

Pentavalent Vanadium Ion-Induced Grafting of Methyl Methacrylate onto Cotton Cellulose

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Synopsis

Graft polymerization of methyl methacrylate (MMA) onto cotton cellulose using vanadium pentanitrate as initiator was studied under a variety of conditions. The graft yield increased with increasing initiator concentration up to 8 mmole/l. and then decreased upon further increase in initiator concentration. Increasing MMA concentration from 1 to 5% was accompanied by a significant increase in the degree of grafting. The latter was also affected by the kind and concentration of the acid incorporated in the polymerization medium. Based on graft yields, the efficiency of the acids follows the order $\text{H}_2\text{SO}_4 > \text{HNO}_3 > \text{HClO}_4$. Replacement of the acid with isopropyl alcohol was also examined. An isopropyl alcohol concentration of 10% constitutes the optimal concentration for grafting. Maximum graft yield depends upon the polymerization temperature; it follows the order $50^\circ\text{C} \geq 60^\circ\text{C} > 40^\circ\text{C} > 30^\circ\text{C} > 70^\circ\text{C}$. Reaction mechanisms for grafting in the presence of acid as well as in the presence of isopropyl alcohol are proposed.

INTRODUCTION

Vinyl graft copolymerization onto cotton could be achieved primarily by a free-radical-initiated process.¹⁻⁵ The most commonly used methods of free radical initiation on cotton are high-energy ionizing radiation, ceric ion, redox systems, and oxidative reagents.^{5,6}

The use of pentavalent vanadium as initiator for vinyl graft polymerization onto cotton has not yet been studied thoroughly. Oxidation of alcohols by transition metals such as pentavalent vanadium ions takes place through a complex formation. This complex dissociates to yield free-radical intermediate.⁷ Thus, if cellulose reacts similarly, initiation of free radicals on the cellulose backbone would occur, and in the presence of a vinyl monomer one may expect grafting. Indeed, a graft yield of 37.33% on cellulose pulp could be obtained when the latter was grafted with methyl methacrylate using vanadium pentanitrate as initiator.⁸

This work was undertaken with a view of studying the feasibility of grafting of cotton with methyl methacrylate using pentavalent vanadium as initiator. For this purpose, the graft polymerization reaction was carried out under different conditions, including initiator and monomer concentration, time and temperature of the reaction, type of acids, as well as incorporation of isopropyl alcohol in the polymerization system.

EXPERIMENTAL

Egyptian Monofi cotton slivers were Soxhlet extracted with petroleum ether at 80–100°C for 48 hr and air dried.

MMA was washed successively with 5% NaOH and water, then dried with anhydrous sodium sulfate, and distilled under reduced pressure in nitrogen before use.

Vanadium pentanitrate was prepared by dissolving ammonium vanadate (1 mole) in nitric acid (6 mole) and then diluted to the desired concentration. Ammonium vanadate, nitric acid, sulfuric acid, and perchloric acid were analytical reagent-grade chemicals.

Unless otherwise stated, the graft copolymerization was carried as follows: A conditioned cellulose sample (0.5 g) was introduced in a glass-stoppered Erlenmeyer flask containing 50 ml of a solution consisting of water, vanadium pentanitrate, and methyl methacrylate at a specific temperature. The flasks were immediately stoppered and kept in a thermostat. After the specific reaction time, the samples were washed thoroughly with distilled water and dried. In order to remove the homopolymer, the grafted samples were extracted repeatedly with acetone to constant weight.

The graft yield and homopolymer percentages were calculated as follows:

$$\% \text{ graft yield} = \frac{\text{dry wt of grafted sample} - \text{dry wt of original sample}}{\text{dry wt of original sample}} \times 100$$

$$\% \text{ homopolymer} = \frac{\text{dry wt of homopolymer}}{\text{wt of monomer used}} \times 100$$

RESULTS AND DISCUSSION

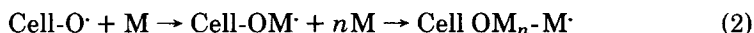
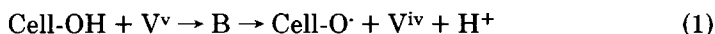
Since the primary objective of this work was to study the feasibility of pentavalent vanadium ion (V^v) in inducing grafting of MMA onto cotton, the graft polymerization reaction was carried out under different conditions. Variables studied include V^v concentration, MMA concentration, incorporation of isopropyl alcohol in the polymerization system, kind of acids, and temperature and reaction time of the polymerization system.

