Grafting Acrylonitrile on Kenaf Fibers Using Ceric Ion-*p*-Xylene Redox Pair

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ABSTRACT: Polyacrylonitrile was grafted onto kenaf fibers in aqueous media by ceric ion-*p*-xylene redox system. The graft yield dependence on *p*-xylene concentration in the range $1.8-45.0 \times 10^{-4}M$ showed a minimum accompanied by an enhanced yield. This suggested the existence of two kinetically distinct grafting reactions associated with two precursor-initiating species, a *p*-xylyl radical and a diradical. The frequency of graft F_g and the average molecular weight of grafted polymer M_v were inversely related at varying concentration on M_v showed that the ion is nonterminating at low concentrations in the range $8.3-33.3 \times 10^{-3}M$. The graft yield showed positive temperature dependence in the region of $30-40^{\circ}$ C and a negative one at higher temperatures, resulting in a decrease in the initial rate of graft at 70°C by a factor of 8 compared to its value at 40°C. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1751–1755, 1999

Key words: grafting acrylonitrile; kenaf fibers; ceric ion-*p*-xylene; redox pair

INTRODUCTION

Previous reports have shown that ceric ion in a redox pair with a number of readily oxidizable organic compounds can initiate the graft copolymerization of vinyl monomers onto cellulosic and noncellulosic substrates.¹⁻⁴ The mechanisms of graft reaction by such redox systems are little understood. However, the grafting characteristics indicate that significant graft levels of up to $212\%^2$ may be achieved depending on the reactivities of the monomer and of the initiating species.

For the ceric-toluene redox pair, it was suggested^{1,2,5} that the initiating specie was a benzyl radical derived from the oxidative abstraction of hydrogen from toluene by ceric ion. Thus, for a ceric ion-*p*-xylene redox pair, a similar reaction may be envisaged.

Preliminary investigation has shown that ceric ion–*p*-xylene redox pair can initiate the graft copolymerization of acrylic acid onto cellulosic fibers,¹ but no detailed studies on the grafting characteristics have been reported.

The present communication is on studies of graft copolymerization of acrylonitrile onto kenaf, *Hibiscus cannabinus* fibers initiated by ceric ion-p-xylene redox pair in aqueous media. The features of the graft reaction and the forms of the initiating species are reported and discussed.

EXPERIMENTAL

Acrylonitrile (Hopkin & Williams) was washed with 5% aqueous sodium hydroxide and then with distilled water to a neutral pH. It was dried over anhydrous calcium chloride and fractionally distilled.

P-xylene was treated with sulfuric acid, washed with distilled water to a neutral pH, and fractionally distilled after drying with anhydrous calcium chloride. Other reagents, that is, ceric ammonium nitrate, nitric acid, glacial acetic acid,

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and N,N'-dimethylformamide (DMF) were used as supplied.

The kenaf plant was obtained from the University's botanical garden at Yola. The bast fibers were air-dried and beaten in a mortar. The methods of preparation of bleached holocellulose from the fibers and of the graft copolymerization were as reported previously.⁶

The fiber-polyacrylonitrile graft copolymer was purified by extraction with DMF to constant weight. The percentage graft and percentage efficiency were calculated from the following relation:

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

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

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

The grafted polymer was removed from the fiber by hydrolysis in 100-mL of boiling 3% sodium hydroxide solution for 30 min.⁷ The resultant mixture was filtered hot on a Buchner funnel and washed with distilled water to a neutral pH. The isolated polymer was dissolved in DMF, and the average molecular weight determined from the viscosity of the DMF solution using the Mark– Houwink equation⁸ as follows: $[n] = 2.09 \times 10^{-4}$ $M_n^{0.75}$.



Figure 1 Effect of (XY) on graft yield at lower concentrations: [AN], 0.63*M*; (Ce(IV)], 33.3 × $10^{-3}M$; [AcOH], 1.17*M*; [H⁺], 0.52*M*; cell, = 0.1 g; time, 3 h; temperature, 30°C. Preoxidation time: 10 min.



