

Graft Copolymerization of Methyl Methacrylate onto Starch Using a Ce(IV)–Glucose Initiator System

N. M. Sangramsingh, B. N. Patra, B. C. Singh, C. M. Patra

P.G. Department of Chemistry, Ravenshaw (Autonomous) College, Cuttack, Orissa 753003, India

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ABSTRACT: Graft copolymerization of methyl methacrylate onto starch was carried out in aqueous medium using Ce(IV)–glucose initiator in the temperature range 40–60°C. Effects of concentration of Ce(IV), glucose, H₂SO₄, monomer, and starch on grafting were investigated. Percentages of grafting were evaluated and compared. The overall energy of activation was calculated from the effects of time and

temperature of polymerization. The reaction mechanism was also discussed. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 981–990, 2004

Key words: graft copolymers; activation energy; initiators; biodegradable; starch

INTRODUCTION

Starch is a natural polymer and is biodegradable. Thus starch-based graft copolymers have been the focus of increased attention because of their tremendous industrial importance.¹ 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.^{2–7} There is ample scope for further research in this area. In this laboratory efforts are being made to induce a characteristic biodegradability in synthetic vinyl polymer by use of natural polymers. The present work was undertaken with this in view: we investigated graft copolymerization of methyl methacrylate onto starch using a Ce(IV)–glucose initiator in aqueous medium at temperatures ranging from 40 to 60°C.

EXPERIMENTAL

Materials

The following substances were used in our experiments: starch, monomer (methyl methacrylate), sulfuric acid, glucose, ammonium ceric sulfate, and water.

Starch was obtained from a local market and used as received. The monomer, a commercial methyl methacrylate (MMA), was washed with 5% sodium hydroxide (NaOH) solution, after which it was washed with water until a clear monomer layer was formed. The monomer was dried overnight over anhydrous CaCl₂ and then stored in a refrigerator.

Grafting procedure

The starch powder was first soaked in an appropriate amount of monomer (MMA) before initiating the graft polymerization. An appropriate quantity of reaction mixture containing starch, MMA, glucose, sulfuric acid, and water was charged to a reaction vessel having B_{24/29} standard joints, equipped with gas inlet and outlet tubes, that was kept in a water bath and maintained at constant temperature with ±0.1°C accuracy. The initiator solution Ce(IV) was kept in a water bath for some time at the required temperature. Then the required amount of ceric ammonium sulfate solution was poured into the vessel containing the reaction mixture. The reactions proceeded for a specified time at three different temperatures: 40, 50, and 60°C. After the specified time, the reaction was arrested by the addition of methanol. The mixture was immediately filtered through a previously weighed G-3 crucible, by vacuum pump, to obtain the precipitate.

The homopolymer, along with the grafted starch, was refluxed with acetone for 5 h, after which the grafted starch was fully dried overnight in an electric oven until a constant weight was obtained.

The percentage of graft yield (%GY) and rate of grafting (Rg) were calculated as follows:

$$\%GY = \frac{\text{Dry wt. of grafted starch} - \text{dry wt. of original starch}}{\text{Dry wt. of original starch}} \times 100$$

$$Rg = \frac{1000w}{vtm}$$

where w is the dry weight of grafted starch less the dry weight of original starch, v is the volume of the reac-

Correspondence to: B. Singh.

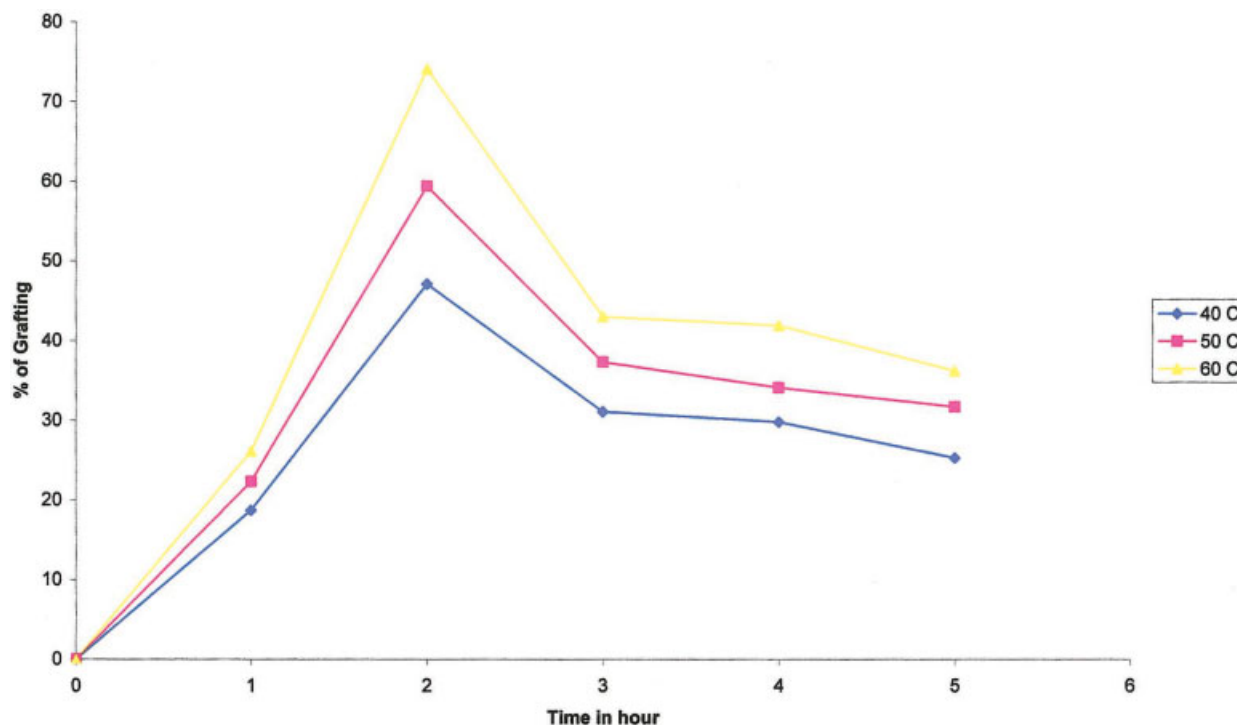


Figure 1 Effect of time on grafting. Starch = 1 g; [MMA] = 0.46M; [Glucose] = 0.025M; [Ce(IV)] = 0.025M; [H₂SO₄] = 0.25M.

tion mixture, t is the time of reaction (in s), and m is the molecular mass of monomer.