Concentration of Pentavalent Vanadium Ion (V^v)

Figure 1 shows the graft yield as a function of vanadium pentanitrate concentration in the presence of sulfuric acid (300 m equiv/l.). It is clear that the graft yield increases significantly by increasing the V^v concentration, attains a maximum at a certain concentration (8 mmole/l.), then decreases with further increase in the V^v concentration.

In a system containing cotton cellulose, MMA, V^v , H_2SO_4 , and water, several reactions are expected to occur. Among these are the following:

(a) Complexation of V^v with cotton cellulose and dissociation of this complex to yield cellulose macroradical capable of initiating grafting as shown by the reactions suggested in eqs. (1) and (2).



where Cell-OH represents cotton cellulose, B is the complex formed between the latter and V^v , and M is the vinyl monomer.

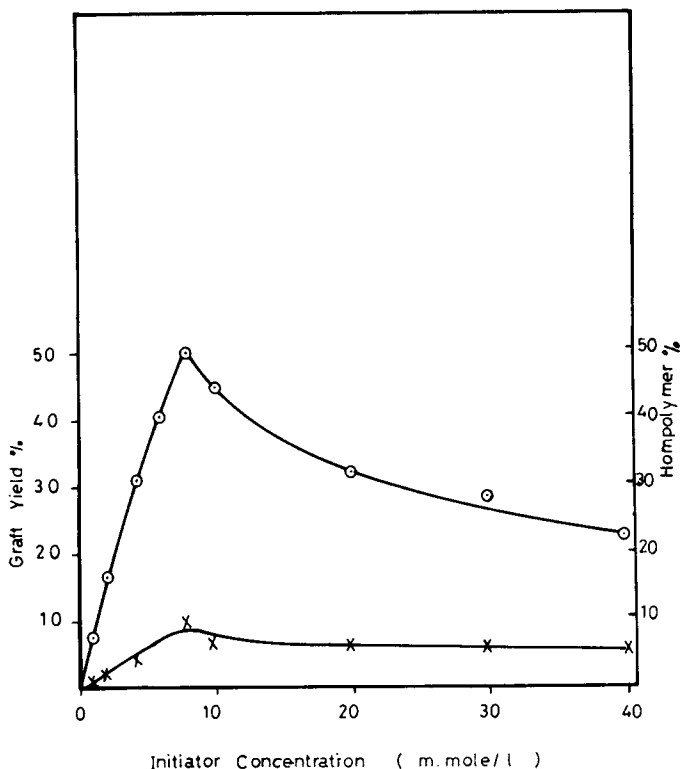
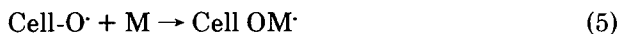
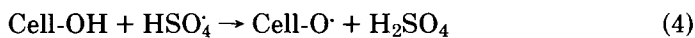
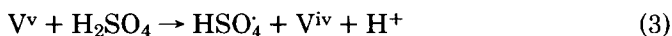
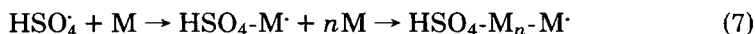
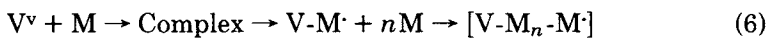


Fig. 1. Variation of graft yield and homopolymer formation with initiator concentration: (O) percent graft yield; (X) percent homopolymer; reaction time, 4 hr; MMA, 4%; H_2SO_4 , 300 m equiv/l.; temperature, 60°C ; M/L ratio, 1:100.

