

Graft Copolymerization of Acrylic Acid onto Methylcellulose by Potassium Permanganate-p-Xylene Redox Pair

C. O. Eromosele, S. P. Nwokata*

Department of Chemistry, University of Agriculture, P. M. B. 2240, Abeokuta, Ogun State, Nigeria

Received 10 June 2002; accepted 28 March 2003

ABSTRACT: Poly(acrylic acid) was grafted onto methylcellulose in aqueous media by a potassium permanganate-p-xylene redox pair. Within the concentration range from 0.93×10^{-3} to $9.33 \times 10^{-3}M$, p-xylene, the graft copolymerization reaction exhibited minimum and maximum graft yields and was associated with two precursor-initiating species, a p-xylyl radical and its diradical derivative. The efficiency of the graft was low, not higher than 12.9% at a p-xylene concentration of $0.93 \times 10^{-3}M$ and suggested the dominance of a competitive homopolymerization reaction under homogeneous conditions. The effect of permanganate on the graft yield was normal and optimal at 135% graft

yield, corresponding to a concentration of the latter of $33.3 \times 10^{-3}M$ over the range from 8.3×10^{-3} to $66.7 \times 10^{-3}M$. The conversion in graft yield showed a negative dependence on temperature in the range 30–60°C and suggested a preponderance of high activation energy transfer reaction processes. The calculated composite activation energy for the graft copolymerization was 7.6 kcal/mol. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 278–281, 2004

Key words: graft copolymers; radical polymerization; activation energy

INTRODUCTION

The initiation of graft copolymerization of vinyl monomers onto cellulosic and non-cellulosic materials by potassium permanganate has been reported.^{1–4} Combined with readily oxidizable organic compounds, potassium permanganate can also form effective redox systems capable of initiating the graft copolymerization of vinyl monomers onto polymeric substrates.^{5–10}

For p-xylene in redox combination with ceric ion, the initiation of graft copolymerization of vinyl monomers onto cellulosic substrates was characterized by minimum and maximum graft yields.

These features were associated with two kinetically controlled reactions, arising from two distinct initiating species, namely, a p-xylyl radical and a diradical.^{11–12} Similar features have been observed for the potassium permanganate-p-xylene redox pair as an initiator of the graft copolymerization of acrylonitrile onto kenaf fiber,¹¹ although no detailed studies were conducted on the overall grafting characteristics.

This article is a report on the grafting characteristics of the graft copolymerization of acrylic acid onto

methylcellulose initiated by the potassium permanganate-p-xylene redox pair in an aqueous medium under homogeneous conditions.

EXPERIMENTAL

The monomer, acrylic acid (Hopkins & Williams) was purified by fractional distillation after it was washed with a 5% (w/v) aqueous sodium hydroxide solution and dried over anhydrous calcium chloride. P-xylene (XY) was treated with concentrated sulfuric acid, washed with distilled water to a neutral pH and fractionally distilled after drying with anhydrous calcium chloride. Other reagents, namely, methylcellulose (MC) (BDH), nitric acid, potassium permanganate, and glacial acetic acid (AcOH) were of analytical grade and were used as supplied. The graft copolymerization reaction was carried out in a 250 mL pyrex conical flask fitted with a standard joint stopper. The required amounts of the reagents, glacial acetic acid, nitric acid, and XY, were introduced into the flask and brought up to 30 mL with distilled water. A quantity of 0.1 g of MC was dissolved in the mixture and was allowed to stand in a thermostated water bath, the temperature of which was regulated to within $\pm 0.05^\circ C$. The required amount of potassium permanganate was put into the flask and allowed to stand for a given period (pre-oxidation time) for the formation of MC macroradicals by the redox reaction between initiating species and MC. This was followed by the

Correspondence to: C. O. Eromosele.

*Present address: Federal University of Technology, Yola, Nigeria.

addition of monomer to the flask to commence 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,¹³ then filtered with a Buchner funnel and washed repeatedly with boiling water.

The graft copolymer was then dried in an oven at 40°C to a constant weight. The percentage graft and percentage efficiency, reproducible to within $\pm 10\%$, 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 MC, the grafted MC and the monomer respectively.

RESULTS AND DISCUSSION

Previous reports on the graft copolymerization of acrylonitrile¹¹ and of acrylic acid¹² on kenaf fibers and MC, respectively, by a ceric ion-XY redox pair showed that they were influenced by two kinetically controlled reactions associated with a p-xylyl radical species and its diradical derivative, resulting in minimum and maximum graft yields.