RESULTS AND DISCUSSION

Graft copolymerization of MMA onto starch using a Ce(IV) initiator system was investigated at three different temperatures: 40, 50, and 60°C. The effects of (1) time, (2) temperature, (3) concentration of initiator, (4) monomer, and (5) amount of cotton were studied. On the basis of experimental findings, a suitable reaction mechanism is proposed.

Effect of time on percentage grafting

Figure 1 and Table I show the effect of time on %GY at 40, 50, and 60°C. In all three cases the graft yield was

found to increase up to 3 h, beyond which there was a decrease in graft yield. This outcome may be attributable to degrafting after a certain time. A similar result⁸ was also obtained in the grafting of acrylonitrile onto jute fiber using a Ce(IV)-*n*-acetyl glycine initiator system.

Effect of initiator concentration

In our present investigation Ce(IV) acts as the initiator. The effect of varying the Ce(IV) concentration while keeping constant concentration of all other reagents, at 40, 50, and 60°C, is shown in Figure 2 and Table II. One may observe that the %GY increases by increasing the concentration of Ce(IV) from 0.005 to 0.045 mol L⁻¹. This increasing trend of graft yield is

TABLE I
Effect of Time on Grafting^{a,b}

Time (h)	40°C		50°C		60°C	
	%GY	Rg × 10 ⁶ (mol L ⁻¹ s ⁻¹)	%GY	Rg × 10 ⁶ (mol L ⁻¹ s ⁻¹)	%GY	Rg × 10 ⁶ (mol L ⁻¹ s ⁻¹)
1.0	18.7	25.941	22.3	30.935	26.1	36.206
2.0	47.1	32.734	59.4	41.209	74.1	51.404
3.0	31.1	14.380	37.3	17.247	43.0	19.883
4.0	29.8	10.334	34.1	11.826	41.9	14.531
5.0	25.3	7.019	31.7	8.795	36.2	10.043

^a Conditions: Starch = 1 g; [MMA] = 0.46M; [Glucose] = 0.025M; [Ce(IV)] = 0.025M; [H₂SO₄] = 0.25M.

^b %GY, percentage of graft yield; Rg, rate of grafting.

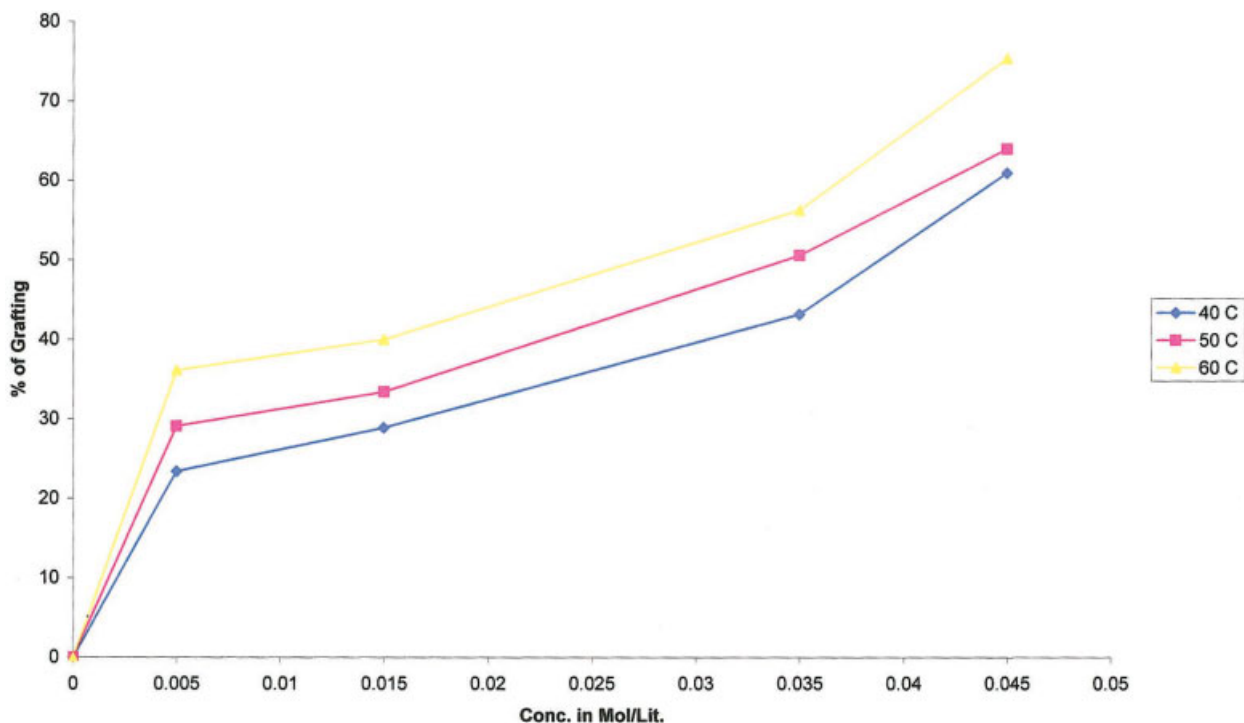


Figure 2 Effect of initiator on grafting. Starch = 1 g; [MMA] = 0.46M; [Glucose] = 0.025M; [H₂SO₄] = 0.25M; time = 2 h.