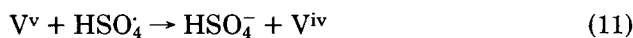
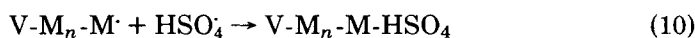
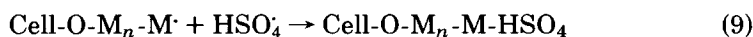
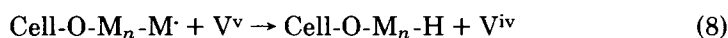
(b) Reaction of V^v with sulfuric acid, in a manner similar to^{9,10} M_n^{iv} to yield sulfate free radical which may participate in graft initiation as suggested by reactions (3)–(5):



(c) Reaction of V^v and/or the sulfate free radical with the vinyl monomer (MMA) to initiate homopolymerization as shown by the reactions suggested by eqs. (6) and (7):



(d) Participation of the V^v and the sulfate free radicals in termination of the graft, homopolymer, as well as free-radical species in the polymerization system as shown by the reactions suggested by eqs. (8)–(11):



Hence, the enhancement in grafting by increasing V^v up to certain concentration (optimal concentration) indicates that reactions (a) and (b) prevail over reactions (c) and (d). The opposite holds true upon exceeding this optimal concentration, where reactions (c) and (d) prevails over (a) and (b).

Figure 1 also shows the homopolymer formed during grafting versus the V^v concentration. Similar to grafting, homopolymer formation increases with increasing V^v concentration up to 8 mmole/l.; but unlike grafting, the magnitude of homopolymer did not decrease with further increase in V^v concentration. Indication of this is that the rate of termination of the homopolymer was not affected by excess V^v in the system, as was the case with grafting. This suggests that above an optimal concentration of V^v , the onset of the gel effect^{10,11} [brought about by dissolution of poly(methyl methacrylate) in its own monomer] on decreasing the rate of termination is more pronounced with the homopolymer than with the graft.

Kind and Concentration of Acids

Figure 2 shows the effect of kind and concentration of acids on the magnitude of grafting of MMA onto cotton cellulose using pentavalent vanadium ion (V^v) as initiator. No grafting occurred in the absence of acid. The latter is essential

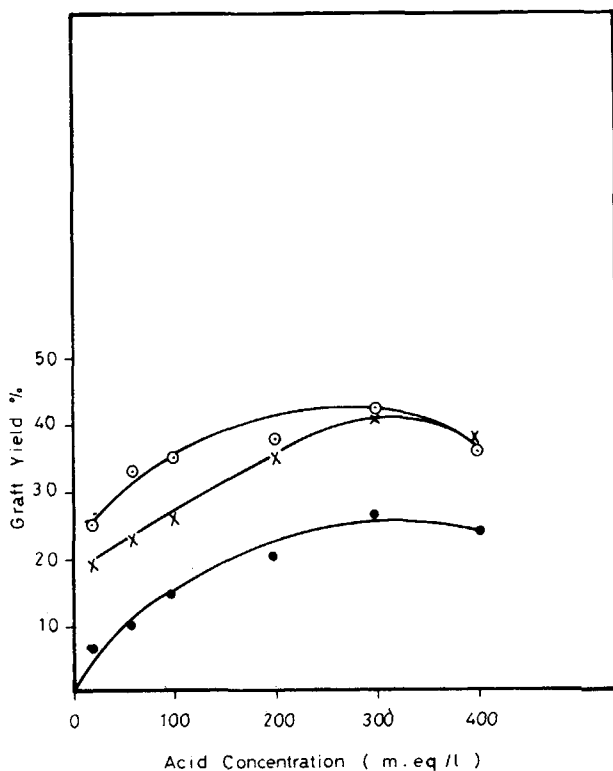


Fig. 2. Effect of kind and concentration of acids on graft yield: (○) H₂SO₄; (X) HNO₃; (●) HClO₄; vanadium pentanitrate, 8 mmole/l.; MMA, 4% temperature, 60°C; reaction time, 5 hr; M/L ratio, 1:100.

for the grafting reaction to proceed, and the magnitude of grafting is dependent on the kind and concentration of the acid. Of the acids used, sulfuric acid proved to be the best, since at equal concentration in the polymerization system, the graft yield obtained with sulfuric acid is higher than that with perchloric and nitric acids. However, irrespective of the acid used, the graft yield increases with increasing concentration of the acid within the range studied, though there is a tendency that above an acid concentration of 300 m equiv/l. the graft yield decreases.

That no grafting occurs in the absence of the acid implies (a) that presence of acid is essential for complexation of V^v with cotton cellulose, and (b) that there is a reaction between V^v and the acid to produce free radical species capable of initiating grafting as postulated above. The tendency of grafting to decrease at higher acid concentration could be associated with a fast rate of termination because of increased rate of generation of free radical species as well as abundance of hydrogen protons. In addition, coagulation of colloidal homopolymer (in solution and within the fibers during grafting) at lower pH values,⁹ would retard diffusion of both monomer and initiator into the fibers, thereby leading to decreased grafting.

