL Aquagel–OH 50 and 40 of Polymer Laboratories, U.K., connected in series was used for the studies. Sodium chloride solution (1*N*) was used as the eluent at a flow rate of 1.0 mL/min. Polyethyleneoxide standard samples from Polymer Laboratories Ltd., U.K., were employed for calibration. A Shimadzu LC-6A liquid chromatograph with RID-6A refractive index detector and PE NELSON 900 data system were used for GPC measurements.

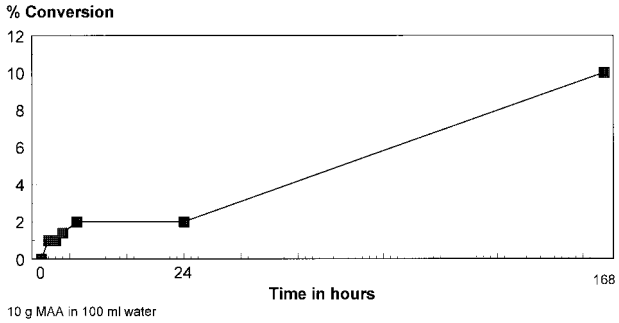

Figure 1 Kinetics of homopolymerization of methacrylic acid.

RESULTS AND DISCUSSION

Matrix Effects on Polymerization of MAA

In order to understand the effect of starch matrix on the polymerization of MAA, the polymerization was carried in water both in presence and absence of starch granules. Fenton's reagent, along with ascorbic acid, was used as the initiator, and the kinetics of the homopolymerization at 30°C are given in Figure 1. The polymerization under these conditions was found to be extremely sluggish, and a monomer conversion of $\sim$ 2% was achieved in 2 h (and only $\sim$ 10% in 168 h). The rate of the reaction was found to be 1% h^{-1} in the initial stages of the reaction. An identical reaction was repeated in presence of starch granules (slurried in water). Monomer conversion into polymer was found to be predominantly in grafted form (on starch) and this was estimated by separation of homopolymer by repeated water washing from the starch granules and estimation of the PMAA content by alkali titration. The homopolymer formed was present in the water medium, and this was separated by precipitation in acetone. The kinetics of formation of homo and grafted polymer in this reaction are given in Figure 2. The rate of monomer conversion to grafted and homopolymer was found to be $\sim$ 89%/10 min and $\sim$ 10%/10 min, respectively. Comparison of results given in Figures 1 and 2 indicate that the rate of polymer-

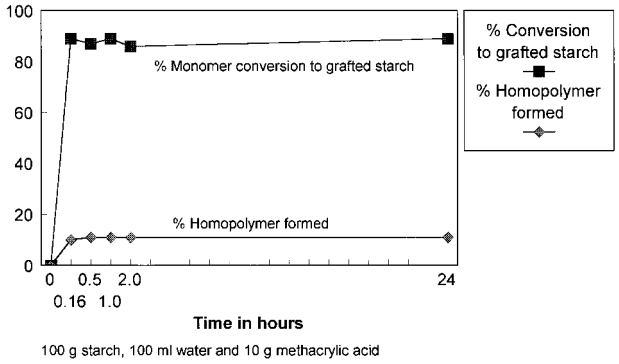

Figure 2 Kinetics of graft copolymerization of granular starch.

ization of MAA in the presence of starch was nearly two orders of magnitude higher than in its absence. The polymerization reaction could be indicated as follows.

Homopolymerization in the absence of starch:

$$M + {}^{\bullet}OH \rightarrow {}^{\bullet}M{-}OH \quad \text{initiation}$$

$${}^{\bullet}M{-}OH + nM \xrightarrow{K_{hp}} {}^{\bullet}M{-}(M)n{-}OH$$

propagation

$${}^{\bullet}M{-}(M)n{-}OH \xrightarrow{K_{ht}} M{-}(M)n{-}OH$$

termination (chain transfer to monomer, solvent, etc.)

Graft copolymerization with starch:

$$ST + {}^{\bullet}OH \rightarrow St{-}O^{\bullet} + H_2O$$

"starch macroradical"

$$St{-}O^{\bullet} + M \rightarrow St{-}O{-}M^{\bullet} \quad \text{initiation}$$

$$St{-}O{-}M^{\bullet} + nM \xrightarrow{K_{gp}} St{-}O{-}M{-}(M)^{\bullet}_{n}$$

propagation

$$St{-}O{-}M{-}(M)^{\bullet}_{n} \xrightarrow{K_{gt}} St{-}O{-}M{-}(M)_{n}$$

termination (chain transfer to monomer, solvent, starch matrix, etc.)

