

Graft Copolymerization of Acrylic Acid on Methylcellulose by Ceric Ion/*p*-Xylene Redox Pair

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Received 16 January 2001; accepted 8 July 2001

ABSTRACT: The graft copolymerization of acrylic acid onto methylcellulose by ceric ion/*p*-xylene redox pair was investigated in aqueous media under homogeneous conditions. The graft yield dependency on *p*-xylene concentration in the range $1.8\text{--}45.0 \times 10^{-5}M$ showed a minimum and an enhanced yield when the methylcellulose interacted with ceric ion and *p*-xylene for an initial period of 10 min (preoxidation time) prior to addition of monomer to the reaction medium. This was attributed to the presence of two kinetically controlled reactions initiated by *p*-xylyl radical and diradical species. At prolonged preoxidation times of 30 and 60 min, the graft yield dependency on *p*-xylene concentration was normal and suggested the presence of only one initiating species. The effect of ceric ion on the graft reaction in the concentration range of $8.33\text{--}83.3 \times 10^{-3}M$ was optimal at 131% graft yield for ceric ion concentration of $16.7 \times 10^{-3}M$ and was reduced significantly by as much as 75% at the highest concentration of the latter. The temperature dependency of graft yield was negative in the region 30–50°C. At 50°C the initial rate of graft was only 37% of the value at 30°C. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 500–504, 2002; DOI 10.1002/app.10200

Key words: ceric ion/*p*-xylene redox pair; graft copolymerization; vinyl monomers

INTRODUCTION

The redox initiation of graft copolymerization of vinyl monomers onto cellulosic substrates under heterogeneous conditions has been extensively studied.^{1–5} For the graft copolymerization of acrylonitrile on kenaf fibers by the ceric ion/*p*-xylene redox system in aqueous media, there were interesting features by the exhibition of minimum and maximum graft yields at varying concentrations of *p*-xylene.⁶ These features were attributed to two kinetically controlled reactions emanating from the activities of two distinct initiating species, that is, a *p*-xylyl radical and a diradical. The

reaction was conducted under heterogeneous conditions and it was not apparent how the latter might have influenced the observed features.

The graft copolymerization of acrylic acid onto cellulosic fibers by the ceric ion/*p*-xylene redox system has been reported, although no detailed studies were carried out on the grafting characteristics.⁴

The present report is on the graft copolymerization of acrylic acid onto methylcellulose by the ceric ion/*p*-xylene redox system under homogeneous conditions in aqueous media. The grafting characteristics are presented and discussed.

EXPERIMENTAL

p-Xylene (XY) (Aldrich, USA) was treated with concentrated sulfuric acid, washed with distilled

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Journal of Applied Polymer Science, Vol. 84, 500–504 (2002)
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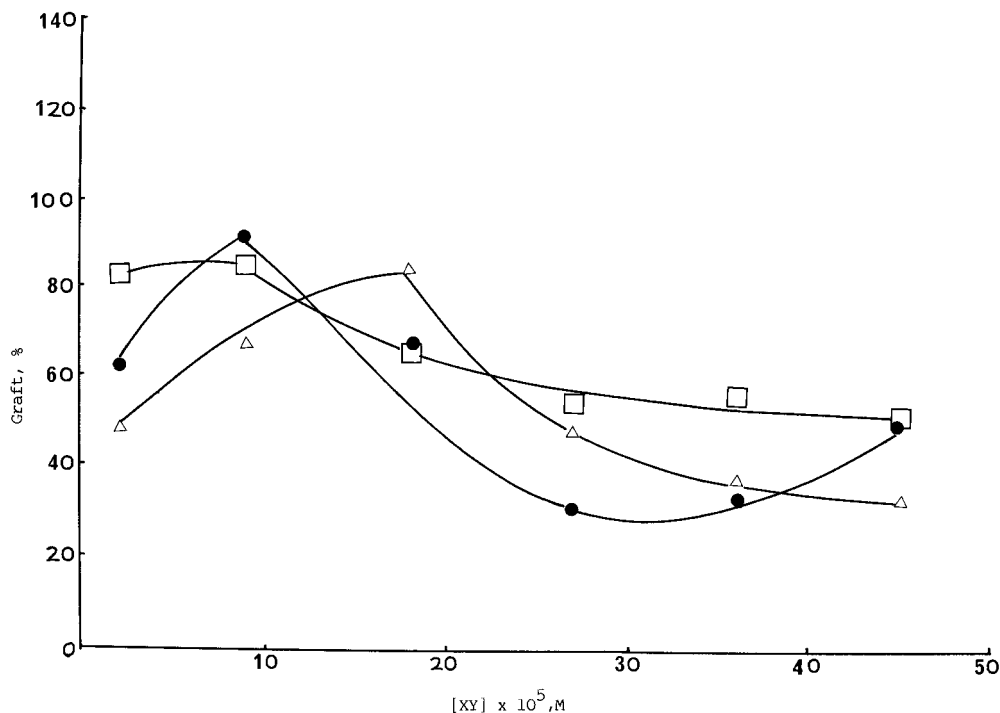