TABLE II
Effect of [Ce(IV)] on Grafting^a

[Ce(IV)] (mol L ⁻¹)	40°C		50°C		60°C	
	%GY	R _g × 10 ⁶ (mol L ⁻¹ s ⁻¹)	%GY	R _g × 10 ⁶ (mol L ⁻¹ s ⁻¹)	%GY	R _g × 10 ⁶ (mol L ⁻¹ s ⁻¹)
0.005	23.4	16.230	29.1	20.184	36.1	25.039
0.015	28.9	20.045	33.4	23.166	40.0	27.744
0.035	43.2	29.964	50.6	35.096	56.3	39.050
0.045	61.0	42.310	64.0	44.391	75.4	52.598

^a Conditions: Starch = 1 g; [MMA] = 0.46M; [Glucose] = 0.025M; [H₂SO₄] = 0.25M; time = 2 h.

attributed to the creation of a greater number of reaction sites arising from an increase in the concentration of Ce(IV) in the reaction vessel. The phenomenon invokes mutual termination of the growing radicals, as proposed by Sudhakar et al.⁹

Effect of amount of starch

In Table III, the effect of starch amount on graft yield at the three experimental temperatures is shown. As shown in Figure 3, the %GY increased by increasing

TABLE III
Effect of Starch on Grafting^a

Weight of starch (g)	40°C		50°C		60°C	
	%GY	R _g × 10 ⁶ (mol L ⁻¹ s ⁻¹)	%GY	R _g × 10 ⁶ (mol L ⁻¹ s ⁻¹)	%GY	R _g × 10 ⁶ (mol L ⁻¹ s ⁻¹)
0.2	5.6	3.844	12.1	8.392	16.5	11.444
0.6	8.9	6.073	15.1	10.473	21.6	14.982
1.4	16.9	11.722	24.5	16.993	31.8	22.056
1.8	14.4	9.988	21.3	14.773	29.6	20.530

^a Conditions: [MMA] = 0.46M; [Glucose] = 0.025M; [H₂SO₄] = 0.25M; [Ce(IV)] = 0.025M; time = 2 h.

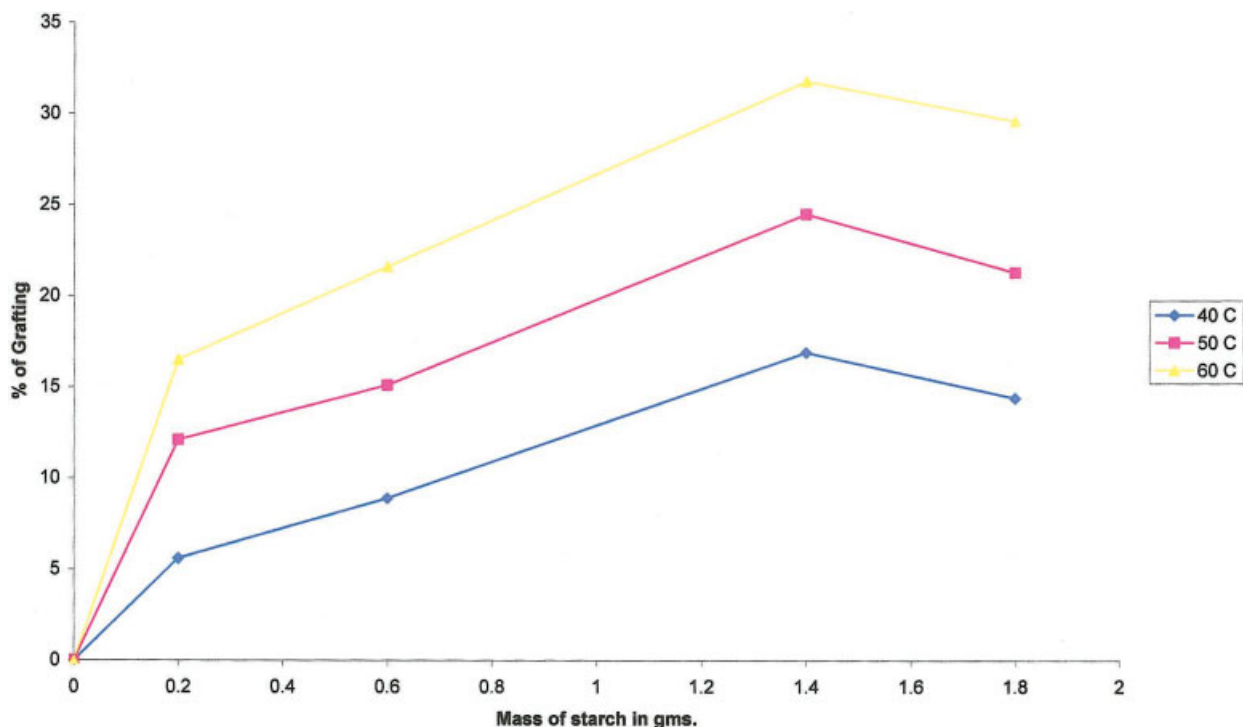


Figure 3 Effect of starch on grafting. [MMA] = 0.46M; [Glucose] = 0.025M; [H₂SO₄] = 0.25M; [Ce(IV)] = 0.025M; time = 2 h.

the amount of starch from 0.2 to 1.4 g, after which the yield decreased. This may be attributed to the fact that, with the increase in starch amount, the number of reaction sites for grafting increases, thus resulting in

an increase in graft yield. However, when the amount of starch is further increased, the amount of other reagents is insufficient to give the required number of reaction sites for grafting; thus there is a decrease in