The mechanism of graft copolymerization is reported to be by formation of "starch macroradicals," which in turn initiates the polymerization of vinyl and acrylic monomers present in the vicinity. Hydroxyl radicals resulting from Fenton's reagent abstract a hydrogen from starch molecule to form "starch macroradicals." The abstraction of hydrogens may be from the hydroxyl (as shown in the scheme above), methylene, or methine hydrogens from starch. When the polymerization takes place within the starch granule (average size $\sim 10\ \mu$m in this case), the availability of the monomer within the granule (via diffusion along with water), stability and reactivity of the "starch macroradical," stability of the propagating species, and the orientation of the monomer within the granule will dictate the nature and rate of polymerization. Results given in Figure 2 indicate that the rate of formation of homopolymer during the grafting reaction itself is much faster (one order of magnitude) than that in the absence of starch. This suggests that the homopolymer in grafting is formed mostly via chain transfer to monomer. The significant difference in rate of propagation ($K_{gp} \gg K_{hp}$) could be argued to be due to the stabilization of the propagating species (increased half-life of the free radicals) within the granule due to the matrix, and/or high local concentration of the monomer. The latter is possible due to the association of carboxyl groups of MMA with starch hydroxyls. Association of MAA molecules within the starch granule with the hydroxyls of amylose and amylopectin could be visualized as given in Figure 3.

This, indeed, could increase the local concentration of the monomer. In fact, use of polyelectrolyte templates are reported to increase the rate of polymerization of monomers like acrylic acid and MAA,[10] and this phenomenon had been explained on similar lines. Higher local monomer concentration within the granule could be expected to lead to formation of higher-molecular weight polymer. This was investigated by isolating the grafted chains (after hydrolyzing the anhydroglucose chains of starch in the grafted polymer), determining the molecular weight by GPC and comparison with molecular weight of polymer formed

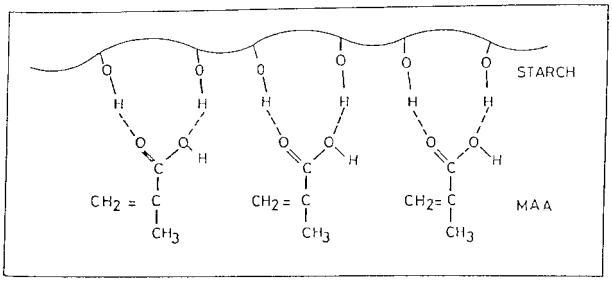

Figure 3 The probable association of methacrylic acid molecules around starch molecule.

Table I Molecular Weight and Polydispersity of Grafted Side Chains of PMAA Homopolymer Formed During Homopolymerization and Grafting

Sample	Molecular Weight	Polydispersity
PMAA formed during homopolymerization	40,624	3.4
Grafted side chain	37,373	3.6
Homopolymer formed during grafting	39,200	3.3

PMAA, polymethacrylic acid.

in the absence of starch. The results are given in Table I. The molecular weights did not differ much and the polydispersity also was found to be approximately the same. This would indicate that stability of the starch macroradical and its increased intrinsic reactivity would be responsible for the higher rate of polymerization.

The local monomer concentration within the granule could be varied by increased dilution of the monomer (with water) and reaction under higher dilutions showed lower percent monomer conversions (Fig. 4).

The starch/monomer ratio was now varied (dilution of the monomer was maintained identical) and the extent of monomer conversion to grafted polymer is given in Figure 5. At higher starch concentrations the percent monomer conversion was found to be higher. The percent PMAA content in the graft copolymer in each case is also shown in Figure 5, and it is interesting to note that the percent polymer content remains the same in all cases. The monomer concentration (in water) in the experiments described here was 10% (weight by weight), and in such a condition the PMAA grafted onto starch remained a constant (19–22%) irrespective of the starch/monomer ratios. A similar experiment was conducted with higher monomer concentration (20% weight by weight and starch/monomer ratio of 1 : 2), and the percent PMAA in grafted starch was found to be 27%. The variation in percent grafted polymer was low and remained in the range of 19–27%, irrespective of the monomer concentration or starch/monomer ratios. This suggests the possibility of limited capacity for starch to associate with the monomer, which eventually dictates the percent polymer add-on.

In order to further establish the influence of the granular nature of the starch matrix to be responsible for the increased rate of polymerization, the reaction was repeated with starch which was dissolved in water (gelatinized starch). Due to the high viscosity of the starch dispersion in water, only a 10% starch solution could be used for the investigation. A control experiment with 10% granular starch slurry was also conducted for comparison. The results are given in Figure 6. A significant difference in the rate of the reaction in the initial stages of the reaction was observed where starch granular reaction was much faster. However, the total conversion after 24 h remained

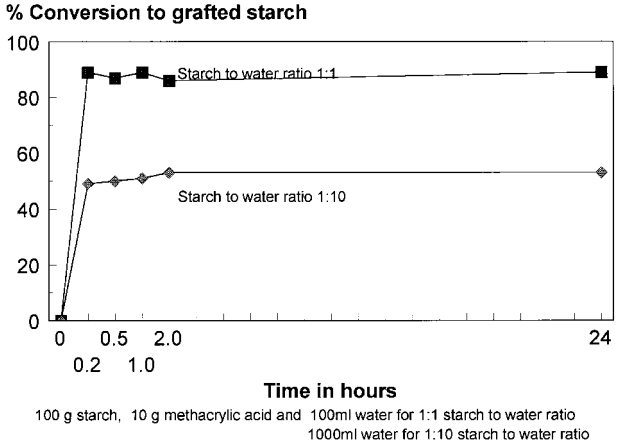

Figure 4 Effect of dilution on percent monomer conversion.