Differences in graft yields obtained when different acids were used (Fig. 2) could be explained in terms of differences in (a) ability to favor formation of a V^v -cellulose complex, (b) affinity of the acid free-radical species for cotton cellulose, (c) efficiency of the initiating species, (d) the half-life of the free radicals formed, and (e) capability of the acid free-radical species to combine and/or participate in cellulose macroradical formation and growing grafted chain.

Incorporation of Isopropyl Alcohol

In the foregoing section we have shown that presence of the acid in the polymerization system plays a key role in the grafting reaction. Here, trials have been made to replace the acid with isopropyl alcohol, bearing in mind that V^v reacts with the latter via a free radical intermediate.⁷ The results obtained are shown in Table I and Figure 3.

Table I shows variation of the graft yield with V^v concentration at a constant concentration of isopropyl alcohol. As is evident, substantial grafting occurs in the presence of isopropyl alcohol; the magnitude of grafting depends upon the concentration of V^v as well as the reaction time. This implies (a) that the V^v

TABLE I
Variation of Graft Yield with Initiator Concentration in Presence of Isopropyl Alcohol^a

Reaction time, min	Graft yield, %				
	2 ^b	4 ^b	8 ^b	12 ^b	20 ^b
15	6	9.6	15	7.5	7.3
30	22	21	25	22	16.4
45	35	35	31	27.4	20.6
60	38	39	40	36.4	34
90	42	41	50	48.6	46.3

^a MMA 4%; isopropyl alcohol 10%; temperature, 50°C; *M/L* ratio, 1:100.

^b Initiator concentration, in mmole.

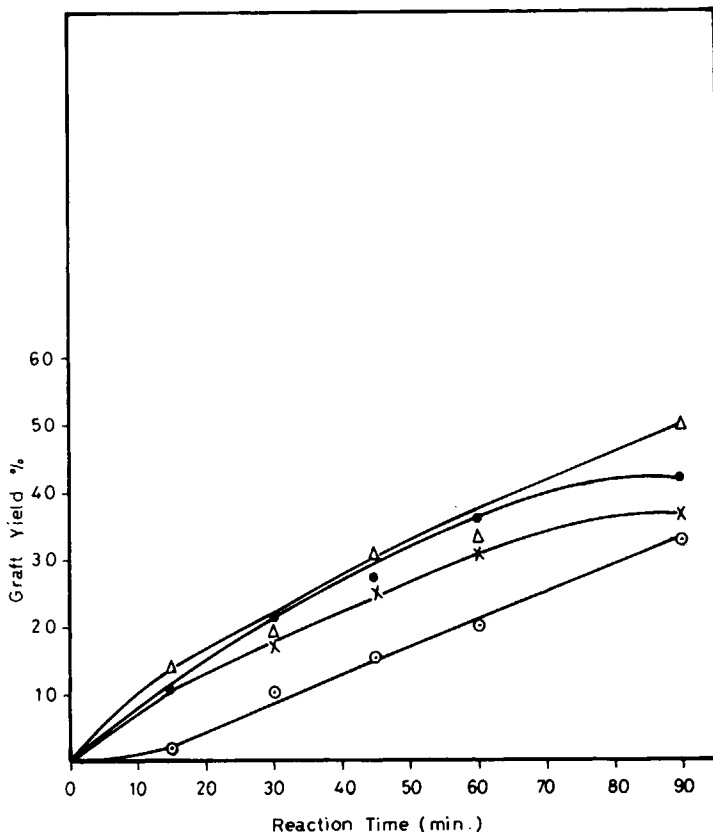


Fig. 3. Influence of isopropyl alcohol concentration on the rate of grafting: (○) 2% isopropyl alcohol; (X) 5% isopropyl alcohol; (Δ) 10% isopropyl alcohol; (●) 15% isopropyl alcohol; vanadium pentanitrate, 8 mmole/l.; MMA, 4%; temperature, 60°C; *M/L* ratio, 1:100.

forms a complex with isopropyl alcohol and this complex dissociates to produce free-radical species capable of attacking cotton cellulose, resulting in cellulose macroradicals which are amenable to graft initiation, and (b) that isopropyl alcohol facilitate complexation of V^v with cotton cellulose which ultimately dissociate to give rise to similar cellulose macroradicals. The behavior of all these radical species seems to follow the known general trends of free-radical polymerization¹¹⁻¹³ such as the enhancement of grafting by prolonging the duration and the decrement in grafting by increasing the initiator concentration above a certain concentration within the range studied.

