Graft Copolymerization of Acrylic Acid on Cellulose: Reaction Kinetics of Copolymerization

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ABSTRACT: Acrylic acid (AA) was grafted to cellulose by using ceric ammonium nitrate (CAN) initiator in aqueous nitric acid solution at 30, 50, 70, and 90°C during reaction periods of 30 to 180 minutes. About 45% of the AA was polymerized at 90°C after 180 minutes. The grafted polymer and homopolymer were isolated by acetone from the reaction mixture, dried, and subjected to Soxhlet extraction with dioxane to separate the homopolymer, poly(acrylic acid), from the graft copolymer. The water absorption capacities and grafting values of grafted cellulose were also determined. The maximum grafting yield was obtained at 30°C. It was also observed that polyacrylic acid-grafted cellulose produced at 30°C had the highest water retention capacity. The time dependence of AA conversion allowed calculation of first-order reaction rate constants. These rate constants were then used to determine apparent activation energies. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 929–934, 1997

Key words: acrylic acid; cellulose; graft copolymerization; reaction kinetics

INTRODUCTION

Cellulose is a naturally occurring complex polysaccharide and the most abundant renewable organic raw material in the world. The properties of cellulose may be modified by changing both physical and chemical structure. The graft polymerization method has gained importance in modifying the chemical and physical properties of pure cellulose and was investigated in the last few decades. Grafting onto cellulose is possible by the growing of a polymer chain on active sites of the cellulose backbone. It is a heterogeneous reaction in which the physical structure and state of aggregation of the cellulose plays an important role. Strong hydrogen bonds between the cellulose chains hinder grafting when vinyl monomers are used without an appropriate swelling agent, such as water. As the swelling power of the solvent or amount of the swelling agent increases, the rate of diffusion of monomer and, in turn, the rate of grafting increases. However, the swelling agent also affects the rate of termination of the graft copolymerization.

During the copolymerization, the radical formation for initiation reaction can occur either on the cellulose backbone or on the monomer to be grafted. The radical formation on the monomer results in homopolymerization. Therefore, initiators capable of creating radicals at various sites on the cellulose backbone are preferred. Depending on the monomer, the radicals can be created by redox type initiators, irradiation, diazotization, or introduction of unsaturated groups.[1] Various initiating systems have been tried with varying degrees of success. Among the redox systematic, ceric ion offers many advantages.
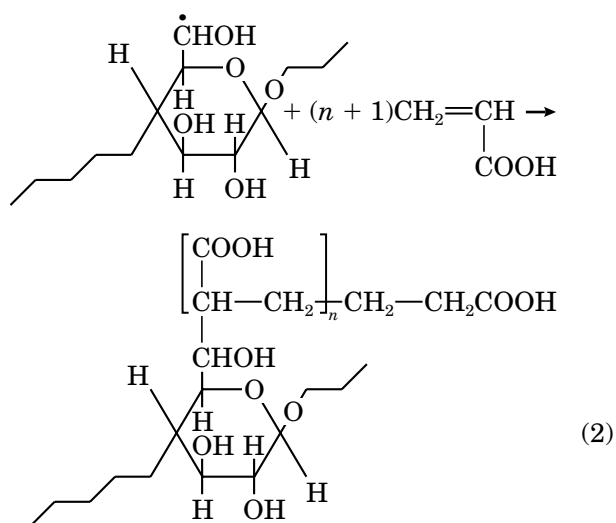
When the ceric salts, such as ceric ammonium nitrate $[Ce(NH_4)_2(NO_3)_6]$, were used as an initiator on the graft copolymerization onto cellulose, it is proposed that a ceric ion–cellulose complex is initially formed as a result of one electron transfer. Then the ceric ion is reduced to cerous ion, and a free radical is created on the cellulose backbone, as shown in eq. (1).[2]