The graft copolymerization of acrylic acid onto MC by a potassium permanganate-XY redox pair in the concentration range from 0.93×10^{-3} to $9.33 \times 10^{-3}M$ XY demonstrates these features, as can be seen in Figure 1. This corroborates an earlier report on the ability of the redox pair to initiate a graft copolymerization reaction.¹¹ The proposed reaction scheme for the process is as follows:

Initiation:

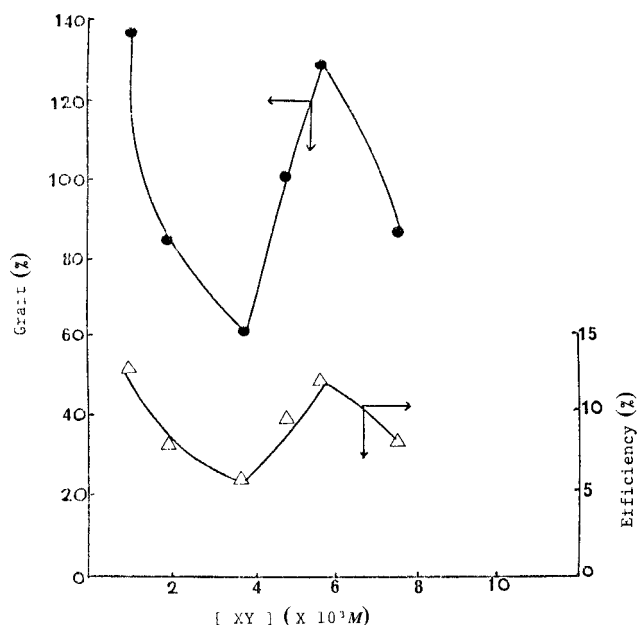
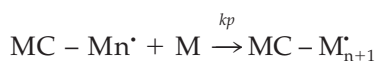
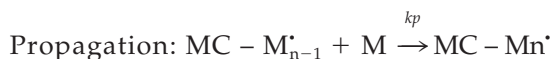
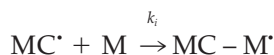
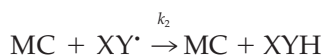
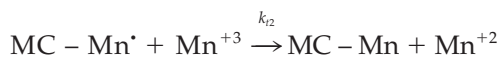
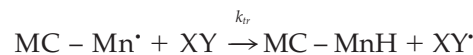


Figure 1 Effect of [XY] on graft yield and efficiency of graft. $[H^+] = 0.52M$; $[AcOH] = 1.17M$; $[AA] = 0.46M$; $[KMnO_4] = 33.3 \times 10^{-3}M$; $MC = 0.1 g$; Pre-oxidation time = 10 min; Time = 3 h; temperature = 30°C.

Termination:

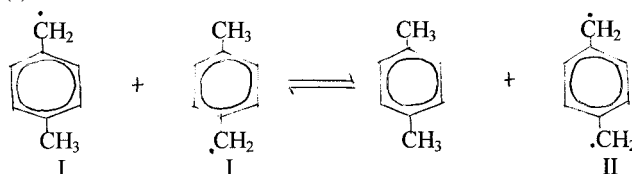


Chain Transfer:



Where MC, XY, XY[·] and M represent methylcellulose, p-xylene, the p-xylyl radical and the monomer respectively.

The minimum and maximum graft yields of 61 and 128% correspond to XY concentrations of 3.73×10^{-3} and $5.60 \times 10^{-3}M$ respectively. The profile of the post minimal graft yield may be associated with initiation of the graft reaction by a diradical species (II) derived from the mutual interactions of two p-xylyl radicals (I):¹¹⁻¹²



