

Graft Copolymerization of Methyl Methacrylate onto Biomedical Polyvinyl Chloride Initiated by Ce(IV)–Glucose Redox System

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ABSTRACT: Graft copolymerization of methyl methacrylate onto PVC was carried out using Ce(IV)–glucose redox system in aqueous sulfuric acid medium under nitrogen atmosphere. To find out the optimum conditions for grafting, effects of concentrations of metal ion, glucose, monomer, and acid on the percentage of grafting was studied. The graft yield was found to be influenced by reaction time, temperature, and amount of PVC. An appreciably high graft

yield could be achieved with the present system. On the basis of the results from the present study, a plausible reaction mechanism has been proposed. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 2105–2111, 2005

Key words: biomedical polymer; PVC; MMA; graft copolymerization; SEM

INTRODUCTION

The traditional definition of a biomaterial is a systematic, pharmacologically inert substance designed for implantation or incorporation into the human body. Polymers have been used in the augmentation and repair of the human body with much success. Even fundamental medical care involves the use of polymers, namely blood bags, disposables, hygienic medical instruments, safer spectacles, contact lenses, and gradual delivery of medicines via capsules and patches. All of these make improved and longer lives a reality.

Polyvinyl chloride is used for a wide range of biomedical applications,^{1–3} including blood bags, blood tubing, surgical gloves, suction pipes, gastrointestinal grafts, oxygenators (extracorporeal heart–lung machines), and dialating catheters in coronary angioplasty.

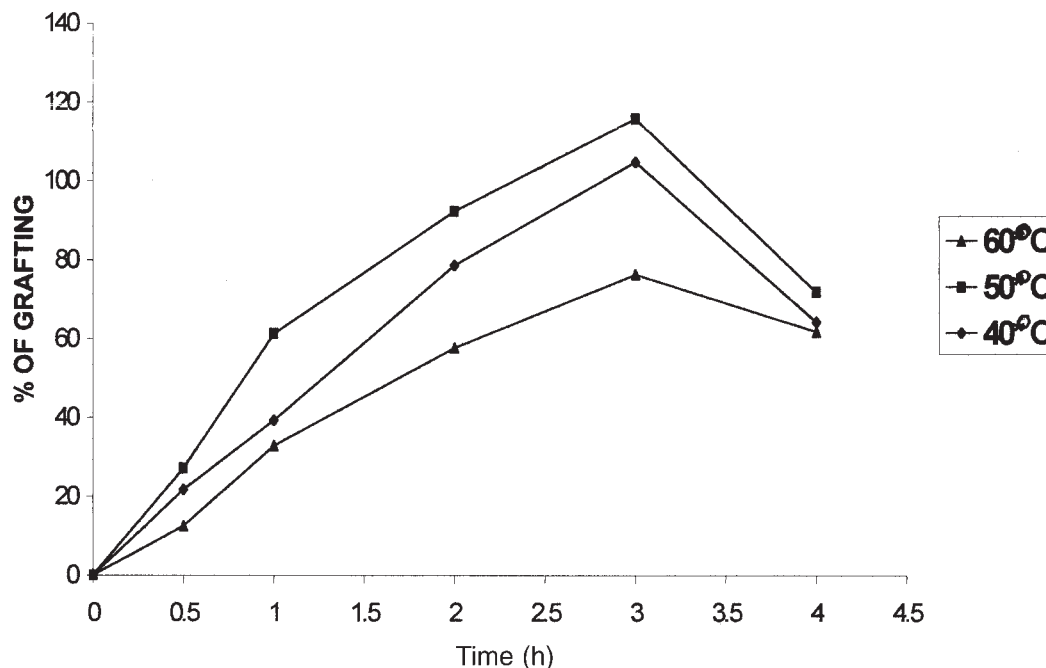
Grafting has long been accepted as an excellent method of upgrading polymers. This technique of graft copolymerization has been successfully adopted in developing novel biomedical polymers in various research laboratories across the globe.^{4–9} Graft copolymerization of natural and synthetic polymers with vinyl monomers has been of special interest to polymer scientists.^{11–14} Sharma et al.,^{15,16} Higa and Gil,¹⁷ and Akira.¹⁹ have studied grafting of vinyl monomers onto polyvinyl chloride. Methyl methacrylate, as an important vinyl monomer, has been successfully

grafted onto holo cellulose by a ceric ion initiator system reported recently.¹⁹ Abu-Ilai²⁰ has recently reported on grafting of methyl methacrylate onto rubberwood fiber using H₂O₂ and Fe²⁺ as the initiator system. Polymethyl methacrylate (PMMA) is very useful in biomedical applications such as dental fillings, contact lenses, eye lens replacement, and other dental and optical applications. Thus, PMMA was chosen for the surface modification of polyvinyl chloride. The present study aims to develop an improved medical grade PVC with better thermal and mechanical properties through the process of graft copolymerization of a vinyl monomer such as methyl methacrylate onto PVC using a Ce(IV)–glucose initiator system.