Figure 3 shows the effect of isopropyl concentration on the extent and rate of grafting. There is an induction period of about 10 min when the grafting reaction was carried out in the presence of isopropyl alcohol at a concentration of 2%. Above this concentration, the grafting reaction proceeds without any induction period, and the rate and extent of grafting increase considerably. Nevertheless, the extent and rate of grafting are favored at an isopropyl alcohol concentration of 10% rather than of 15%, particularly at the last stage of the reaction. Indication of this is that there is an optimal concentration of isopropyl alcohol at which maximum grafting occurs. Two possibilities may be considered in explaining this. First, abundance of free-radical species may take place at higher concentration of isopropyl alcohol, leading to acceleration of rate of ter-

mination. Second, the decreased swellability of cellulose at higher concentrations of isopropyl alcohol may lead to retardation of diffusion of both monomer and initiator. It is understandable that fast rate of termination of the graft, and cellulose macroradicals and free radical species in the polymerization medium, together with decreased initiator and monomer diffusion, would certainly lead to decreased grafting.

Monomer Concentration

Figure 4 shows the effect of MMA concentration on the extent and rate of grafting. It is seen that the extent and rate of grafting increase significantly as MMA concentration increases. This is in accordance with previous reports¹⁰ which ascribed this to the gel effect brought about by the solubility of poly(methyl methacrylate) in its own monomer. The gel effect seems to be more pronounced at higher MMA concentration. As a result, termination of the growing grafted chain radicals by coupling is hindered, while the swellability of cotton cellulose is enhanced. The ultimate effect of this is increased grafting.

It is also likely that besides the gel effect, at higher MMA concentration complexation of MMA with cotton cellulose is favored. Once this is the case, activation of MMA will occur via formation of a donor-acceptor complex in which

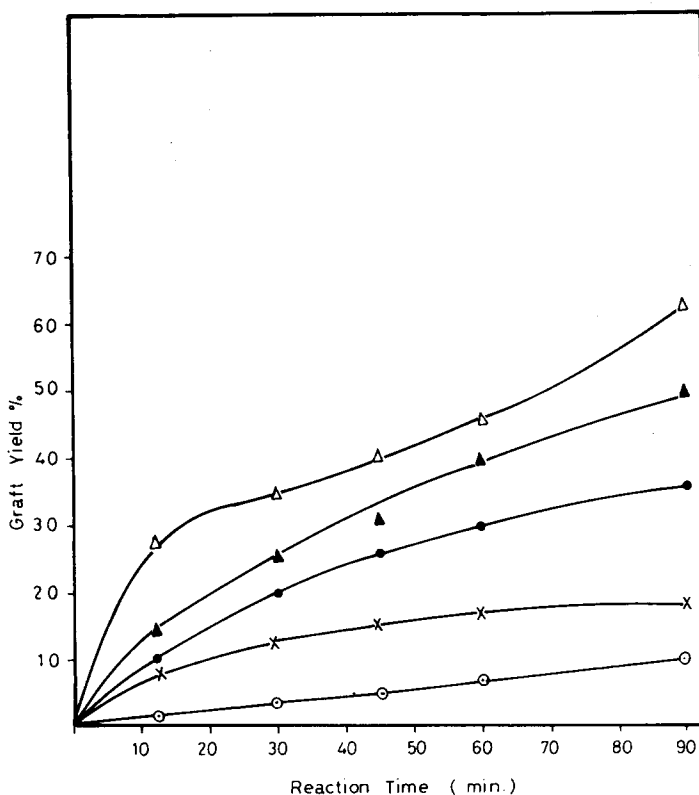


Fig. 4. Effect of methyl methacrylate concentration on the rate of grafting: (○) 1% MMA; (X) 2% MMA; (●) 3% MMA; (▲) 4% MMA; (△) 5% MMA; vanadium pentanitrate, 8 mmole/l.; isopropyl alcohol, 10%; temperature, 50°C; *M/L* ratio, 1:100.

the uncomplexed MMA, though normally an electron acceptor, behaves as a donor relative to the complexed MMA, which has been converted to a stronger acceptor. Enhanced monomer reactivity is also apparently due to association of complexed monomer into an organized array, since cotton cellulose acts as a matrix for such alignment. Naturally, the enhanced monomer reactivity means increased grafting. A similar assumption has been reported for grafting cellulose,¹²⁻¹⁴ wool,¹⁵⁻¹⁷ and nylon¹¹ with MMA using different initiators.