$$\text{(cellulose structure)} + Ce^{4+} \rightarrow$$

$$\text{(cellulose radical, } \dot{C}HOH) + Ce^{3+} + H^+ \quad (1)$$
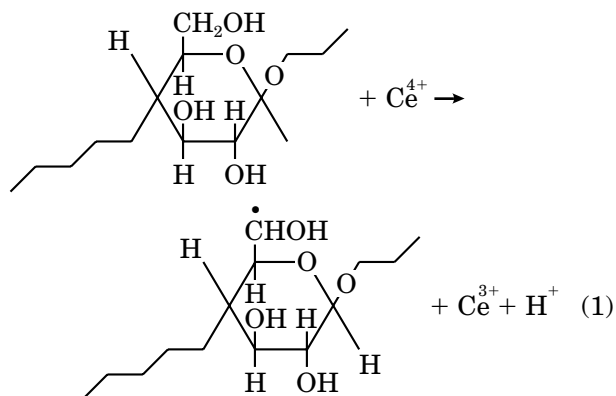
The radical site on the cellulose then initiates graft copolymerization of a polar vinyl monomer, which is present in the reaction mixture.

$$\text{(cellulose radical, } \dot{C}HOH) + (n+1)CH_2{=}CH{-}COOH \rightarrow$$

$$\begin{bmatrix} COOH \\ | \\ CH{-}CH_2 \end{bmatrix}_n CH_2{-}CH_2COOH \text{ on } \dot{C}HOH \text{ cellulose} \quad (2)$$
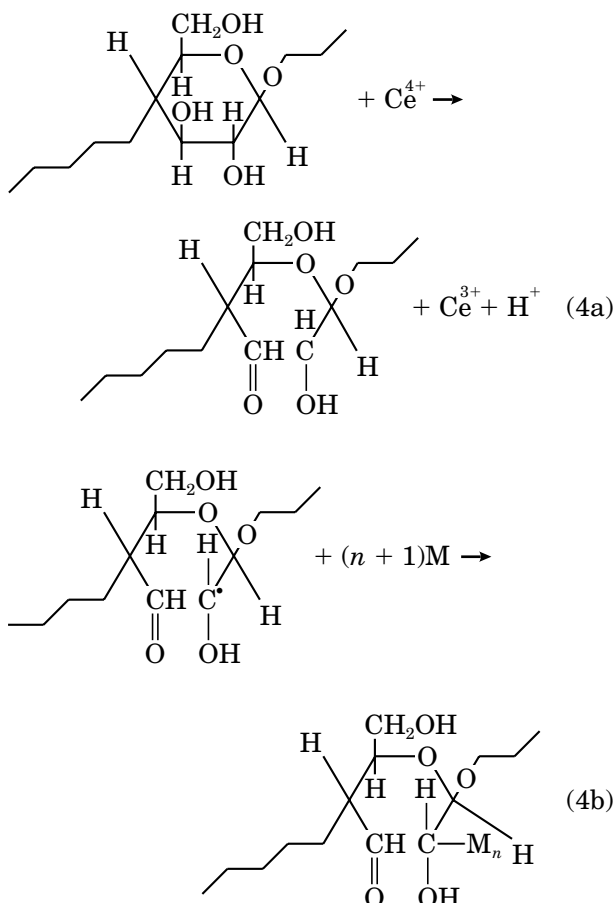
The homopolymer formation during the copolymerization is attributed to the chain transfer from the growing graft copolymer to the monomer.

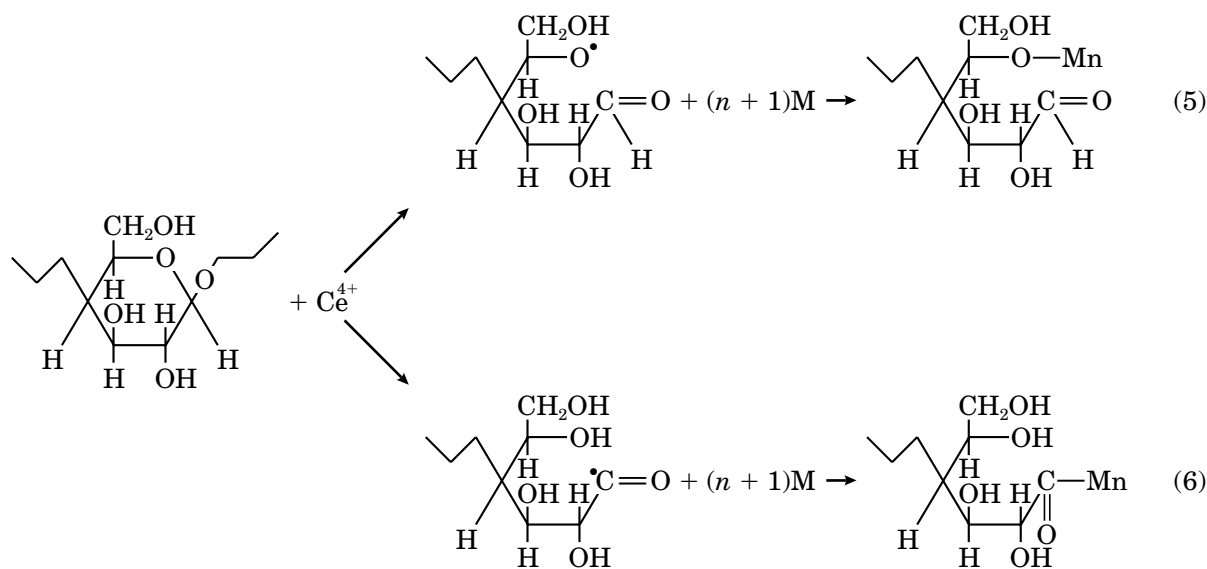As it is shown in eq. (3), the formation of an oxygen radical at the primary methylol group of the cellulose backbone is also possible.[3]