Figure 1 Effect of *p*-xylene on graft yield at different preoxidation times. $[H^+] = 0.52M$; $[Ce(IV)] = 33.3 \times 10^{-3}M$; $[AA] = 0.46M$; $MC = 0.1$ g; $[AcOH] = 1.17M$. Preoxidation time: 10 min (●); 30 min (△); 60 min (□). Time = 3 h; temperature = 30°C.

water to a neutral pH, and fractionally distilled after drying with anhydrous calcium chloride.

Acrylic acid (AA; Hopkin and Williams) was washed with 5% aqueous sodium hydroxide solution, dried over anhydrous calcium chloride, and fractionally distilled. The other reagents, that is, methylcellulose (MC, low substitution; BDH, Poole, UK), nitric acid, ceric ammonium nitrate, and glacial acetic acid (AcOH) (Aldrich) were used as supplied.

The method of the graft copolymerization reaction was as reported in a previous communication.⁷ Specifically, the reaction was conducted in a 250-mL Pyrex stopper. The required amounts of the reagents, that is, glacial acetic acid, nitric acid, and *p*-xylene, were put into the flask and the solution made up to 30 mL with distilled water. A 0.1-g sample of the MC was dissolved in the solution while the flask was kept in a thermostated water bath, regulated to within $\pm 0.05^\circ C$.

The required amount of ceric ammonium nitrate was introduced into the flask, swirled gently, and allowed to stand for a given period (preoxidation time), to permit formation of MC macroradicals by the redox reaction between ini-

tiating species and MC. The monomer was then added to the flask to start the graft reaction process. The graft copolymer was precipitated at the end of the reaction by raising the temperature of the solution to 60°C, filtered on a Buchner funnel, and washed repeatedly with boiling water.⁸ The percentage graft and percentage efficiency were calculated from the following relations:

$$\% \text{ Grafting} = [(W_2 - W_1)/W_1] \times 100$$

$$\% \text{ Efficiency} = [(W_2 - W_1)/W_3] \times 100$$

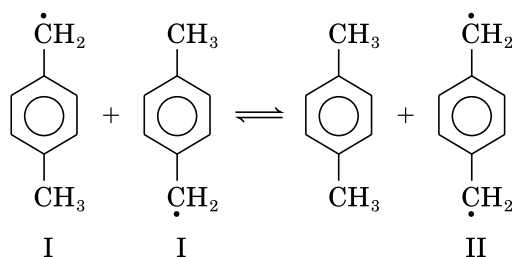
where W_1 , W_2 , and W_3 are the weights of the methylcellulose, grafted methylcellulose, and the monomer, respectively.

RESULTS AND DISCUSSION

Effect of *p*-Xylene Concentration on Graft Yield

Figure 1 represents plots of graft yields at varying XY concentrations and preoxidation times. The latter is the period of interaction between the MC,

ceric ion, and XY prior to addition of the monomer to the reaction medium. At 10 min preoxidation time, the effect of XY is characterized by maximum and minimum graft yields at its concentrations of 9.0 and $27.0 \times 10^{-5}M$, respectively, over the concentration range of 1.8 – $45.0 \times 10^{-5}M$. These features corroborate a previous report⁶ on the effect of XY on the graft copolymerization of acrylonitrile onto kenaf fibers under heterogeneous conditions, and which was ascribed to the presence of two kinetically controlled reactions initiated by two radical species of the forms I and II. At high concentrations of XY, a preponderance of *p*-xylyl radicals may lead to their mutual interactions to yield an unstable and reactive diradical species (II). For a redox interaction with MC, the latter species is expected to be more active than I, resulting in an enhanced macroradical formation and graft yield.



The observance of this phenomenon in the present system under homogeneous conditions suggests that the effect of XY on the graft copolymerization is independent of the physical property of the reaction medium.