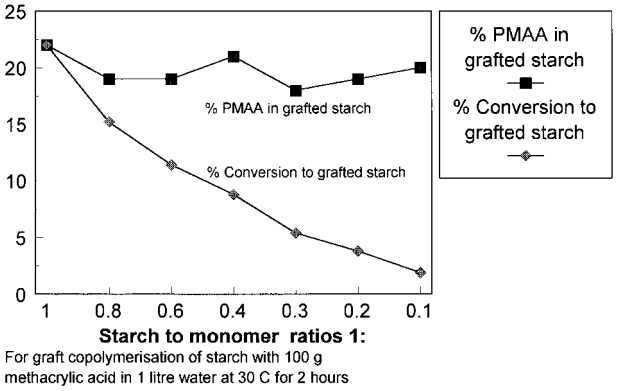

Figure 5 Effect of monomer starch ratios on extent of monomer conversion to grafted starch and percent PMAA content of grafted starches.

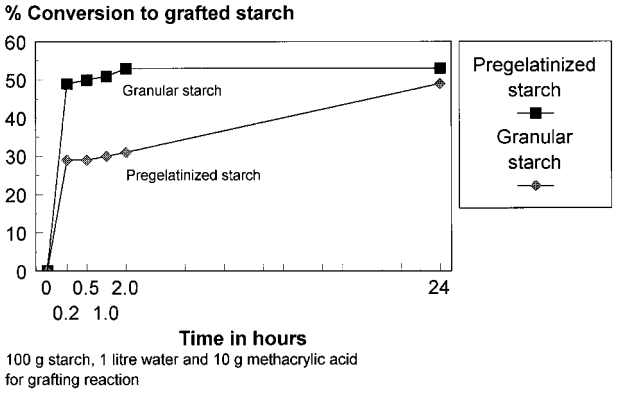

Figure 6 Kinetics of graft copolymerization of pregelatinized starch compared with granular starch.

about the same in both the cases. As compared to the homopolymerization (Fig. 1) the polymerization rate was much faster even in the case of starch solution. The effects of increased intrinsic reactivity of the "starch macroradical" and higher local monomer concentration are possible for dissolved starch as well. However, in the case of starch granules the effect is magnified due to the heterogeneity, and thereby enhanced influence, due to the matrix.

Alignment of monomer molecules within the starch matrix was earlier shown[8] to influence the stereoregularity of the grafted chain. We had earlier reported[8] higher isotactic content at low monomer conversions for grafting of starch with MAA (10% isotactic content for 14% monomer conversion to grafted starch in comparison to 1% for the homopolymer).

Control on Molecular Weight During Graft Copolymerization

Mercaptosuccinic acid and triethylamine were evaluated as chain transfer agents to vary the molecular weight of the grafted chains. The molecular weight of the PMAA-grafted chains and the level of chain transfer agents are given in Table II. The percent monomer conversion (to grafted starch) was found to be detrimentally affected by use of chain transfer agents. This was indeed expected, as increased chain transfer could lead to formation of higher amounts of homopolymer. Increasing levels of chain transfer agent resulted in lowering of the molecular weight. In addition, the polydispersity of the grafted chains improved significantly (1.1 as compared to 3.6 in the absence of chain transfer agents). The chain transfer constants were determined from Mayo plots[11] and the results are given in Table II. These results suggest diffusion of chain transfer agents also into starch granules during graft copolymerization.

CONCLUSIONS

Spontaneous grafting of MAA onto starch occurred on addition of the initiator. The polymerization was found to be two orders of magnitude faster during grafting on starch granules as compared to the reaction in the absence of starch. The conversion was very low in the case of homopolymerization ($\sim$ 10% in 168 h), in comparison to graft copolymerization (>85% in 10 min). Graft copolymerization of pregelatinized starch with MAA gave low conversion. The conversion was 29% after 10 min for pregelatinized starch in comparison to $\sim$ 50% for the granular reaction, under the same dilution. Increased intrinsic reactivity of the "starch macroradical," the stability of the propagating free radical species, high local monomer concentration within the starch granule (due to the possible association of MAA with hydroxyls

Table II Effect of CTA on Percent Conversion to Grafted Starch, Molecular Weight, and Polydispersity

Sample Description	Molecular Weight	Polydispersity	Conversion to Grafted Starch (%)	Chain Transfer Constant Cs
SPMAA without CTA	37,373	3.6	88	
CTA: Triethyl amine (TEA)				
SPMAA with 0.002*M* TEA	9,648	1.1	43	0.5
CTA: Mercaptosuccinic acid (MSA)				
SPMAA with 0.007*M* MSA	12,196	2.3	45	0.1
SPMAA with 0.011*M* MSA	9,648	1.2	21	

CTA, chain transfer agent.

of starch), etc. induced by the starch matrix were argued to be the reasons for the above phenomena. The molecular weight and polydispersity of the grafted PMAA chains could be controlled by use of chain transfer agents like mercaptosuccinic acid and triethylamine.

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