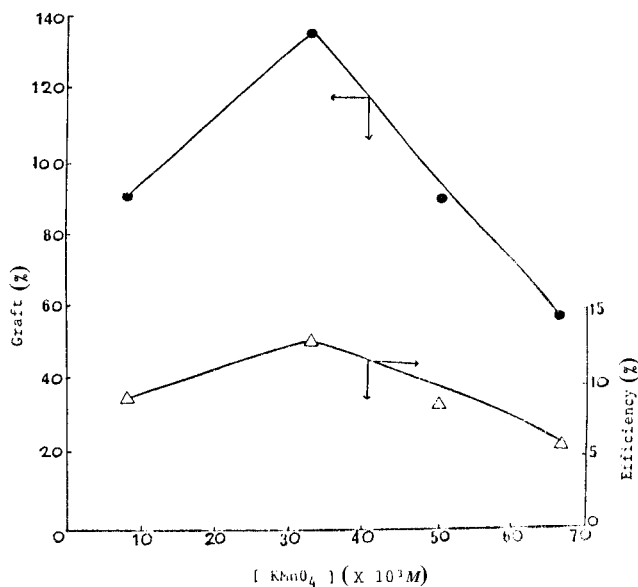


Figure 2 Effect of $[\text{KMnO}_4]$ on graft yield and efficiency of graft. $[\text{H}^+] = 0.52\text{M}$; $[\text{AcOH}] = 1.17\text{M}$; $[\text{AA}] = 0.46\text{M}$; $[\text{XY}] = 5.60 \times 10^{-3}\text{M}$; $[\text{AA}] = 0.46\text{M}$; $\text{MC} = 0.1\text{ g}$; Pre-oxidation time = 10 min; time = 3 h; temperature = 30°C .

Ceric ion in combination with XY appears to be more effective for the graft copolymerization of vinyl monomers onto cellulosic substrates than the analogous permanganate-XY redox pair under identical reaction conditions.

For the latter, the XY concentration range required for graft reaction is an order of magnitude higher than its value for ceric ion-XY redox pair.¹¹

The efficiency of the graft as a function of XY concentration follows the same pattern as the corresponding plot for percentage graft yield and is not higher than 12.9% at on XY concentration of $0.93 \times 10^{-3}\text{M}$, as shown in Figure 1.

The low percentage efficiency reflects the low reactivity of acrylic acid monomer and perhaps the preponderance of a competitive homopolymerization reaction under homogeneous conditions.

The effect of permanganate on the graft yield, shown in Figure 2, is normal; that is, it shows an initial increase in graft yield followed by a fall in the value at higher concentrations of permanganate, as has been demonstrated for a number of graft reactions.¹

The maximum graft yield of 135% corresponds to a permanganate concentration of $33.3 \times 10^{-3}\text{M}$, and an efficiency of 12.7% at 30°C . A fall in the graft yield with an increase in the permanganate concentration may be associated with a number of possible reactions involving the latter,¹⁴ namely

- (1) enhanced termination of grafted polymeric radicals and oxidation of radical sites on the cellulose by Mn^{+4} ,

- (2) oxidation of p-xylyl radicals by Mn^{+4} , which makes them ineffective for initiation of graft copolymerization on the cellulose and
- (3) rapid formation of Mn^{+2} from the oxidation reactions of Mn^{+4} , which may autocatalyze the initiation of homopolymerization.

For the present system, it seems likely that the low percentage efficiency is attributable to the occurrence of a homopolymerization reaction accentuated by the possible presence of Mn^{2+} as a catalyst for the process.

This is consistent with the observation from Figure 2 that, over the range from 33.3×10^{-3} to $66.7 \times 10^{-3}\text{M}$ of permanganate concentration, there is a marked reduction in the efficiency of the graft by 57%.

The conversions for the graft copolymerization reactions at temperatures in the range $30\text{--}60^\circ\text{C}$ are presented in Figure 3. The graft yield shows a negative temperature dependence, and the value at 60°C after 4 h of reaction time is only 60% of the corresponding value at 30°C .

For permanganate-thioacetamide⁹ and ceric-ion-thioacetamide¹⁵ redox initiations of graft copolymerization of vinyl monomers onto cellulosic fibers, the graft yield showed positive temperature dependence. The observance of negative temperature dependence for the permanganate-XY redox initiated system is consistent with a previous report on ceric-ion-XY initiated graft copolymerization of acrylic acid onto methylcellulose.¹² It would seem that the negative temperature dependency of the graft reactions is trace-