$$\text{(cellulose, } CH_2OH) + Ce^{4+} \rightarrow$$

$$\text{(cellulose, } CH_2O^{\bullet}) + Ce^{3+} + H^+ \quad (3)$$
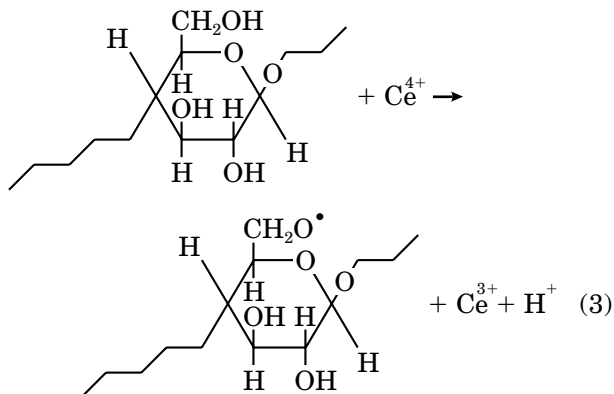
Another grafting site subsequently proposed[3] involves the oxidation of the anhydroglucose unit, as shown in eq. (4).

$$\text{(anhydroglucose unit, } CH_2OH) + Ce^{4+} \rightarrow$$

$$\text{(oxidized unit with } CH{=}O, C{-}OH) + Ce^{3+} + H^+ \quad (4a)$$

$$\text{(radical unit } CH{=}O, \dot{C}{-}OH) + (n+1)M \rightarrow$$

$$\text{(grafted unit } CH{=}O, C{-}M_n) \quad (4b)$$

$$\text{Mn: } {-}[CH_2{-}\overset{COOH}{\underset{|}{CH}}]_n CH_2{-}\overset{COOH}{\underset{|}{CH_2}}$$

The following initiation mechanism has also been proposed, causing to the formation of a block copolymer,[3] as shown in eqs. (5) and (6).

$$CH_2OH\text{—}O^\bullet \cdots C=O + (n+1)M \rightarrow CH_2OH\text{—}O\text{—}Mn \cdots C=O \quad (5)$$

$$CH_2OH\text{—}OH \cdots {}^\bullet C=O + (n+1)M \rightarrow CH_2OH\text{—}OH \cdots C\overset{||}{\underset{O}{\text{—}}}Mn \quad (6)$$

$+ Ce^{4+}$

A lot of work has been reported on grafting of various vinyl monomers onto cellulosic materials using different types of initiators.[4–20] According to the nature of the vinyl monomer grafted on cellulose, it gains different physical and/or chemical properties. To increase the hydrophilicity, the monomers containing hydrophilic groups must be grafted onto cellulose.

