Graft Copolymerization of Acrylonitrile onto Cotton Cellulose by Potassium Permanganate–Thioacetamide Redox System

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SYNOPSIS

The graft copolymerization of acrylonitrile onto cotton, initiated by the $KMnO_4$–thioacetamide redox system in an aqueous medium, has been investigated. The percentage graft yield was determined by varying the concentrations of $KMnO_4$, acrylonitrile, thioacetamide, and temperature. The percentage graft yield increased initially and then decreased with increasing concentrations of $KMnO_4$ and thioacetamide, with an optimum yield not greater than 21%. The percentage graft yield, however, was greatly enhanced with a value of up to 66% as the concentration of acrylonitrile was increased. The percentage graft yield increased with temperature in the range of 35–70°C with a calculated activation energy of 8.33 Kcal/mol. The effects of solvents and amines on the percentage graft yield were also investigated. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Potassium permanganate is an effective initiator of the graft copolymerization of some vinyl monomers onto cellulosic and noncellulosic materials.[1-4] In combination with a number of organic compounds, potassium permanganate forms potent redox systems, which are capable of initiating the graft copolymerization of vinyl monomers onto polymeric substrates.[5-8]

Organic sulfur compounds, which are readily oxidizable substances under suitable conditions, have been used as components of many redox systems. Specifically, thiourea,[9-13] cysteine,[14-15] thiomalic acid,[16] and thioglycolic acid,[17] in combination with a number of oxidants, have been shown to be effective initiators of the graft copolymerization of methylmethacrylate onto polymeric substrates. The graft yield for some of the systems[9] were in excess of 200% and the presence of additives, such as amines,[17] solvents, and neutral inorganic salts,[9,11,14] appears to influence the percentage graft yield.

This article presents the results of a study on the graft copolymerization of acrylonitrile on cotton cellulose by the potassium permanganate–thioacetamide redox system in an aqueous medium. The effects of amines and solvents on the copolymerization are presented and discussed.

EXPERIMENTAL

Materials

Potassium permanganate and thioacetamide were of analytical grade and were used as supplied.

The cotton sample (Gosspium hirsutum) was obtained from Afcott Agricultural Farms in Yola, Nigeria, and was refluxed consecutively in methanol and then in distilled water for a period of 3 h. The sample was then washed with distilled water and was air-dried to constant weight.

Acrylonitrile (Aldrich Corp, U.S.A.) was washed with 5% aqueous sodium hydroxide and sodium chloride solutions, was dried over anhydrous calcium chloride, and then was fractionally distilled. The middle fraction of the monomer was collected and was stored under refrigerated conditions. Sulfuric acid, (BDH, 18 M) was used as supplied. Triply-distilled water was used in all cases for the copolymerization reactions.

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Graft Copolymerization

The graft-polymerization reaction was conducted in a 250 mL pyrex conical flask, fitted with a standard joint stopper. The flask, containing 50 ml of distilled water and the required amount of sulfuric acid, was immersed in a thermostated water bath, regulated to within ±0.05°C. 0.5 g of the purified cotton sample was then dispersed in the acid solution and was followed by the addition of the required amount of the redox initiator. The flask was allowed to stand, after gentle mixing, for 10 min before the required amount of monomer was added to it. Polymerization proceeded for 3 h before it was stopped by the addition of 5 mL of 1% hydroquinone solution.

The cotton graft was filtered, washed copiously with distilled water, and then was purified by soxhlet extraction with N,N'-dimethylformamide for 8–10 h to remove ungrafted homopolymers, until a constant weight was obtained.

The percentage graft and percentage efficiency were calculated from the relation:

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

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

where W_1, W_2, and W_3 are the weights of cotton, the cotton graft, and monomer, respectively.