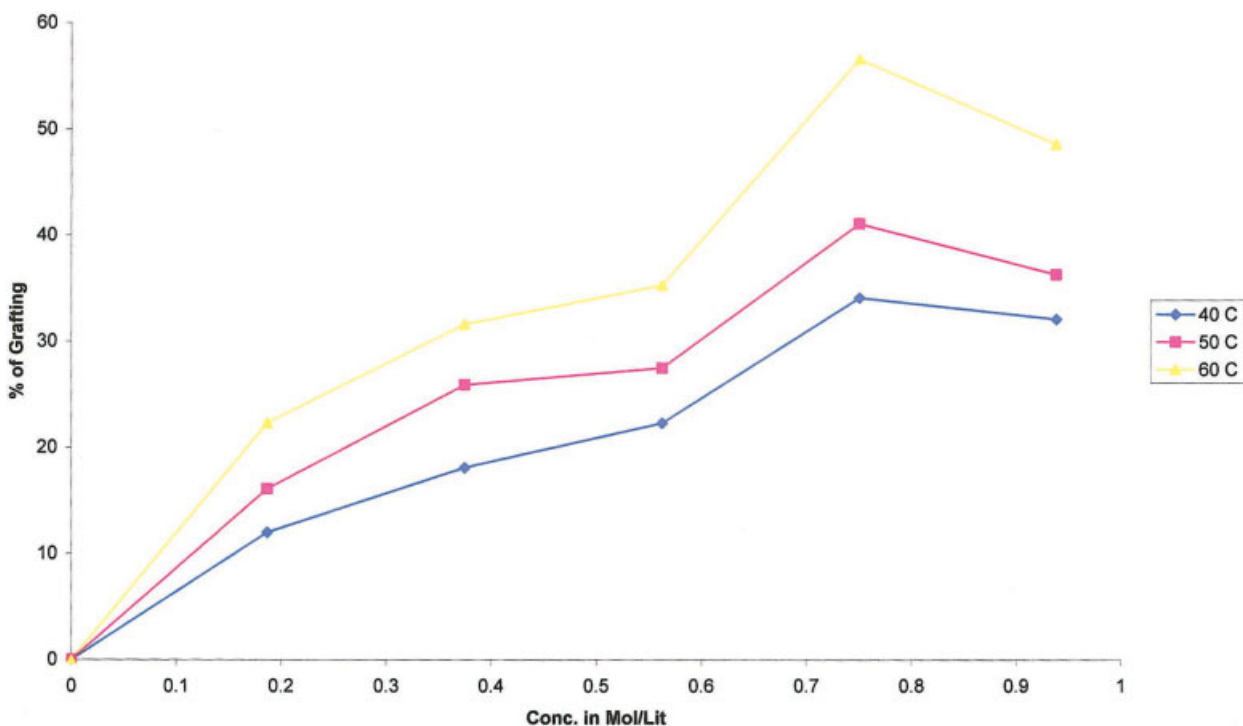


Figure 4 Effect of monomer on grafting. Starch = 1 g; [Glucose] = 0.025M; [H₂SO₄] = 0.25M; [Ce(IV)] = 0.025M; time = 2 h.

TABLE IV
Effect of [MMA] on Grafting^a

[MMA] (mol L ⁻¹)	40°C		50°C		60°C	
	%GY	R _g × 10 ⁶ (mol L ⁻¹ s ⁻¹)	%GY	R _g × 10 ⁶ (mol L ⁻¹ s ⁻¹)	%GY	R _g × 10 ⁶ (mol L ⁻¹ s ⁻¹)
0.187	12.0	8.323	16.1	11.097	22.3	15.259
0.375	18.1	12.485	25.9	17.340	31.6	21.501
0.563	22.3	15.259	27.5	18.727	35.3	24.276
0.751	34.1	23.582	41.1	28.438	56.6	38.842
0.939	32.1	22.195	36.3	24.970	48.6	33.293

^a Conditions: Starch = 1 g; [Glucose] = 0.025M; [H₂SO₄] = 0.25M; [Ce(IV)] = 0.025M; time = 2 h.

the percentage of grafting when the amount of starch is increased beyond a certain limit. The rate of termination becomes faster than initiation. This result is in agreement with the observations of Sudhakar et al.⁹ and Nayak et al.¹⁰

Effect of monomer concentration

The effect of monomer (MMA) concentration on %GY, keeping constant the concentration of all other reagents, at 40, 50, and 60°C, is shown in Figure 4 and Table IV. The %GY increases with increases in monomer concentration from 0.187 to 0.751M, after which it increases slowly. The slow increasing trend of graft yield after a certain optimum concentration may be attributable to the fact that, at higher monomer con-

centration, there might be competition between homopolymerization and grafting, and it is the homopolymerization that prevails over the grafting.

At higher MMA concentration, the combination and disproportionation of macroradicals occur more frequently, the grafting of which onto cotton fiber¹¹ causes a decrease in graft yield.

The higher rate of grafting observed by increasing the monomer concentration was attributed to the familiar gel effect, which not only hinders termination by coupling of the growing polymer chain but also causes swelling of the cotton fiber, thus facilitating diffusion of the monomer into the growing grafted chains.

The result obtained here using the Ce(IV)–glucose initiator system is similar to that obtained using the