EXPERIMENTAL

MMA was washed with 5% NaOH solution followed by conductivity water. After drying with anhydrous calcium chloride, it was distilled under reduced pressure and stored in the refrigerator for use. Ammonium ceric sulfate, glucose, PVC, and other reagents were used as received. Graft copolymerization was carried out in a constant temperature water bath maintained at the required temperature with an accuracy of $\pm 0.1^\circ\text{C}$. PVC was soaked with monomer (MMA) for about 15 min. Pyrex vessels with B_{24/29} standard joints fitted with gas inlet and outlet tubes were used to carry out the experiments. The reaction mixture containing PVC, monomer, glucose, sulphuric acid, and water were taken in the reaction vessel and nitrogen gas was passed through it for 30 min. The reaction vessels and ceric ammonium sulfate solution were then thermostated for 10 min to attain the temperature

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[MMA] = 0.47 mL⁻¹, [Ce(IV)] = 0.025 mL⁻¹, Glucose = 0.025 mL⁻¹,
[H₂SO₄] = 0.25 mL⁻¹, PVC = 0.1g.

Figure 1 Effect of time on graft yield.

of the bath. Ceric ammonium sulfate solution was added and the time was noted. The experimental details are given in Figures 1–6. The reaction was carried out at three different temperatures: 40, 50, and 60°C. After the required reaction time, reactions in each vessel were arrested by quenching the vessel with ice-cold water. Finally the samples were extracted with toluene in a Soxhlet apparatus for 6 h to dissolve all of the homopolymers until a constant weight of grafted polyvinyl chloride was obtained. The percentage of graft yield was calculated as follows:

% graft yield

$$= \frac{\text{dry wt. of grafted PVC} - \text{dry wt. of original PVC}}{\text{dry wt. of original PVC}} \times 100$$

RESULTS AND DISCUSSION

The dependence of grafting on reaction variables such as monomer and initiator concentration and time and temperature was studied in detail.²¹

Effect of variation of time on graft yield

The percentage of graft yield versus reaction time was studied at 40, 50, and 60°C, as shown in Figure 1. It was recorded that graft yield increased steadily over time for up to 3 h and then decreased.²² It is obvious

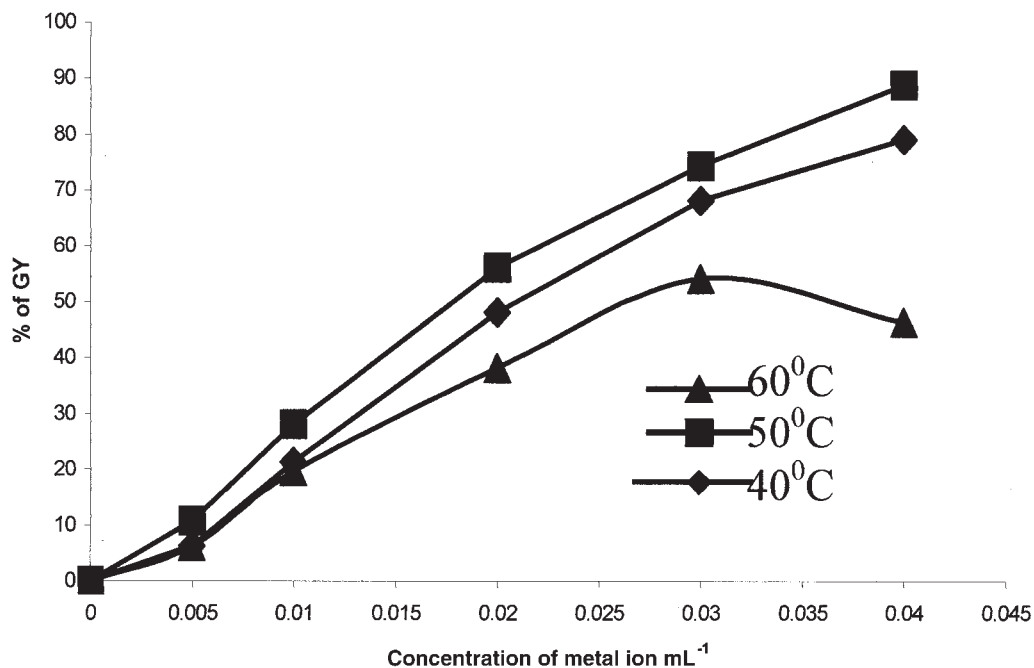
that the higher the contact time of the monomer molecule with the PVC macro radical sites, the higher the grafting. But the decrease in the percentage of graft yield after 3 h can be attributed to the depletion of initiator and monomer concentration with the progress of the reaction.²³