Reaction Temperature

Figure 5 shows the effect of polymerization temperature on the extent and rate of grafting. At 30°C, the grafting reaction is accompanied by an induction period of ca. 45 min. The same holds true for grafting at 40°C, but the induction period is much shorter (about 10 min). However, the extent and rate of grafting are much higher at 40°C than at 30°C. Raising the polymerization temperature up to 50°C enhances significantly the grafting reaction, which proceeds without any induction period. No significant change in the magnitude of grafting could be achieved when the polymerization temperature was raised to 60°C. On the other hand, raising the temperature up to 70°C is accompanied by a significant decrease in the magnitude of grafting, particularly during the later stages of the reaction.

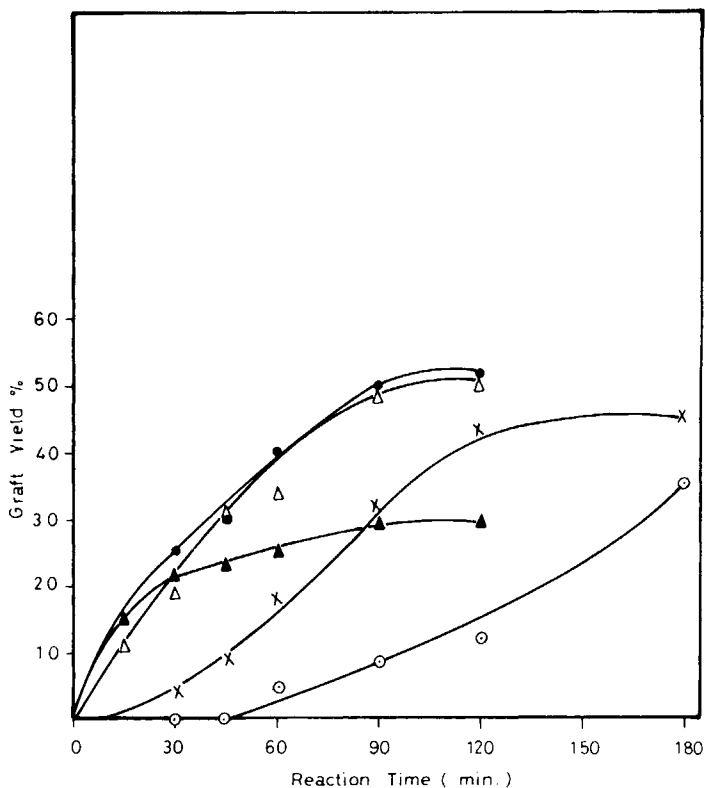


Fig. 5. Variation of rate of grafting with polymerization temperature: (○) 30°C; (X) 40°C; (●) 50°C; (△) 60°C; (▲) 70°C; vanadium pentanitrate, 8 mmole/l.; MMA, 4%; isopropyl alcohol, 10%; M/L ratio, 1:100.

The enhancement in grafting by raising the temperature could be associated with the favorable effect of temperature on (a) concentration of free-radical species in the polymerization system, (b) swelling properties of cotton cellulose, (c) solubility of MMA, (d) diffusion of MMA from the polymerization medium to the fiber phase, and (e) rate of initiation and propagation of the graft. Decrement in grafting at higher temperature (i.e., 70°C) could be ascribed to faster rate of termination, as with other initiators.⁹⁻¹⁸

Reaction Time

The effect of increasing the polymerization time on the graft yield may be realized from Table I and Figures 3-5. It is clear that within the range studied, prolonging the duration of polymerization is generally accompanied by a significant enhancement in the graft yield. The magnitude of this enhancement however, is governed by the polymerization temperature and concentration of monomer, initiator, and isopropyl alcohol.

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