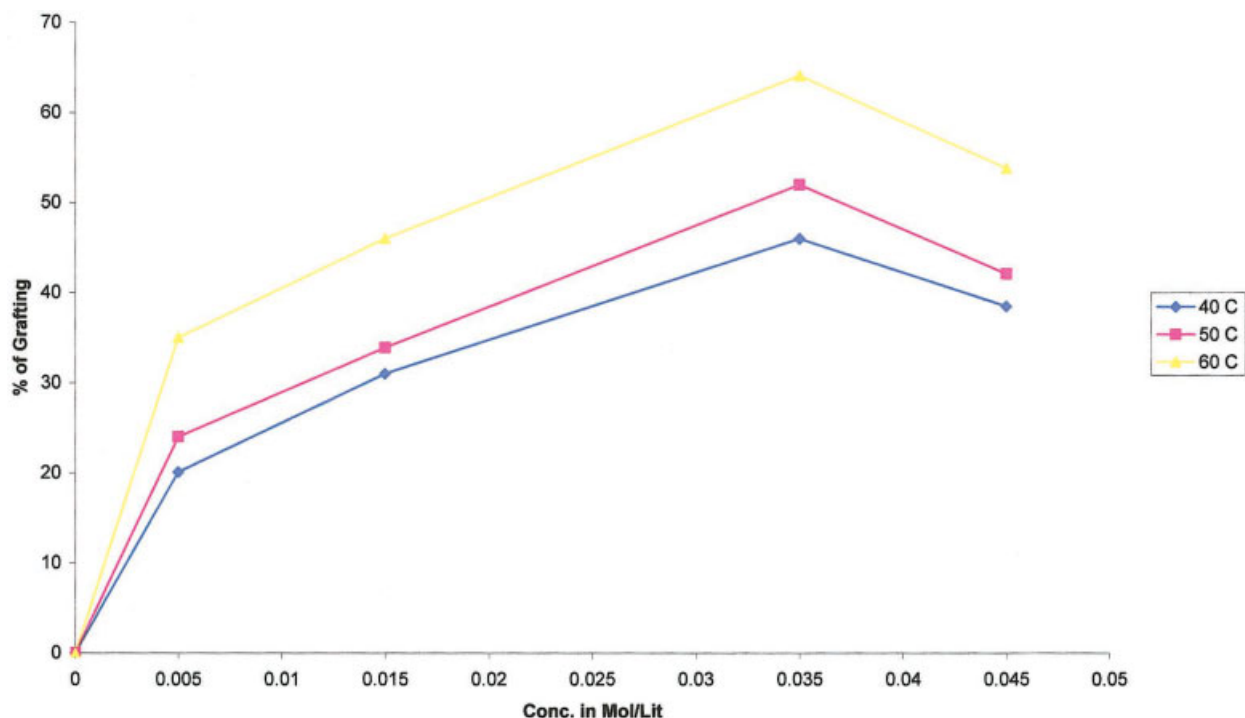


Figure 5 Effect of glucose on grafting. Starch = 1 g; [MMA] = 0.46M; [H₂SO₄] = 0.25M; [Ce(IV)] = 0.025M; time = 2 h.

TABLE V
Effect of [Glucose] on Grafting^a

[Glucose] (mol L ⁻¹)	40°C		50°C		60°C	
	%GY	R _g × 10 ⁶ (mol L ⁻¹ s ⁻¹)	%GY	R _g × 10 ⁶ (mol L ⁻¹ s ⁻¹)	%GY	R _g × 10 ⁶ (mol L ⁻¹ s ⁻¹)
0.005	20.1	13.941	24.0	16.646	35.0	24.267
0.015	31.0	21.501	33.9	23.513	46.0	31.906
0.035	46.0	31.906	52.0	36.067	64.1	44.391
0.045	38.5	26.704	42.1	29.201	53.8	37.316

^a Conditions: Starch = 1 g; [MMA] = 0.46M; [H₂SO₄] = 0.25M; [Ce(IV)] = 0.025M; time = 2 h.

V⁵⁺-cyclohexanol initiator system for grafting of MMA onto jute fiber, as reported by Mohanty et al.¹²

Effect of glucose

Figure 5 and Table V depict the effect of variation of glucose concentration on %GY, keeping constant and concentration of the other reagents, at the three experimental temperatures. By varying the glucose concentration from 0.005 to 0.035M, the %GY initially increases but thereafter decreases. The decrease is attributed to the formation of radical scavengers at higher glucose concentrations and/or a faster rate of termination. Nearly identical results were obtained¹³ on grafting of MMA onto jute fiber using a Ce(IV)-glucose initiator system.

Effect of reaction medium

The reaction medium plays an important role in graft copolymerization. Here the graft copolymerization was carried out in aqueous sulfuric acid medium. It was demonstrated that an increase in sulfuric acid concentration from 0.05 to 0.25M causes an increase in graft yield, although by increasing the acidity of the system the grafting efficiency decreases.¹⁴ These results are shown in Figure 6 and Table VI. The decrease of %GY at higher acid concentration is probably attributable to formation of species unfavorable for grafting.

Effect of temperature

The graft copolymerization of MMA onto cotton was investigated at 40, 50, and 60°C. When the concentra-

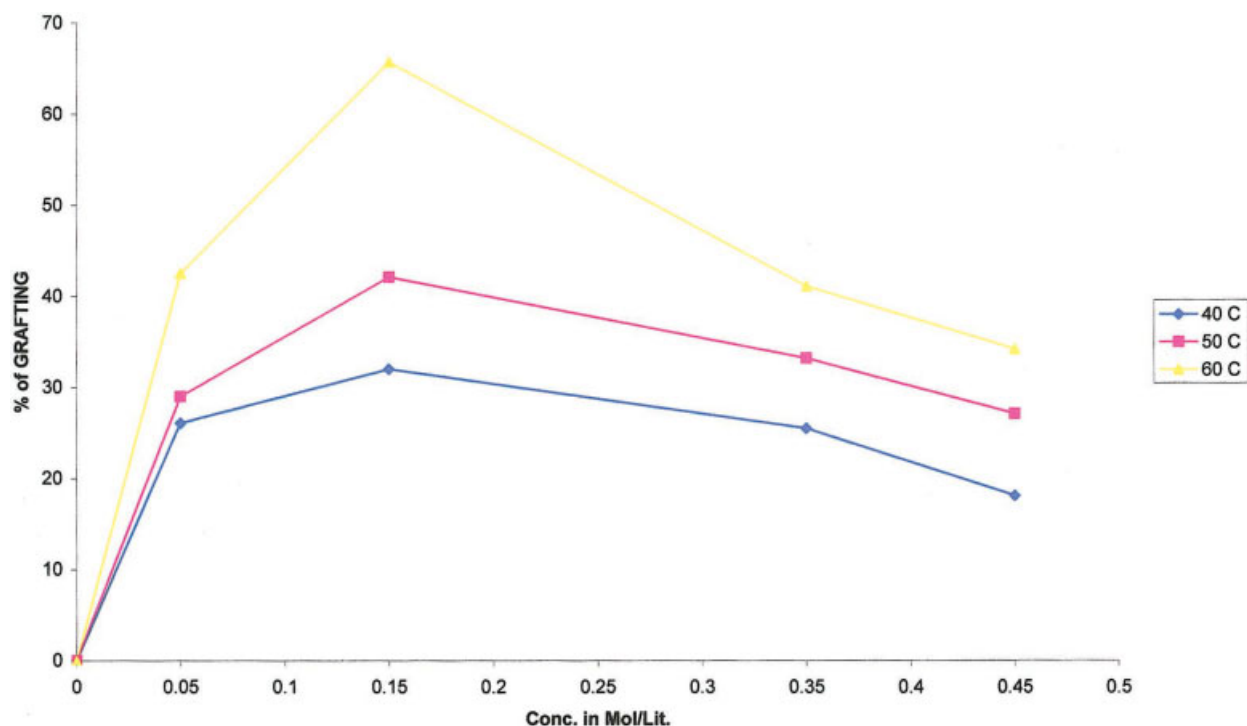


Figure 6 Effect of acid on grafting. Starch = 1 g; [MMA] = 0.46M; [Glucose] = 0.025M; [Ce(IV)] = 0.025M; time = 2 h.