Effect of metal ion concentration

Concentration of Ce(IV) was varied from 0.005 to 0.04 mL⁻¹ at three different temperatures. The graft yield was found to increase steadily with increasing initiator concentration, as shown in Figure 2. This trend may be attributed to the prevalence of either radical or mutual termination over the linear one.²⁴ Again, the steady increase in graft yield with increasing initiator concentration was due to the increase of active sites on the backbone of PVC arising from the attack of different amounts of Ce(IV) on polymer matrix. The decrease in percent graft yield (at 60°C) for the highest initiator concentration may be ascribed to (i) excess Ce⁴⁺ that may act as a terminator²⁵ and, (ii) hindrance to the diffusion of monomer molecules to the active sites on PVC due to the excess of Ce⁴⁺ ions present in the reaction mixture, resulting in preferential homopolymerization.²⁶

Effect of glucose concentration

Ce(IV) coupled with glucose constitutes the redox initiator system for the graft copolymerization reaction in



[MMA] = 0.47 mL⁻¹, [Glucose] = 0.025 mL⁻¹, [H₂SO₄] = 0.25 mL⁻¹, PVC = 0.1g
Time = 3 h

Figure 2 Effect of variation of metal ion concentration.

this case. Concentration of glucose was varied from 0.005 to 0.045 mL⁻¹ at three different temperatures- (Figure 3). The percentage of graft yield increases with

the concentration range studied. The increasing concentration of radicals with increasing concentration of glucose may contribute to the higher graft yield.²⁷

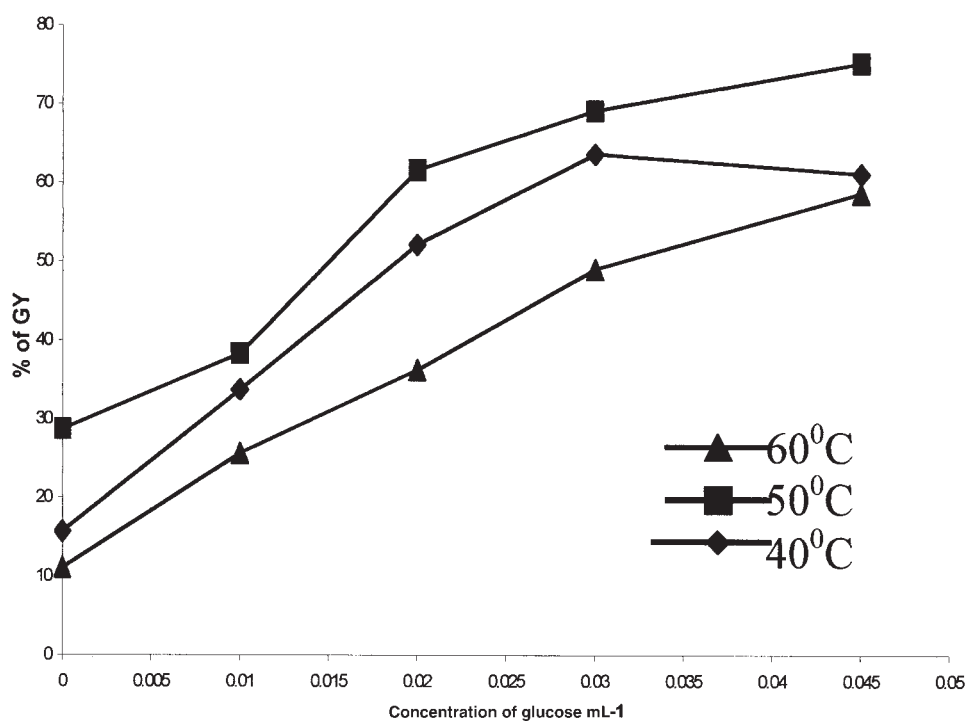


Figure 3 Effect of variation of glucose concentration.

