Graft Copolymerization of Acrylonitrile on Kenaf Fibers by Ceric Ion in the Presence of Allyl Compounds

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ABSTRACT: Graft copolymers of acrylonitrile on kenaf fibers were obtained in an aqueous medium by the use of allyl alcohol and allyl chloride in combination with ceric ion as redox pairs. The graft copolymerization reactions showed distinct features that were associated with different initiating species derived from the redox pairs. For a cericallyl-chloride-initiated reaction, a minimum graft yield was observed, accompanied by an enhanced graft yield. This suggested the existence of two kinetically controlled grafting reactions arising from two different initiating species. For the ceric-allylalcohol-initiated reaction, the grafting profile showed a maximum yield and suggested the presence of one active initiating species. High concentrations of acrylonitrile were favorable to grafting with values of up to 150%, but they also resulted in decreased efficiency in monomer conversion to grafted polymer. The frequency of grafting increased with the concentration of allyl alcohol but the molecular weight of grafted polymer of up to 4.46×10^4 decreased by a factor of one and half over the concentration range $1.8-9.0 \times 10^{-4}M$ of the latter. The presence of 10% (v/v) N,N'-dimethylformamide resulted in zero graft, but the same vol % of formic acid had no apparent effect on the graft yield. A negative temperature dependence in the graft yield was found in the temperature range of 50-70°C. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1757-1761, 1999

Key words: graft copolymerization; acrylonitrile; kenaf fibers; ceric ion; allyl compounds

INTRODUCTION

The use of redox couples as initiators of graft copolymerization of vinyl monomers onto cellulosic and noncellulosic substrates has received considerable attention.¹⁻¹⁰ Such studies are, for the most part, aimed at achieving optima graft yields and at improving the physicochemical properties of polymeric substrates.

For the graft copolymerization of vinyl monomers onto plantain pulp by ceric ion, chemical modification of the pulp by the introduction of an allylic moiety into the polymeric backbone-enhanced grafting, albeit nominally, by 15% for methyl methacrylate¹¹ and, substantially, by up to 50% in the case of acrylonitrile.¹²

The present communication is on the use of allyl alcohol and allyl chloride in redox couples with ceric ion for the initiation of graft copolymerization of acrylonitrile onto kenaf, *Hibiscus cannabinus*, fibers. The features of the graft reaction are reported, and the probable initiating species of the graft reactions proposed and discussed.

EXPERIMENTAL

Acrylonitrile (Hopkin & Williams) was purified by fractional distillation after it was washed with 5%

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aqueous sodium hydroxide solution and dried over anhydrous calcium chloride. Other reagents, that is, ceric ammonium nitrate, nitric acid, glacial acetic acid, and allyl alcohol were used as supplied.

The pretreatment of kenaf fibers, and the methods of graft copolymerization and isolation of grafted polymer from the fibers, were as reported in previous communications.^{2,5} The graft percentage and the efficiency percentage were calculated from the following relations:

% 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 molecular weight of the isolated polymer was determined from the viscosity of its solution in *N*,*N'*-dimethylformamide (DMF) at 30°C using the following Mark–Houwink equation¹³: (n) = $2.09 \times 10^{-4} M_v^{0.75}$.

The frequency of graft F_g , defined as the number of moles of grafted polymer (N_g) per 10^4 anhydroglucose unit (AGU), was calculated from the following relation¹¹: $F_g = N_g M_o \times 10^4$. N_g is given by the weight of grafted polymer per gram of the fiber, divided by the molecular weight of the grafted polymer, and M_o is the molecular weight of one AGU.

RESULTS AND DISCUSSION

Figure 1 shows the effect of allyl alcohol (AA) on graft yield. The graft yield shows a positive dependence on allyl alcohol in the concentration range of $1.8-18.0 \times 10^{-4}M$ of the latter. A negative dependence of graft yield is evident at higher concentrations of allyl alcohol. The initial increase in graft yield at low concentrations of allyl alcohol may be ascribed to the presence of an initiating radical species (1) derived from the redox interactions of allyl alcohol and ceric ion; that is,

$$\begin{array}{c} \operatorname{Ce}(\mathrm{IV}) + \operatorname{CH}_{2} = \operatorname{CH} - \operatorname{CH}_{2} \rightleftharpoons \operatorname{Ce}(\mathrm{III}) + \operatorname{CH}_{2} = \operatorname{CH} - \operatorname{CH}_{2} + \operatorname{H}^{+} \\ 1 & & 1 \\ OH & & 0. \\ (1) & & (1) \end{array}$$

The radical species (1) cannot be stabilized and is expected to be reactive in the redox initiation of



Figure 1 Effect of [AA] and [AC] on the graft yield: [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; (\bullet) AA; (\triangle) AC.