Although some research on acrylic acid (AA) grafting onto cellulose, also involving preirradiation techniques, has been carried out previously, relatively little has focused on the evaluation of water retention capacities.[14–21]

Lepoutre et al.[4] obtained the sodium polyacrylate–polyacrylamide grafted cellulose fibers by hydrolyzing the poly(acrylonitrile)-grafted cellulose fibers and investigated the water and saline retention values. Williams and Stannett[16] investigated the water retention values of poly(acrylic acid)–grafted cellophane obtained by using $FeSO_4/H_2O_2$ initiator. Okieimen and Ebhoaye[17,18] have investigated the water and saline retention capacities of poly(acrylic acid)–grafted holocellulose and obtained the maximal values of 9 and 7 g g, respectively.

In the current work, the effects of reaction temperature on the graft copolymerization of AA onto cellulose using a ceric ammonium nitrate (CAN) initiator were investigated. The temperature is one of the most important factors to affect the extent of grafting. This effect depends upon the type of initiator and monomer and their concentrations. In early laboratory experiments, the effects of concentration of monomer (AA) and $FeSO_4/H_2O_2$ and CAN initiators were studied. Satisfactory grafting yield with the $FeSO_4/H_2O_2$ initiator system could not be obtained. Therefore, the experiments in this work were performed on the predetermined monomer concentration with a CAN initiator.

EXPERIMENTAL

Chemicals

The AA monomer was distilled under vacuum and stored at $-8°C$ until used. Ceric Ammonium Nitrate (Merck) was used as initiator. Cellulose was obtained from Sigma. The bidistilled water was used. Nitric acid and acetone were reagent grade. Nitrogen was purified by passing it through a freshly prepared alkaline pyrogallol solution and concentrated sulfuric acid.

Graft Copolymerization Experiments

Four grams of cellulose was added to 320 mL of $2.5 \times 10^{-3}M$ HNO_3 solution in a three-necked flask, then stirred and purged by passing nitrogen for 30 min. CAN and 20 mL of AA were then added into reaction mixture. Bubbling of nitrogen through the reaction mixture was continued for the duration of reaction, which was carried out by placing the flask in a water bath at 30, 50, 70, and 90°C and for 30 to 180 minutes. After the desired reaction time had elapsed, the polymer-

ization was stopped by adding hydroquinone to the reaction flask. The graft copolymer and homopolymer were separated by adding acetone into the reaction mixture. The solution was filtered, the polymer precipitated was washed with acetone, and the precipitate then dried under vacuum at 40°C. Unreacted AA in acetone solution was determined by titration with 0.1N NaOH and phenolphthalein indicator. Dried homopolymergraft copolymer samples were subjected to extraction with dioxane in a Soxhlet apparatus for 40 h to separate the homopolymer poly(acrylic acid). Grafting yield was determined by titration. The graft copolymer in a 0.1N NaBr solution was titrated with solution of 0.1N NaOH solution. Subtracting the weight of unreacted AA from the initial weight of AA gave the weight of total synthetic copolymer. After the titration of graft copolymer with NaOH, the obtained Na form of graft copolymer was subjected to swelling by holding it in the distilled water at room temperature. Water retention capacity (WRC) results were reported as the ratio of swelled copolymer weight minus the initial copolymer weight to initial copolymer weight. The amount of homopolymer in the reaction mixture was calculated by subtracting the weight of AA grafted from the weight of AA reacted.

RESULTS AND DISCUSSION

The goal of our work was to provide a comparison of graft polymerization of AA on cellulose at different reaction temperatures. Reactions were conducted at temperatures of 30, 50, 70, and 90°C for 30, 60, 90, 120, 150, and 180 minutes. The results are presented below for comparison of AA conversion, grafting, homopolymer formation, and water retention capacity at the four reaction temperatures.

Acrylic Acid

Figure 1 summarizes the temporal variations of AA for the four reaction temperatures. Note that curves drawn through experimental data are for visual purposes and don't present model fit. As the temperature increased, the conversion rate of AA increased at 30 and 50°C, while the conversion rate was almost the same for 70 and 90°C.