RESULTS AND DISCUSSION

Effect of Thioacetamide Concentration

The effect of varying concentrations of thioacetamide (TAS) on the percentage graft yield and percentage efficiency is represented in Figure 1. It can be seen clearly that the percentage graft yield increases and then decreases after an optimum value of 21% at a TAS concentration of 1.6×10^{-3} mol/L. The corresponding percentage efficiency is not higher than 10%, indicating a low conversion of the monomer into grafted polymer. In some polymerization reactions involving potassium permanganate,[1,18,19] the active initiator was indicated as MnO_2. If this is assumed to be so for this system, then the mechanism for the formation of thiol radicals from thioacetamide may be represented as follows:

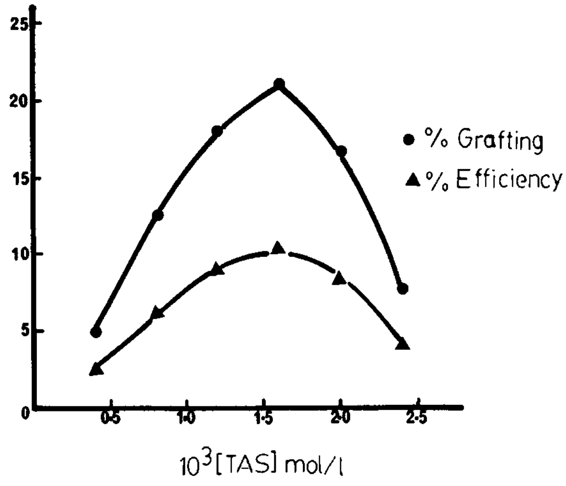
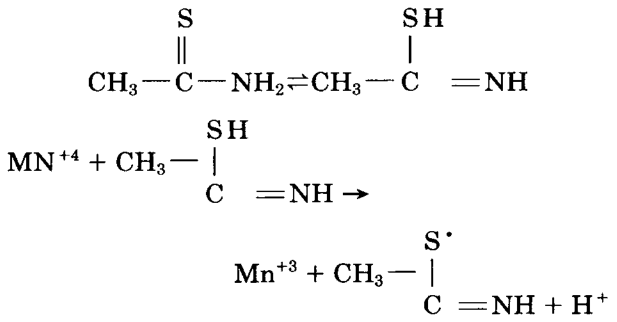


Figure 1 Effect of Thioacetamide on graft yield and efficiency: $[H^+] = 0.2$ mol/L, $[KMnO_4] = 4 \times 10^{-3}$ mol/L, $[AN] = 0.37$ mol/L, cotton = 0.50 g, time = 6 h, temperature = 35°C.



$$CH_3-\overset{\overset{S}{\|}}{C}-NH_2 \rightleftharpoons CH_3-\overset{\overset{SH}{|}}{C}=NH$$

$$MN^{+4} + CH_3-\overset{\overset{SH}{|}}{C}=NH \rightarrow$$

$$Mn^{+3} + CH_3-\overset{\overset{S^{\cdot}}{|}}{C}=NH + H^+$$

Thus, the decrease in the graft yield may be associated with increasing termination of graft copolymerization by thiol radicals at high concentrations of thioacetamide. It may also be due to an enhanced formation of homopolymer, initiated by the thiol radicals. The latter is corroborated by the low percentage efficiency found for this system. Third, the decrease in graft yield may be due to increased mutual termination reactions by propagating macroradicals as conversion increases. This is, however, unlikely, since the overall conversion is low and the reaction is heterogeneous.

Effect of Permanganate Concentration

Figure 2 represents the effect of permanganate on the percentage graft yield and percentage efficiency. The graft yield increases and then decreases after an optimum value of 20% at the permanganate concentration of 12×10^{-3} mol/L. The corresponding percentage efficiency is not higher than 10%. The decrease in the graft yield may be rationalized as follows:

1. Enhanced termination of grafted polymeric radicals and oxidation of radical sites on the cellulose by Mn^{+4}.
2. Oxidation of thiol radicals by Mn^{+4}, thereby rendering them ineffective for initiation of graft copolymerization on the cellulose.

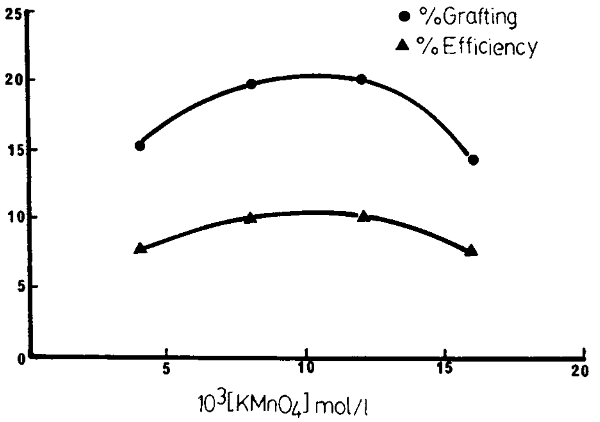


Figure 2 Effect of permanganate on graft yield and efficiency: [H^+] = 0.2 mol/L, [AN] = 0.37 mol/L, [TAS] = 2×10^{-3} mol/L, cotton = 0.50 g, time = 6 h, temperature = 35°C.