TABLE VI
Effect of $[H_2SO_4]$ on Grafting^a

$[H_2SO_4]$ (mol L ⁻¹)	40°C		50°C		60°C	
	%GY	Rg × 10 ⁶ (mol L ⁻¹ s ⁻¹)	%GY	Rg × 10 ⁶ (mol L ⁻¹ s ⁻¹)	%GY	Rg × 10 ⁶ (mol L ⁻¹ s ⁻¹)
0.05	26.1	18.033	29.0	20.114	42.5	29.478
0.15	32.0	22.195	42.1	29.201	65.7	45.570
0.35	25.5	17.687	33.2	23.027	41.1	28.507
0.45	18.1	12.554	27.1	18.796	34.2	23.721

^a Conditions: Starch = 1 g; [MMA] = 0.46M; [Glucose] = 0.025M; [Ce(IV)] = 0.025M; time = 2 h.

tion of all reagents was kept constant, it was observed that the percentage of grafting increased with increases in temperature from 40°C. This effect, shown in Figure 1, can be ascribed to the enhanced diffusion rate of monomer at higher temperature.⁹ The Arrhenius plot (Fig. 7) of log Rg versus 1/T is a straight line. From the slope of the plot, the activation energy was computed to be 4.145 kcal/mol.

Mechanism

In the system containing Ce(IV), MMA, glucose, and starch, Ce⁴⁺ may interact with glucose to form a complex that dissociates to give a free radical. This radical

abstracts hydrogen from the starch molecule [CH] yielding a macroradical C.

Initiation

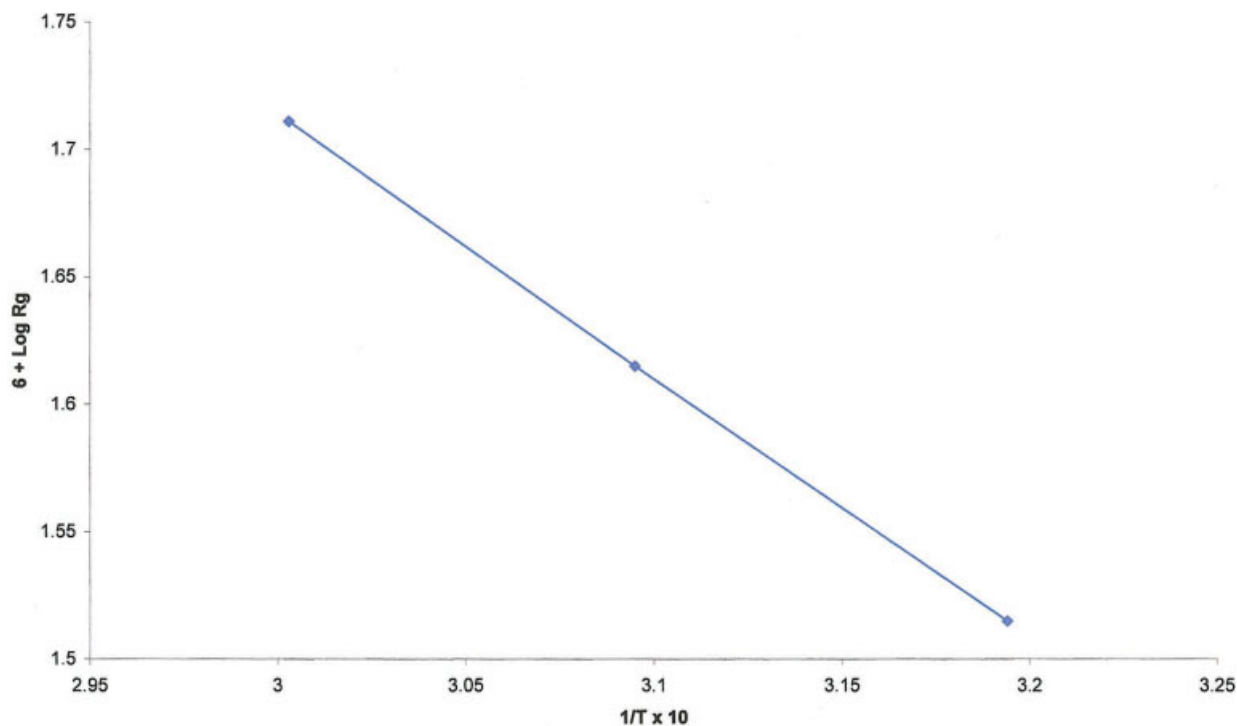
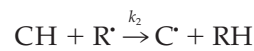
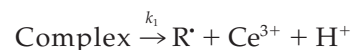
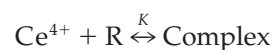


Figure 7 Arrhenius plot. Starch = 1 g; [MMA] = 0.46M; [Ce(IV)] = 0.025M; [Glucose] = 0.025M; time = 2 h.