The effect of temperature on the grafting of AA onto cellulose is shown in Figure 2. One observes that the rate of grafting increased sharply during the initial period of the reaction; but as the poly-
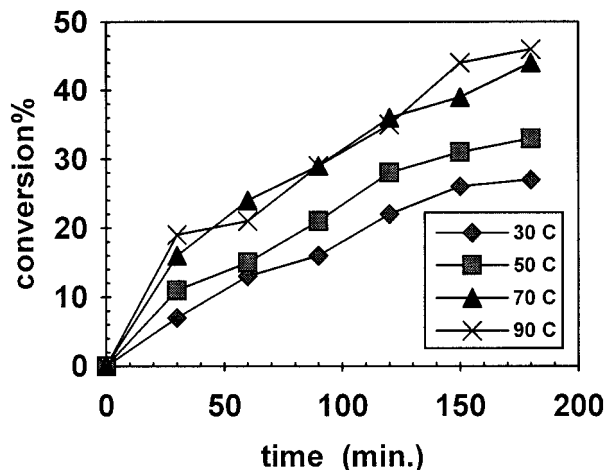

Figure 1 Temporal variations of AA conversion for graft copolymerization.

merization proceeded, the rate decreased, and higher grafting degrees in general were obtained at 30°C. As the temperature rose from 30 to 90°C for 180 minutes of grafting time, the grafting decreased from 44.1 to 13.85%. The grafting yield remained almost the same at reaction temperature of 90°C after the initial period. As can be seen in Figures 1 and 2, AA conversion increased, and the grafting percentage decreased as the temperature increased. These results indicate that homopolymer formation is favored over grafting at high reaction temperatures.

It is well known that during the graft copolymerization onto cellulose with a redox type initiator, some of the radicals resulting from decomposition of the initiator creates active centers on the cellulose to initiate the graft copolymerization, while the rest of them initiate the homopolymerization in the aqueous medium. Therefore, the graft yield depends greatly upon the active centers created by initiator on the cellulose. Higher temperatures probably decreased the amount of CAN complex ion in solution, resulting in a higher amount of homopolymer formation.

Water Retention Capacity

The variations of the swelling ratio are illustrated in Figure 3. The swelling ratio was roughly constant at reaction temperatures of 50, 70, and 90°C, while greater values of swelling ratio were obtained at 30°C. The maxima exhibited at 30°C and 150 minutes of reaction is indicative of a copolymer having short graft chains with high grafting
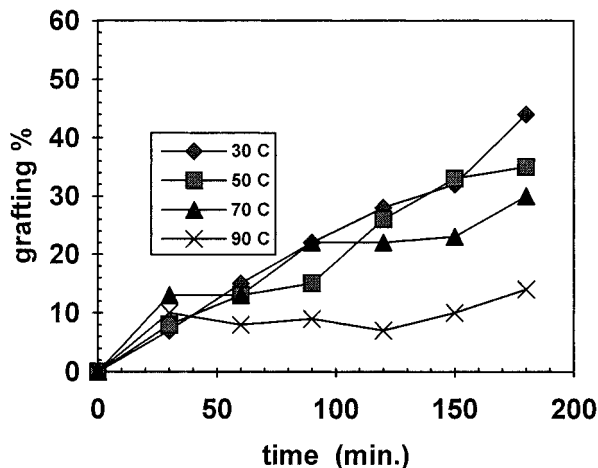
Figure 2 Grafting yields at various reaction temperatures.

density. The results show that grafting the AA monomer on the cellulose backbone at 30°C increases both water retention capacity and grafting yield of the product polymer.

It is known that the grafting of hydrophilic monomers onto cellulose impart the water absorption property to the cellulosic material. The water retention properties of cellulosic materials are thought to result from interaction through bonding of the hydroxyl groups on the cellulose with water molecules. Although it has been seen, there is almost no difference between the WRC values of the copolymers obtained at 50, 70, and 90°C; the copolymer obtained at 30°C has high WRC values in comparison with others.
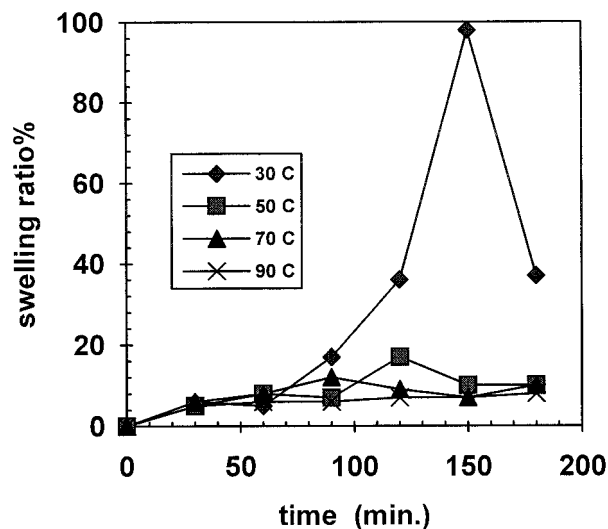
It can be speculated that the short graft chains in high grafting density have a greater effect on the swelling property of the graft copolymer than long graft chains in low grafting density in equal grafting percentage. The copolymers obtained at 50 and 70°C, especially at 50°C, have close grafting values with the copolymer obtained at 30°C. But their WRC values are quite different from each other. The reason for this difference may arise from the fact that the copolymer obtained at 30°C has small graft chains in high grafting density, but the copolymers obtained at 50 and 70°C have long graft chains in low grafting density. At 90°C, grafting values are low, and, therefore, WRC values of the copolymer are also low.