The graft reactions at preoxidation times of 30 and 60 min were intended to test the effectiveness of the diradical species over a prolonged period of interaction with MC, given that, as previously mentioned, it is unstable and reactive. As can be seen in Figure 1, the graft yield profiles at these preoxidation times do not show any minima, suggesting that a diradical species may be absent in the reaction medium. This is contrary to the results for the graft copolymerization of acrylonitrile on cellulosic fibers by the ceric ion/*p*-xylene redox system under the same conditions and preoxidation times.⁶ It would seem, therefore, that for the present system, the instability of the diradical at higher preoxidation times is more likely a function of the nature of the reaction medium. Specifically, the monomer that is acidic is expected to influence the pH of the reaction

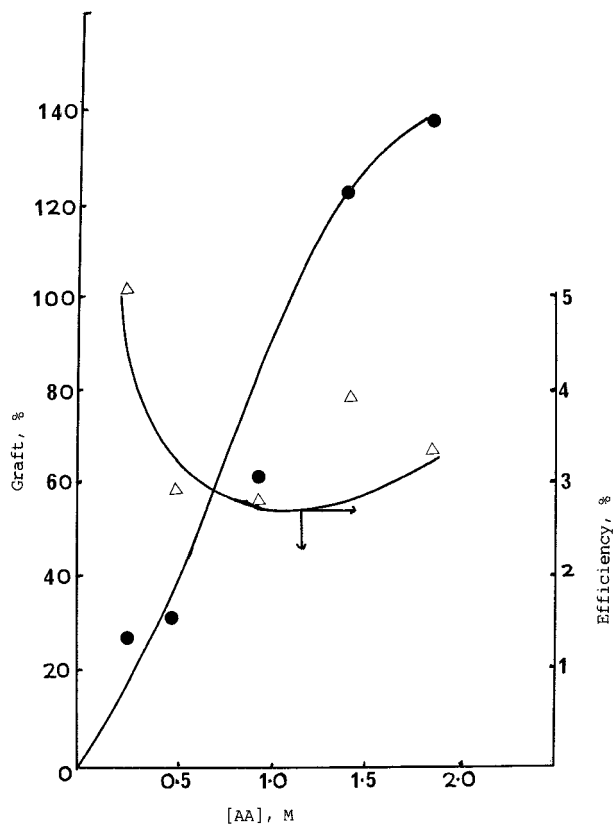


Figure 2 Effect of [AA] on graft yield. $[H^+] = 0.52M$; $[Ce(IV)] = 33.3 \times 10^{-3}M$; MC = 0.1 g; $[AcOH] = 1.17M$; $[XY] = 1.8 \times 10^{-5}M$. Preoxidation time = 10 min; time = 3 h; temperature = $30^\circ C$.

medium and may have significant impact on the stability of the diradical species.

Effect of Monomer Concentration on Graft Yield

The effect of the monomer on the graft reaction was investigated in the concentration range of 0.23 – $1.85M$, as shown in Figure 2. The graft yield increases with monomer concentration, even though it approaches a plateau at high concentrations. The grafting efficiency suggests that the graft reaction is complex, notwithstanding the positive dependency of graft yield on monomer concentration. Increase in graft yield with monomer concentration is expected, provided of course that the monomer is nonterminating and is inactive in transfer reactions.

Effect of Ceric Salt Concentration on Graft Yield

Figure 3 shows the effect of ceric ion on the graft yield over the concentration range of 8.33 – 83.3

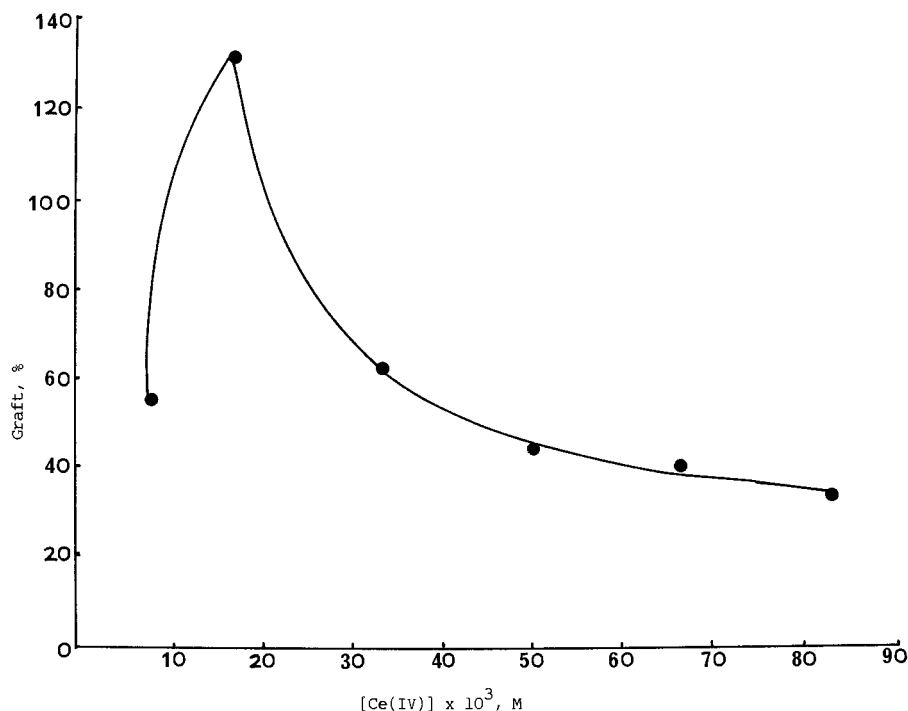


Figure 3 Effect of [Ce(IV)] ion on graft yield. $[H^+] = 0.52M$; MC = 0.1 g; [AcOH] = 1.17M; [XY] = $1.8 \times 10^{-5}M$; [AA] = 0.46M. Preoxidation time = 10 min; time = 3 h; temperature = 30°C.