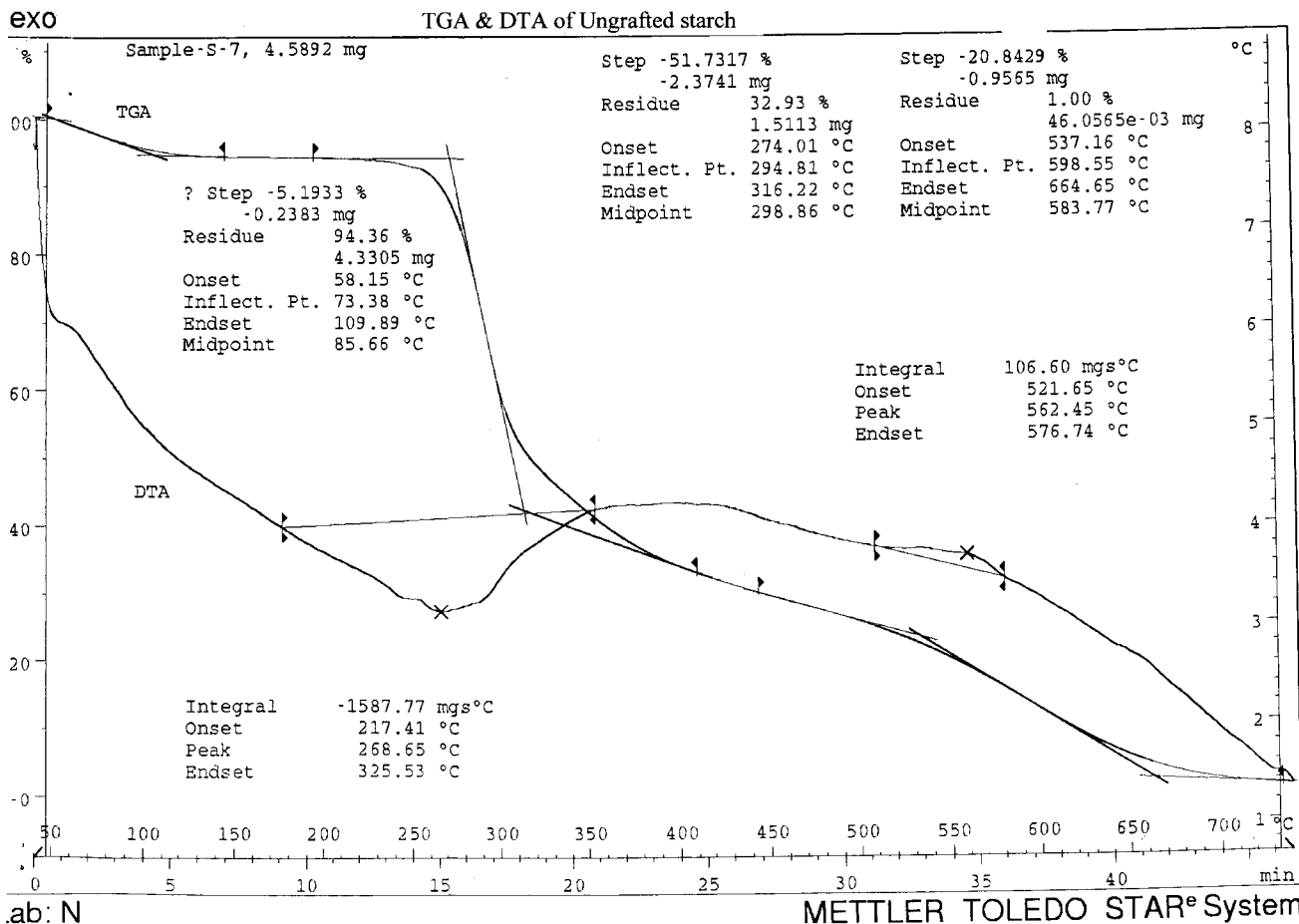


Figure 8 TGA and DTA of ungrafted starch.

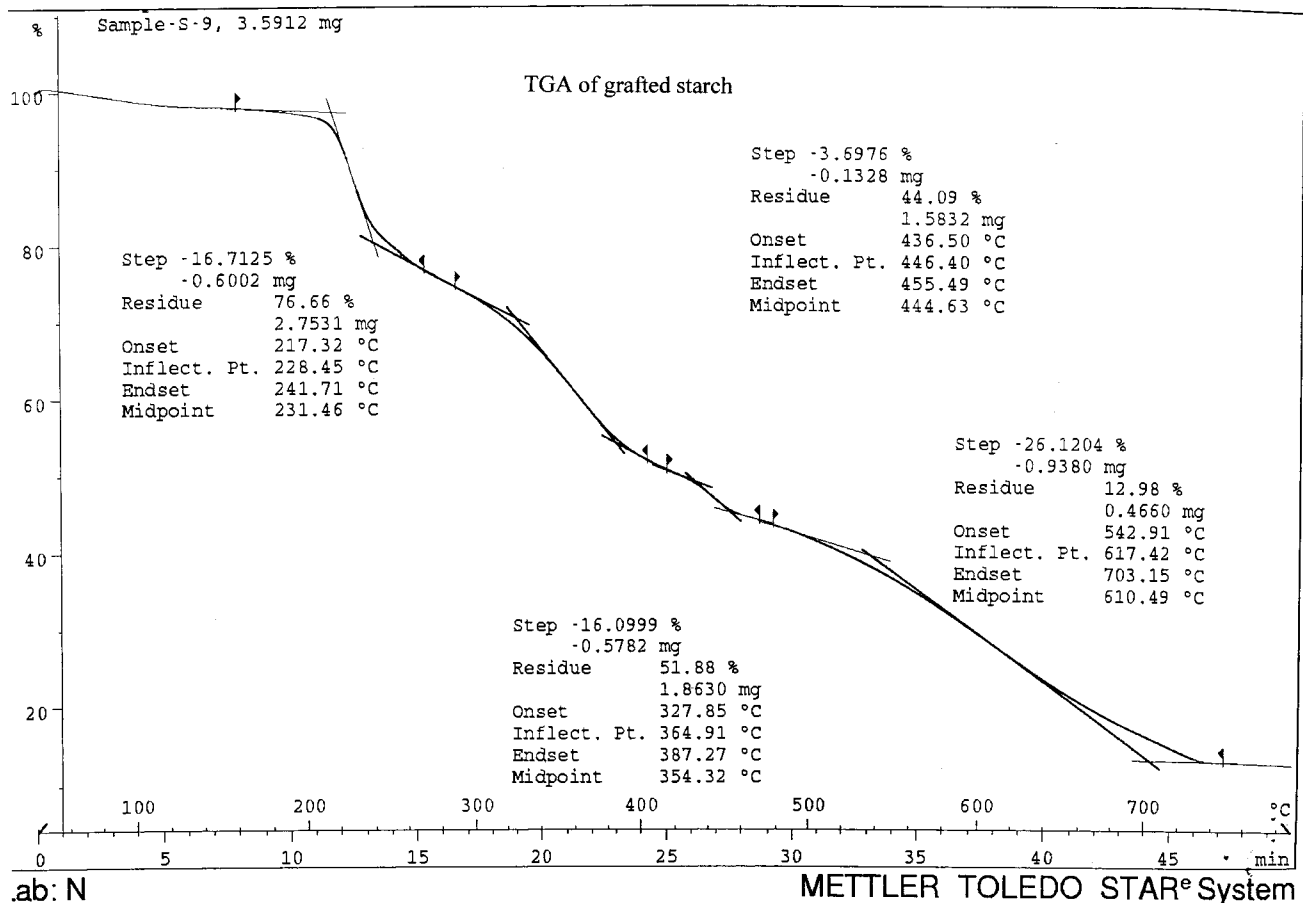


Figure 9 TGA of grafted starch.