Homopolymer Formation

Homopolymer formation is important at high reaction temperatures. In the graft copolymerization, the radical formation on the monomer results in the homopolymerization. The homopolymer results were reported as the temporal variations of the ratio of homopolymer to AA at four reaction temperatures (Fig. 4). Results show that homopolymer yield increased at 90°C and remained almost the same at 70°C. The rate of change of homopolymer formation decreased at 30 and 50°C. The yield of homopolymer formation was the lowest at 30°C.

REACTION KINETICS

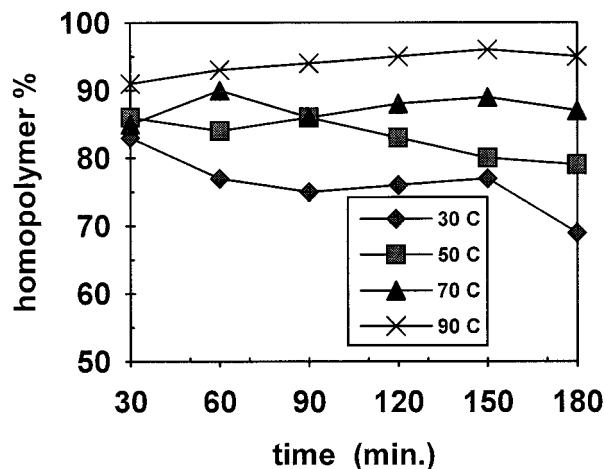Simple measurements of the effect of reaction environment on the graft copolymerization of AA

Figure 3 The swelling ratio of graft copolymer.

Figure 4 Temporal variations of homopolymer formation.

Table I   Acrylic Acid Disappearance Rate Constants

Temperature (°C)	k (min^{-1})	r^2
30	0.018	0.98
50	0.022	0.98
70	0.030	0.97
90	0.033	0.97

onto cellulose was the apparent first-order AA disappearance rate constants. Results are summarized in Table I. These rate constants were then used to determine apparent activation energy. The overall activation energy (E) for polymerization can be expressed with eq. (7), which is the difference between the sum of the activation energies for propagation (E_p) and decomposition of initiator (E_d) and the activation energy of termination (E_t)

$$E = E_p + E_d/2 - E_t/2 \qquad (7)$$

These values for the peroxide systems have been given as $E_d = 30-40$ kcal mol, $E_p = 5-10$ kcal mol, and $E_t = 2-5$ kcal mol. E consisting mainly of E_d and E_t has a small effect on E. The decomposition reaction of initiator for this system is an ionic reaction, and the activation energy for the decomposition has a small value; therefore, the step determining the overall activation energy is the propagation step. In this study, the overall activation energy in the graft copolymerization of AA onto cellulose for the first-order reaction was found to be 2.313 kcal mol. It is known that the value of overall activation energy (E) is determined mainly by the activation energy of decomposition. But since decomposition activation energies for ionic reactions is small, the activation energy (E) calculated from AA disappearance rate constants represents mainly the activation energy of propagation. Apparent first-order rate constants with satisfactory regression constant yielded a low activation energy of 2.3 kcal mol.

CONCLUSIONS

(1) Monomer conversion increases as reaction temperature increases.

(2) Grafting yield decreases as reaction temperature decreases.

(3) High temperatures favor homopolymerization more than grafting.

(4) The step determining the overall activation energy is the propagation step.

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