Figure 2 Effect of [XY] on graft yield: [AN], 0.63*M*; [Ce(IV)], 33.3 × 10⁻³*M*; [AcOH], 1.17*M*; [H⁺], 0.52*M*; cell, 0.1 g; time, 3 h; (●) Ce(IV)-XY, 30°C; (■) Ce(IV)-XY, 70°C; (△) KMnO₄-XY, 30°C. Preoxidation time: 10 min.

The molar number of grafted polymer per gram of fiber N_g was determined from the weight of the grafted polymer W_g (in g/g fiber) and the average molecular weight M_v was determined by the following relationship⁹: $N_g = W_g/M_v$.

The frequency of grafting F_g defined as the number of moles of grafted polymer (N_g) per 10⁴ anhydroglucose unit (AGU) was determined from the following equation¹⁰: $F_g = N_g M_o \times 10^4$, where M_o is the molecular weight of one AGU.

RESULTS AND DISCUSSION

Effect of *P*-Xylene Concentration on Graft Yield, Molecular Weight, and Frequency of Graft Polymer

Analogous to the dual effect of toluene on graft copolymerization and homopolymerization reactions of vinyl monomers,^{1,2,5} *P*-xylene (*XY*) appears to enhance and to retard the graft copolymerization of acrylonitrile on kenaf fibres in the



Figure 3 Effect of [XY] on graft yield at varying preoxidation time: [AN], 0.63*M*; [Ce(IV)], 33.3 $\times 10^{-3}M$; [AcOH], 1.17*M*; [H⁺], 0.52*M*; cell, 0.1 g; time, 3 h; temperature, 30°C; (\triangle) 30 and (\bigcirc) 60 min.

concentration range of 0.19–2.7 \times 10⁻⁴M, as shown in Figure 1. Interestingly, however, at higher concentrations of XY (Fig. 2), there is a point of inflexion showing a minimum graft yield corresponding to the XY concentration of 18.0 $\times 10^{-4}M$ and beyond which graft yield is again enhanced. This phenomenon is observed also at 70°C albeit at lower graft yields. Further, in combination with $KMnO_4$ in a redox pair, the same phenomenon in graft yield as a function of XYconcentration is observed. The fibers were preoxidized at varying times prior to addition of monomer to the reaction medium. Yet, as can be seen in Figure 3, the form of the graft yield, that is, showing a minimum, is independent of the preoxidation time. Similarly, the graft copolymerization reaction in 50% (v/v) DMF—water mixture (Fig. 4) shows the same features having a minimum graft yield at an XY concentration of 27.0 \times 10⁻⁴*M*. However, the graft yields are lower than the values obtained from aqueous media. No graft reaction was observed in pure DMF solvent

media. Thus, the *p*-xylene conversion profile may be associated with the existence of two kinetically distinct grafting reactions, proceeding sequentially, and arising from the activities of two different initiating species.

In combination with ceric ion, a *p*-Xylyl radical of the form,



may be formed from *XY*. At low concentrations of *XY*, the radical (I) may be the dominant initiating



Figure 4 Effect of (*XY*) on graft yield in 50% (*v*/*v*) DMF-H₂O media: [AN], 0.63*M*; [Ce(IV)], 33.3 $\times 10^{-3}M$; [AcOH], 1.17*M*; [H⁺], 0.52*M*; cell, 0.1 g; time, 3 h; temperature, 30°C. Preoxidation time: 10 min.

$[XY] imes 10^4 \ (M)$	Graft (%)	$M_v imes 10^{-4}$	F_g (Ng/10 ⁴ AGU)
0.18	68	5.18	21.22
1.8	61	3.76	26.24
27	59	4.47	21.38
36	58	2.08	45.19

Table IEffect of [XY] on the Frequency andMolecular Weight of the Grafted Polymer

species of the graft reactions. Of course, this is to				
be expected since the radical species (1) may be				
stabilized by resonance, a factor which could en-				
hance its formation at the initial stages of the				
graft reactions. However, at higher concentra-				
tions of XY, an unstable di-radical (II) may be				
formed by the mutual interactions of two <i>P</i> -Xylyl				
radicals, that is,				



The presence of a di-radical (II) may lead to a kinetically distinct grafting reaction, being highly unstable and, hence, more reactive than the *P*-Xylyl



Figure 5 Effect of [Ce(IV)] on graft yield: [AN], 0.63*M*; [*XY*], 1.8 \times 10⁻⁴*M*; [AcOH], 1.17*M*; [H⁺], 0.52*M*; cell, 0.1 g; time, 3 h; temperature, 30°C. Preoxidation time: 10 min.