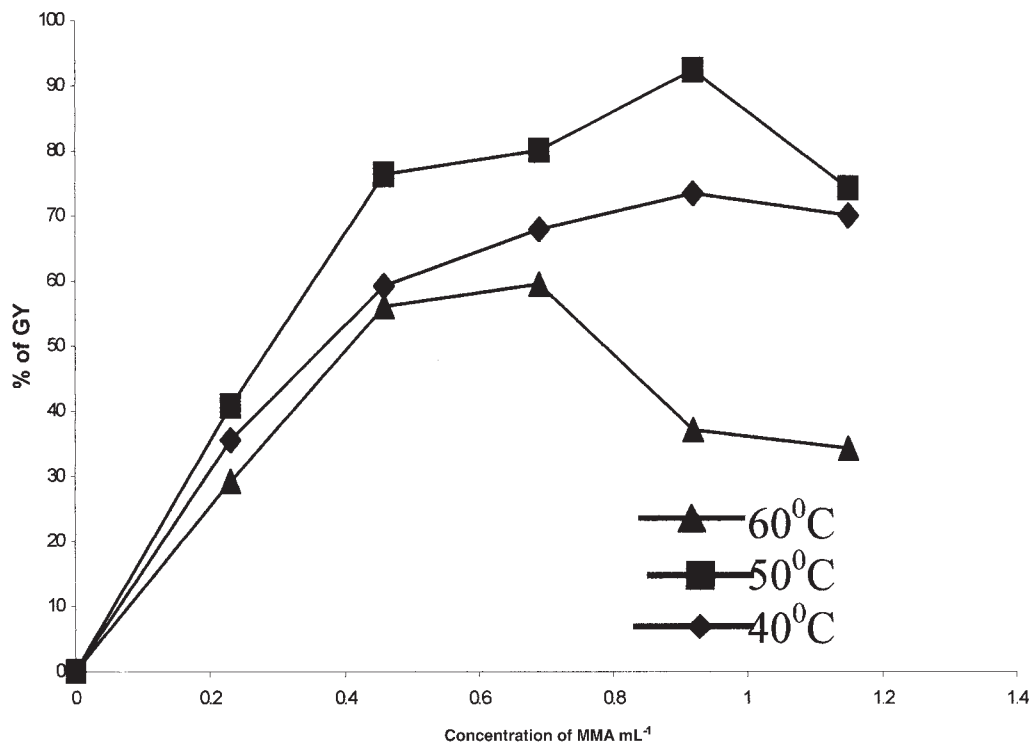


Figure 4 Effect of variation of MMA concentration.

Effect of monomer concentration

The effect of variation of monomer (MMA) concentration on graft yield at three different temperatures is shown in Figure 4. Initially there was an increase in the graft yield with increasing monomer concentration in the range of 0.2354 to 0.9418 mL⁻¹. The growth in graft yield with increase in concentration of methyl methacrylate might be due to the formation of a higher number of radicals (PMN), which in turn might generate more grafting sites on polyvinyl chloride. The decreasing trend in graft yield after certain concentrations of the monomer might be due to the competition between homopolymerization and grafting, where the former prevailed over the latter at higher monomer concentrations.^{28,29}

Effect of amount of polyvinyl chloride

The dependence of graft yield on the amount of polyvinyl chloride was studied in the range of 0.05–0.3 g at three different temperatures (Figure 5). Initially, the graft yield was found to increase and then decreased with the increase in the amount of polyvinyl chloride. The increase in the graft yield might be due to the formation of a higher number of radical sites on the backbone of the polymer. Subsequent decrease was attributed to the increase in surface area and viscosity of the polymer.³⁰ This relates to earlier work on this problem.³⁰ The increase in the amount of polymer