3. Mn^{+2} is believed to be rapidly formed[18] in a series of oxidation reactions involving Mn^{+4} and it may autocatalyse the initiation of homopolymerization.

Effect of Acrylonitrile Concentrations

The percentage graft increases with acrylonitrile (AN) concentration over the range 0.2–0.75 mol/L, as shown in Figure 3. At the highest graft yield of 66%, the percentage efficiency is not higher than 16.5%. Since the copolymerization is heterogeneous, increasing concentration of the monomer may increase the solubility of polyacrylonitrile, both grafted and ungrafted, and, consequently, results in increased viscosity of the reaction medium. The phenomenal increase in the graft yield may then be associated with reduced termination processes, particularly by coupling between grafted polymeric chains and between grafted and ungrafted polymeric chains. This is in agreement with similar results reported for some systems.[7]

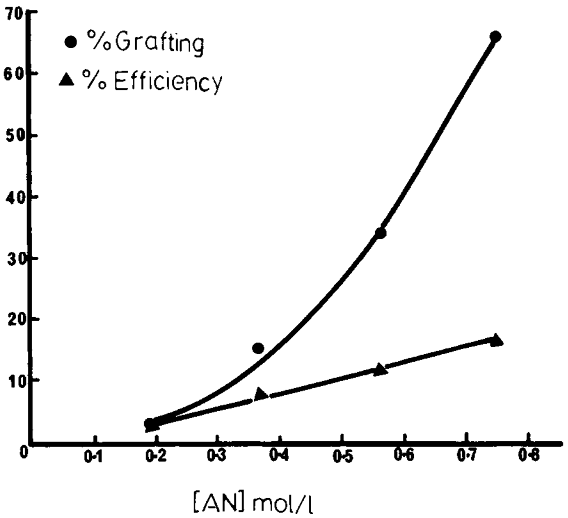


Figure 3 Effect of acrylonitrile on graft yield and efficiency: [H^+] = 0.2 mol/L, [$KMnO_4$] = 4×10^{-3} mol/L; [TAS] = 1.6×10^{-3} mol/L; cotton = 0.50 g; time = 6 h; temperature = 35°C.

Effect of Temperature

The effect of temperature on the graft copolymerization was investigated over the range 35–70°C. The results are presented as time–conversion curves in Figure 4(A). As can be seen in Figure 4(A), the yield increases with time and with temperature, but

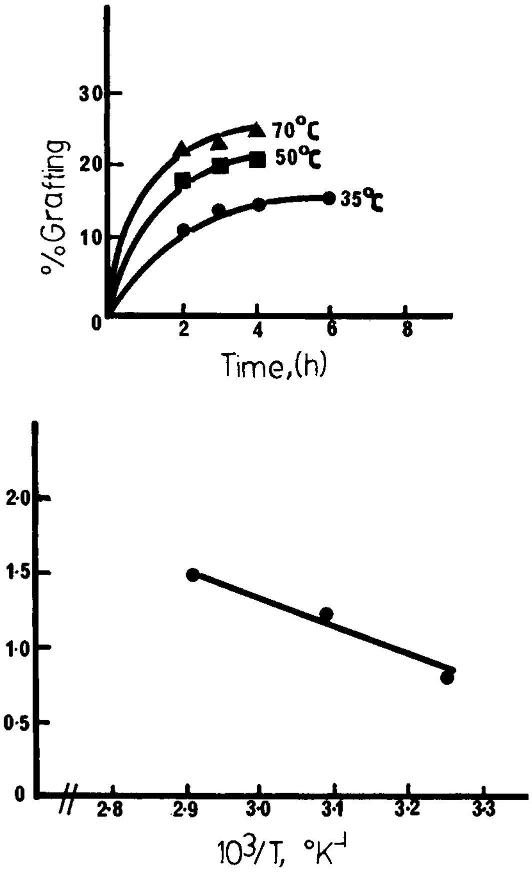


Figure 4 (A) Effect of temperature on graft yield and efficiency: [H^+] = 0.2 mol/L, [$KMnO_4$] = 4×10^{-3} mol/L; [TAS] = 1.6×10^{-3} mol/L, [AN] = 0.37 mol/L, cotton = 0.50 g. (B) Arrhenius plot for graft copolymerization of AN onto cotton by potassium permanganate–thioacetamide redox system.