$\times 10^{-3}M$. An optimum graft yield can be seen at a ceric ion concentration of $16.7 \times 10^{-3}M$, beyond which there is a significant reduction in the yield. The negative dependency of graft yield at higher ceric ion concentrations suggests that the latter is terminating the graft reactions, as was demonstrated for many systems involving ceric ion as a component of redox initiators.⁹⁻¹¹ The decrease in graft yield is more profound when compared with the results for grafting of acrylonitrile on cellulosic fiber⁶ under identical reaction conditions. This would seem to suggest that the polyacrylic acid macroradical is less reactive and more susceptible to termination by ceric ion. In part this may be attributed to the solubility of polyacrylic acid graft polymer in the reaction medium, which may render it more vulnerable to radical diffusion processes and transfer reactions.

Effect of Temperature on Graft Yield

The time-temperature conversions for the graft reactions are presented in Figure 4. The graft yield decreases with temperature in the range 30–50°C. At 50°C, the initial rate of graft is only

37% of the value at 30°C. The negative temperature dependencies of the graft yield and rate of graft clearly show that the insolubility of the graft copolymer in aqueous media at high temperature is inimical to the graft reactions.

CONCLUSIONS

The graft copolymerization of acrylic acid onto methylcellulose by the ceric ion/*p*-xylene redox pair under homogeneous conditions is characterized by minimum and maximum graft yields at varying concentrations of *p*-xylene and at the low preoxidation time of 10 min. This feature is associated with the presence of two kinetically controlled reactions initiated by a *p*-xylyl radical and its diradical derivative. The graft yield, however, is normal (i.e., exhibiting no minima after prolonged preoxidation times of 30 and 60 min), suggesting the presence of only the *p*-xylyl radical species for the initiation process.

The effect of the ceric ion on the graft reaction is optimal at 131% graft yield, corresponding to

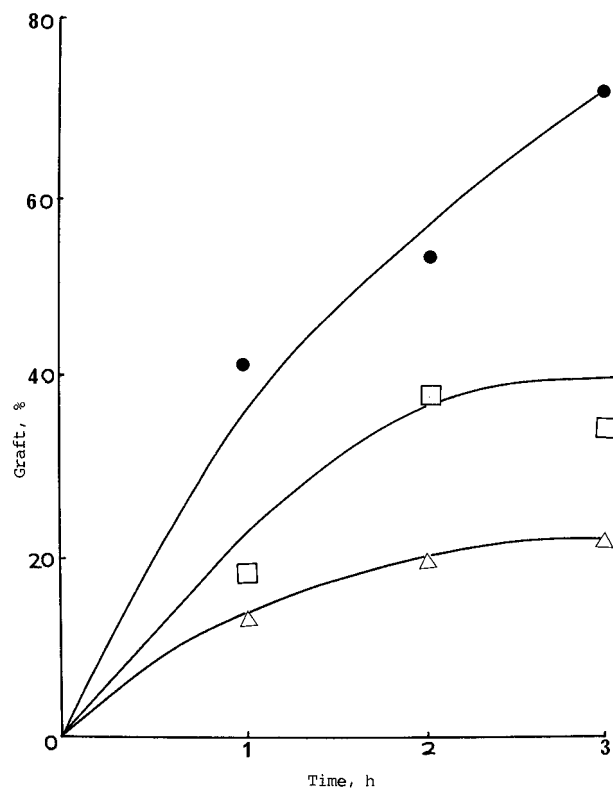


Figure 4 Effect of temperature on graft yield. $[H^+] = 0.52M$; $MC = 0.1$ g; $[AcOH] = 1.17M$; $[XY] = 1.8 \times 10^{-5}M$; $[AA] = 0.46M$; $[Ce(IV)] = 33.3 \times 10^{-3}M$. Preoxidation time = 10 min. Temperature: 30°C (●); 40°C (□); 50°C (△).

its concentration of $16.7 \times 10^{-3}M$ over the range $8.33\text{--}83.3 \times 10^{-3}M$. The graft yield, however, is reduced significantly by as much as 75% at the highest concentration of the ion.

The graft yield shows negative temperature dependency in the region 30–50°C and the initial rate of graft at 50°C is only 37% of the value at 30°C.

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