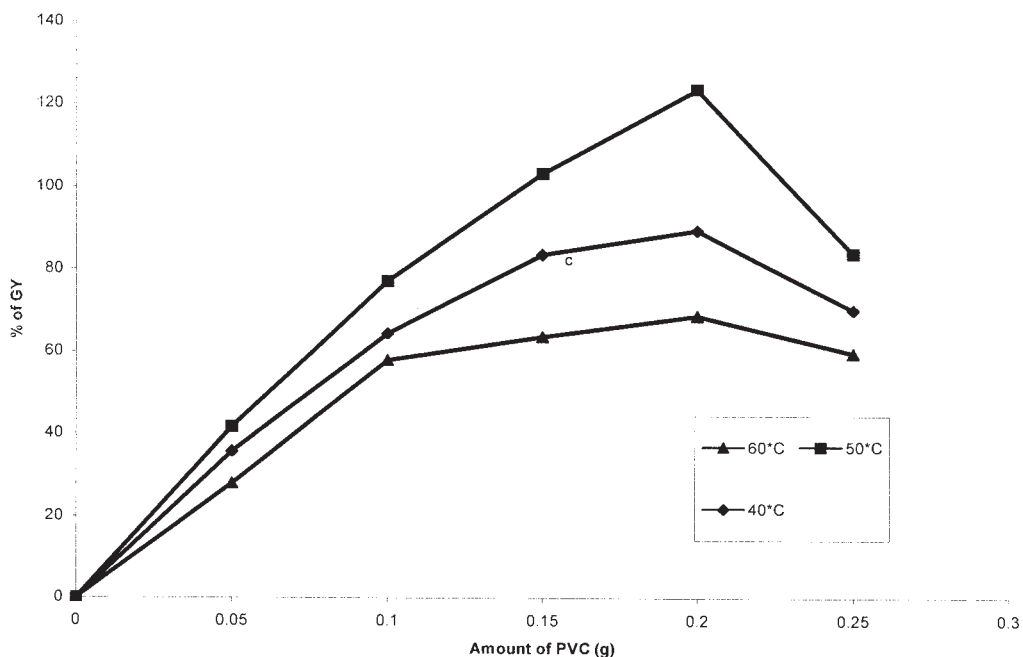
beyond a certain limit puts an adverse effect on graft yield. It increases the viscosity of the medium and the higher viscosity limits the mobility of the polymer chain.³¹

Effect of temperature

The graft copolymerization of methyl methacrylate onto polyvinyl chloride has been studied at temperatures ranging from 40 to 60°C. The graft yield was found to increase with the increase in temperature from 40 to 50°C and subsequently decreased at 60°C. A decrease of rate of grafting with increase of temperature has been attributed to coagulation of polymer and degradation of polyvinyl chloride at higher temperatures.³²

Effect of acid

The effect of sulfuric acid on graft yield was studied in the concentration range of 0.05 to 0.45 mL⁻¹ at three different temperatures (Figure 6). Though percent grafting increases with increase in acid concentration initially, the higher concentration of acid is not only unfavorable for grafting but it also destroys some useful properties of polymer. For this reason, the concentration of acid has been kept as low as possible in all our studies.



[MMA] = 0.47 mL^{-1} , [Ce (IV)] = 0.025 mL^{-1} , [Glucose] = 0.025 mL^{-1}
 [H₂SO₄] = 0.25 mL^{-1} , Time = 3 h.

Figure 5 Effect of variation of PVC amount.

Mechanism

On the basis of the foregoing results, a suitable mechanism is given here. Rigorous kinetic analysis is not

attempted because of the complex and heterogeneous nature of reaction. The reaction proceeds through the following steps.