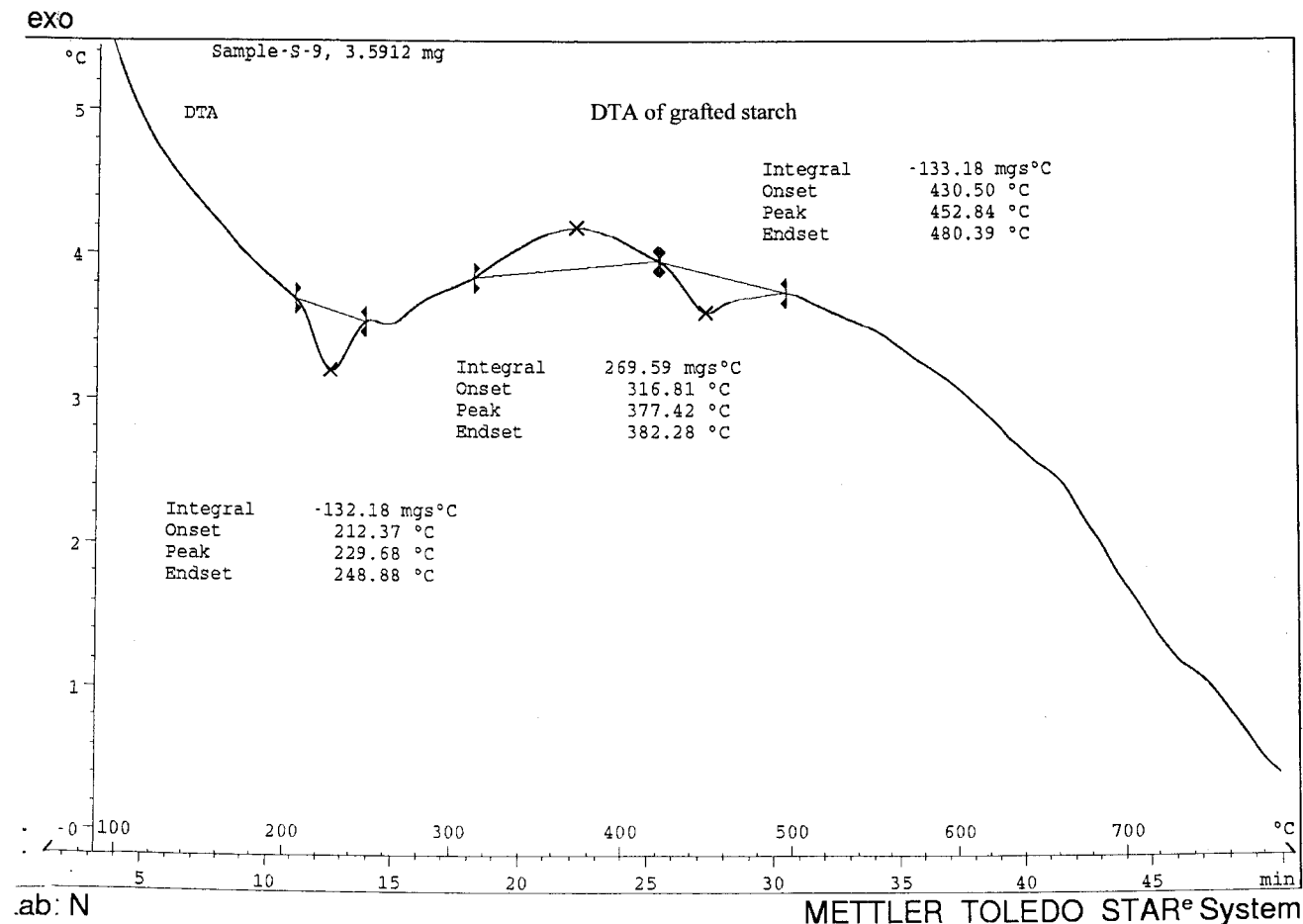
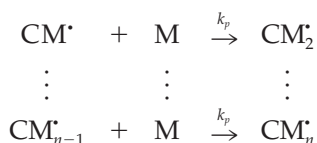
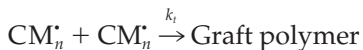


Figure 10 DTA of grafted starch.

Proagation



Termination



Oxidation



where Ce^{4+} is the ceric ion; CH represents the starch molecule; C represents the starch macroradical; M represents monomer; R represents glucose; and $K, k_1, k_2, k_i, k_p, k_t,$ and k_o are different rate constants.

Characterization

Figures 8, 9, and 10 depict TGA and DTA analyses of ungrafted starch and starch 30% grafted with MMA, respectively. These figures clearly illustrate that the grafted starch is more thermally stable than the ungrafted starch. Similar results were obtained in an earlier study.¹⁰

CONCLUSIONS

Graft copolymerization is a novel technique for the development of the properties of polysaccharides. For natural polymers like starch to survive in competition against synthetic polymers consumers must continually express their preference for the natural material; thus to retain preferred status, natural polymers must be constantly developed and improved. The graft polymerization of vinyl monomer onto polymers, particularly onto starch, has gained considerable importance in recent years because it is a fascinating field of research with seemingly unlimited potential. In the present case it was observed that $Ce(IV)$ with glucose

forms a suitable redox system for graft copolymerization of MMA onto starch. Results of this present investigation are sufficient to study the mechanism of the process: experimental results are in substantial agreement with the proposed mechanism.

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