Table II	Effect of [[Ce(IV)] on	the Fre	equency
and Mole	cular Weig	ght of the (Grafted :	Polymer

$\begin{array}{l} [Ce(IV)] \\ \times \ 10^3 \ (M) \end{array}$	Graft (%)	$M_v imes 10^{-4}$	F_g (Ng/10 ⁴ AGU)
8.3	51	1.79	46.17
16.7	66	3.70	28.84
33.3	80	7.13	18.14
83.3	75	2.11	57.51

radical species (1). In redox interactions with the cellulosic fibers for the generation of radical sites in the latter, species (II) is expected to be more active than (I), resulting in an enhanced graft yield.

Thus, because the initiating system for the graft reaction is composite, the effects of XY concentrations on molecular weight and frequency of grafted polymer are, as expected, complex and not clear cut. However, as can be seen in Table I, the average molecular weight of grafted polymer decreases as the frequency of graft increases. This trend is self-consistent but is contrary to the observed one for the graft copolymerization of polymethylmethacrylate onto a holocellulose initiated by ceric ion, for which the average molecular weight of grafted polymer decreased with decrease in the frequency of graft.¹¹

Effect of Ceric Salt Concentration on Graft Yield, Molecular Weight, and Frequency of Graft Polymer

The graft yield increases initially and decreases with increasing concentration of the Ce(IV) ion,



Figure 6 Effect of [AN] on graft yield: [XY], 1.8 $\times 10^{-4}M$; [Ce(IV)], 33.3 $\times 10^{-3}M$; [AcOH], 1.17*M*; [H⁺], 0.52*M*; cell, 0.1 g; time, 3 h; temperature, 30°C. Preoxidation time: 10 min.

Figure 7 Effect of temperature on graft yield: [AN], 0.31*M*; [*XY*], 27.0 × 10⁻⁴*M*; [Ce(IV)], 33.3 × 10⁻³*M*; [AcOH], 1.17*M*; [H⁺], 0.52*M*; cell, 0.1 g; (△) 30, (●) 40, (□) 50 and (■) 70°C. Preoxidation time: 10 min.

as shown in Figure 5. In the concentration range of $8.3-33.3 \times 10^{-3}M$, the average molecular weight of the grafted polymer increases with the Ce(IV) ion concentration, as shown in Table II. The frequency of grafting over this concentration range shows an inverse relationship with the average molecular weight of grafted polymers. At a higher concentration of Ce(IV) ion, the average molecular weight of the grafted polymer decreases.

The increase in the average molecular weight with the Ce(IV) ion at the low concentration range suggests that the latter is nonterminating or that the termination reaction by it is insignificant. This argument is strengthened by the apparent drop in the average molecular weight of grafted polymer at higher Ce(IV) ion concentration. For the graft copolymerization of methylmethacrylate onto plantain pulp,¹⁰ an inverse relationship was found for the average molecular weight of the grafted polymer and the Ce(IV) ion concentration and was associated with termination of the graft copolymerization by electron transfer to the Ce(IV) ion. For the present system, it would seem that the graft yield, the average molecular weight, and the frequency of grafted polymer are

influenced to a greater extent by the initiating species generated by the redox interaction of the Ce(IV) ion and XY.

Effect of Monomer Concentration on Graft Yield

The graft yield increases with monomer concentration [AN] over the range 0.31-1.89M at 30°C, as shown in Figure 6. At higher concentrations of the monomer, the graft yield approaches a plateau and the efficiency of monomer conversion into graft polymer decreases, resulting in more homopolymer formation.

Effect of Temperature

In the region of 30-40°C, the graft polymerization is positively dependent on temperature but shows a negative dependence at higher temperatures, as can be seen in Figure 7. The latter dependence in graft yield may be associated with instability of the initiating Xylyl radicals at high temperatures. The di-radical is expected to become more unstable at high temperatures and, consequently, to accentuate premature termination of growing graft polymer chain via electron transfer reactions. At 70°C, the initial rate of graft decreases by a factor of 8 from its value at 40°C.

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