graft copolymerization via hydrogen abstraction from the cellulosic fiber. However, other radical species (II) and (III) may be formed but are expected to be less active for the initiation of graft reaction on account of resonance stabilization; that is

$$Ce(IV)+CH_2=CH-CH_2 \iff Ce(III)+CH_2=CH-CH+H^+$$

$$I \qquad OH \qquad OH$$

$$(II)$$

A preponderance of the latter species (II) and (III) may account in part for the fall in graft yield at high concentrations of allyl alcohol. A classical test of whether the radical species (I) is an active initiating species, as postulated for allyl alcohol, may be seen by the effect of allyl chloride (AC) on the graft copolymerization reaction (Fig. 1), where over the same concentration range, the graft yield shows contrasting dependence on AC. Clearly, the results suggest that the active initiating species derivable from the two allyl compounds are different. reactions, which may involve the initiating species (IV) and (V), derived as follows:

For allyl chloride, the grafting characteristics suggest the existence of two kinetically controlled

species (IV) and (V) derived as follows:- $Ce(IV)+CH_{2}=CH-CH_{2} \implies Ce(III)+CH_{2}=CH-\dot{C}H+H^{+}$ $Cl \qquad Cl \qquad Cl$ (IV) $CH_{2}=CH-\dot{C}H \implies \dot{C}H_{2}-CH=CH$ $Cl \qquad Cl$ $(IV) \qquad (V)$

The initial fall in graft yield also suggests a pos*teriori* the existence of a maximum graft yield at lower concentrations of allyl chloride, probably due to the initiating activities of the radical species (IV). The latter species may be dominant at the early stages of the reaction being more easily formed but less active as a result of the inductive effect of a chlorine atom in the vicinity of the radical. The enhancement in graft yield at higher concentrations of allyl chloride may thus arise from the participation in the graft reaction of the more active initiating species (V). The frequency of grafting F_g increases with the concentration of allyl alcohol, but the molecular weight of the grafted polymer decreases over the concentration range of the latter, as shown in Table I.

Figures 2 and 3 show the effects of ceric ion and monomer on the graft yield, respectively. The graft yield profile for ceric ion is consistent with a previous report,³ that is, an increase in yield in the concentration range of $8.3-66.7 \times 10^{-3}M$, followed by a drop in yield at higher concentrations. A decrease in yield with ceric ion concentration is usually associated with a chain termination reaction involving ceric ion and growing

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

$[{ m AA}] imes 10^4 \ (M)$	Graft (%)	F_g $(N_g/10^4$ AGU)	$M_{_{v}} imes$ 10^{-4}
1.8 9.0	78 79	$\begin{array}{c} 28.3 \\ 50.9 \end{array}$	$4.46 \\ 2.51$

polymer chain. For the monomer (Fig. 3), the graft yield increases by a factor of 4 in the concentration range of 0.31-1.57M. The grafting ef-



Figure 2 Effect of [Ce(IV)] on the graft yield: [AN] = 0.63M; [AA] = $1.8 \times 10^{-4}M$; [AcOH] = 1.17M; [H⁺] = 0.52M; cell = 0.1 g; time = 3 h; temperature = 30° C.



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

ficiency, however, decreases significantly at high concentration of the monomer ostensibly due to homopolymer formation, which was evident.



Figure 4 Effect of temperature on the graft yield: [AA] = $1.8 \times 10^{-4}M$; [Ce(IV)] = $33.3 \times 10^{-3}M$; [AcOH] = 1.17M; [AN] = 0.31M; [H⁺] = 0.52M; Cell = 0.1 g; (△) 30° C; (●) 50° C; (■) 70° C.



Figure 5 Effect of 10% (*v*/*v*) formic acid on the graft yield: [AN] = 0.31*M*; [AA] = $1.8 \times 10^{-4}M$; [Ce(IV)] = $33.3 \times 10^{-3}M$; [AcOH] = 1.17M; [H⁺] = 0.52M; cell = 0.1 g; temperature = 30° C; (△) formic acid; (●) control.

The effect of temperature on graft yield is shown in Figure 4. A negative temperature dependence in graft yield is observed beyond 50°C. Graft yields at 70°C are significantly low compared to values at 50°C, that is, not higher than 18%.

Graft copolymerization reaction was conducted in the presence of 10% (v/v) formic acid and DMF. The results are shown in Figure 5. In relation to the control, formic acid appears to have no effect on the graft yield, but the presence of DMF results in zero graft yield.

In the classical study of homopolymerization of acrylonitrile in an aqueous medium initiated by a ceric ion-thioacetamide redox system, a decrease in the yield of polymer was observed in the presence of organic solvents,¹⁴ namely, acetic acid, formic acid, methanol, and ethanol. The depression in the yield was ascribed to the following:

- 1. A decrease in the area of shielding of strong hydration layer in an aqueous medium by the solvent, resulting in premature termination of the radical and the growing chain;
- 2. an increased regulated rate of production of primary radicals, which may render the termination rate relatively fast, compared with the rate of growth of the polymer chains; and

3. an increased tendency toward mutual termination of the polymer chain in the presence of the solvents.

From the effect of formic acid on the graft copolymerization reaction, it may seem that transfer reactions involving the acid is not marked, as was demonstrated previously for the graft copolymerization of methacrylonitrile on Kenaf fibers initiated by the ceric ion-toluene redox pair.²

For DMF, the ability to solubilize polyacrylonitrile is expected to result in low graft yield.¹⁵ However, the observance of zero graft yield in the presence of the solvent may be ascribed to enhanced termination reactions since the latter is diffusioncontrolled in free radical polymerization reactions.

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