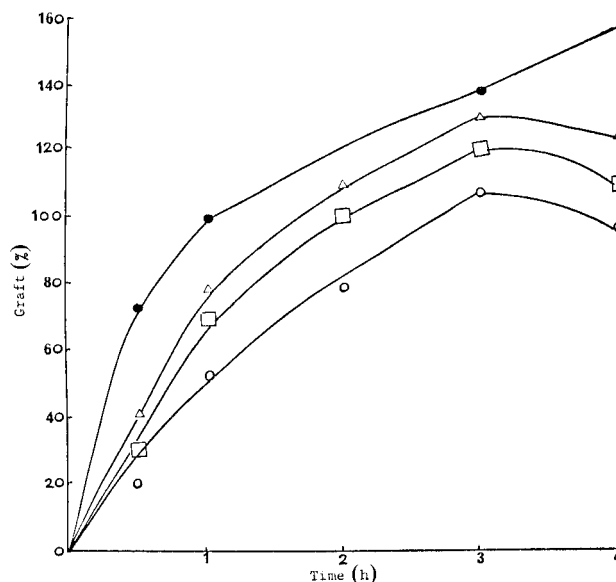


Figure 3 Effect of temperature on graft yield. $[\text{H}^+] = 0.52\text{M}$; $[\text{AcOH}] = 1.17\text{M}$; $[\text{AA}] = 0.46\text{M}$; $[\text{KMnO}_4] = 33.3 \times 10^{-3}\text{M}$; $[\text{XY}] = 3.73 \times 10^{-3}\text{M}$; $\text{MC} = 0.1\text{ g}$; Pre-oxidation time = 10 min; temperature: (●) 30°C ; (Δ) 40°C ; (□) 50°C ; (○) 60°C .

able to the reactivities of XY and its diradical derivative, both of which are expected to participate in transfer reactions. The negative dependence of graft yield on temperature suggests that the composite activation energy for the process is positive and that transfer reactions of high activation energy are favored as temperature increases.

The calculated overall activation energy, based on the initial rates of the graft copolymerization reaction, is 7.6 kcal/mol.

CONCLUSIONS

The graft copolymerization of acrylic acid onto methyl cellulose by the potassium permanganate-p-xylene redox pair under homogeneous conditions exhibits minimum and maximum graft yields associated with two kinetically controlled reactions of the p-xylyl radical and its diradical derivative.

The efficiency of the graft is low, not higher than 12.9% at a p-xylene concentration of $0.93 \times 10^{-3}M$, reflecting a dominant competitive homopolymerization reaction under homogeneous conditions.

The effect of permanganate on graft yield is normal and optimal at 135% graft yield, corresponding to the latter concentration of $33.3 \times 10^{-3}M$ over the range from 8.3×10^{-3} to $66.7 \times 10^{-3}M$, and a p-xylene concentration of $5.6 \times 10^{-3}M$.

The conversion in graft yield shows negative dependence on temperature and suggests a preponderance of high activation energy transfer reaction process with a calculated composite activation energy of 7.6 kcal/mol.

References

1. Mishra, M. K.; Tripathy, A. K. *J Appl Polym Sci* 1982, 27, 1845.
2. Parti, N. C.; Pradhan, A. K.; Nayak, P. L. *J Macromol Sci Chem* 1982, A17(3), 501.
3. Carisohn, H.; Hartmann, M. *Acta Polymerica* 1982, 33(11), 640.
4. EL-Shinawy, N.; Allam, E.; Hebeish, A. *Cellul Chem Technol* 1979, 13(5), 565.
5. Panda, G.; Pati, N. C.; Nayak, P. L. *J Appl Polym Sci* 1980, 25(7), 1479.
6. Nayak, P. L.; Pati, N. C.; Panda, G. *J Macromol Sci Chem* 1981, A 16(4), 829.
7. Pradhan, A. K.; Pati, N. C.; Nayak, P. L. *J Appl Polym Sci* 1982, 27, 2131.
8. Tripathy, S. S.; Jena, S.; Misra, S. B.; Padhi, N. P.; Singh, B. C. *J Appl Polym Sci* 1985, 30(4), 1399.
9. Eromosele, I. C. *J Appl Polym Sci* 1994, 51, 1817.
10. Eromosele, I. C.; Hamagadu, T. J. *J Appl Polym Sci* 1993, 50, 645.
11. Eromosele, I. C.; Agbo, A. *J Appl Polym Sci* 1999, 73, 1751.
12. Eromosele, I. C.; Eromosele, C. O.; Zanna, H. K. *J Appl Polym Sci* 2002, 84, 500.
13. Mukhopadhyay, S.; Mitra, B. C.; Palit, S. R. *J Polym Sci A-1* 1969, 7, 2079.
14. Palit, S. R.; Konar, R. S. *J Polym Sci* 1962, 58, 85.
15. Eromosele, I. C.; Kolapo, A. *Iranian Polym J* 1998, 7(3), 143.