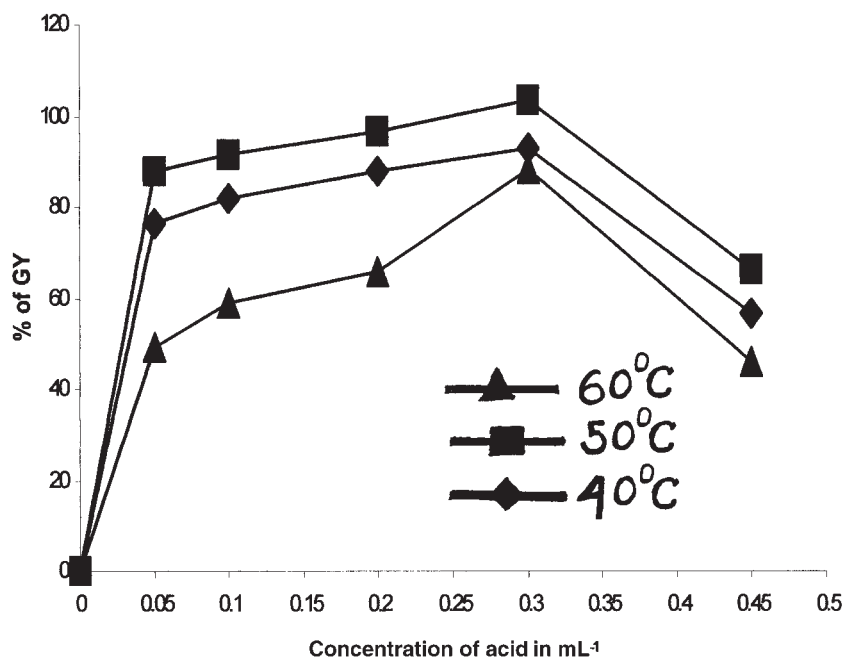
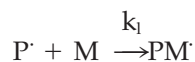
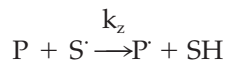
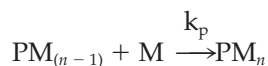
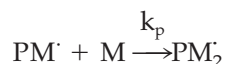


Figure 6 Effect of variation of acid concentration.

Initiation



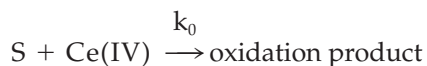
Propagation



Termination



Oxidation



where the organic substrate, glucose, is denoted as S; and Ce(IV), P, P[·], M, S[·]; k, k₁, k₂, k_i, k_p, k_t are ceric ion, polyvinyl chloride, polyvinyl chloride macroradical,

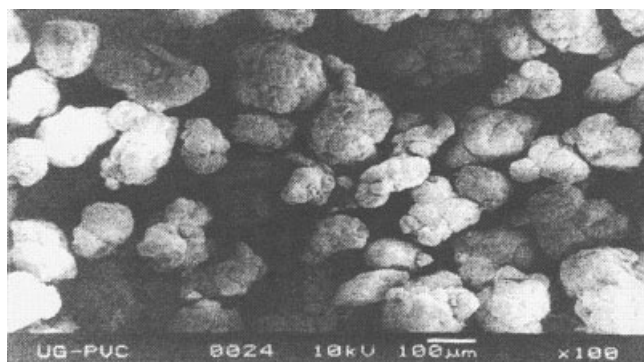


Figure 7 Scanning electron micrographs of ungrafted PVC.

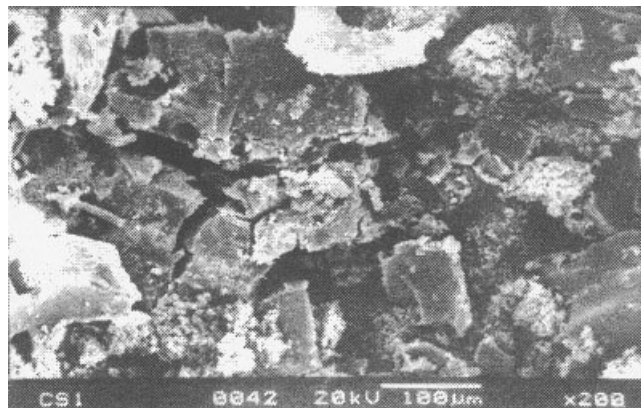


Figure 8 Scanning electron micrographs of grafted PVC.

monomer(methylmethacrylate), organic substrate free radical, and different rate constants, respectively.

CONCLUSION

Results of the present investigation are significantly helpful in suggesting the optimum conditions for effective grafting of methyl methacrylate onto biomedical polyvinyl chloride. The percentage of graft yield is found to be optimum at the following levels: time, 180 min; Ce(IV), 0.04 mL⁻¹; glucose, 0.04 mL⁻¹; MMA, 0.9418 mL⁻¹; PVC, 0.2 g; sulfuric acid, 0.3 mL⁻¹; and temperature, 50°C. Scanning electron micrographs of polyvinyl chloride before grafting and after grafting are given here(Figures 7 and 8). A comparison of SEM micrographs of ungrafted PVC (Figure 7) and grafted PVC (Figure 8) indicates that the surface morphology of PVC before grafting is quite smooth but shows fibrillar topography after grafting. Thus, comparison of these figures clearly reveals that grafting has taken place. In the course of research, sufficient experimental evidence could be gathered in favor of the mechanism suggested.

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