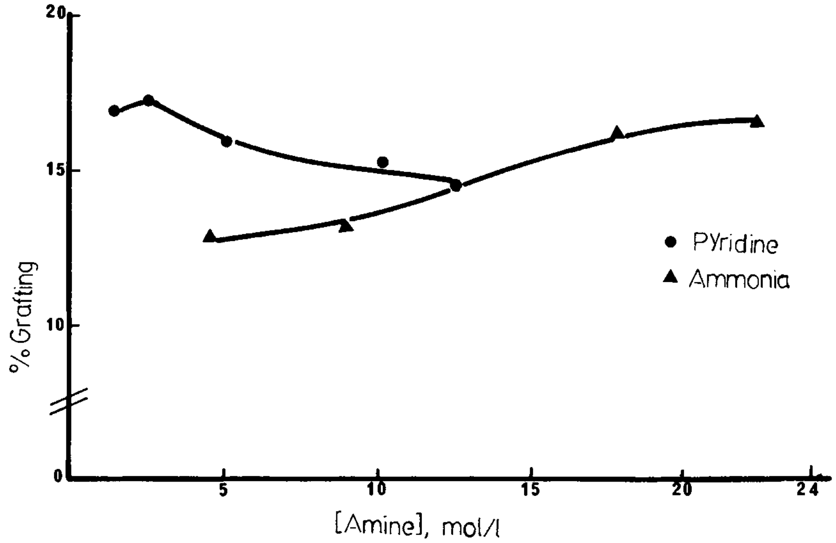


Figure 5 Effect of Amines on graft yield: $[H^+] = 0.2$ mol/L, $[KMnO_4] = 4 \times 10^{-3}$ mol/L, [TAS] = 1.6×10^{-3} mol/L, [AN] = 0.37 mol/L, cotton = 0.50 g, time = 6 h, temperature = 35°C.

with less than 30% yield after 4 h at 70°C. The overall increase in graft yield with temperature may be influenced by an enhanced degree of swelling of the cotton cellulose in aqueous medium as the temperature increases, plus increased diffusion of the monomer to the radical sites on the cellulose and on the graft polymer.

An Arrhenius plot of the initial rate of the graft copolymerization vs. the reciprocals of the temperatures is represented in Figure 4(B), from which the activation energy for the polymerization is derived to be 8.33 Kcal/mol.

Effect of Pyridine and Ammonia

Figure 5 represents the effect of pyridine and ammonia on the percentage graft yield. Over the concentration range 2.5–12.6 mol/L, pyridine appears to depress the percentage graft yield in a manner that is similar to that reported for the graft copolymerization of methylmethacrylate onto wool.[17] In contrast, ammonia appears to enhance the percentage graft yield over the concentration range of 4.5–22.4 mol/L.

However, in relation to the control percentage graft of 15.4% that is, in the absence of added amine, pyridine showed a slight increase of not greater than 10.3% on the percentage graft over the concentration range of 2.5–5.1 mol/L and then decreases the yield at higher concentrations.

For ammonia, there is significant depression on the percentage graft yield of up to 17% in the concentration range of 4.5–8.9 mol/L, and a nominal increase of about 6.5% at the higher concentration of 22.4 mol/L.

The effects of the amines may be associated with their relative basicities, which are expected to influence the pH of the medium and hence the rate of formation of thiol radicals.

Effect of Solvents

Table I shows the effect of the addition of 10% (V/V) of different solvents on the percentage graft yield. Relative to the control percentage graft yield of

Table I Effect of Solvents on Graft Yield[a]

Solvent 10% (V/V)	% Graft Yield
Control	15.4
Acetone	19.0
Mathanol	5.6
Carbon Tetrachloride	17.4
1,4-Dioxane	12.2
Acetic Acid	10.6

[a] $[H^+] = 0.2$ mol/L, $[KMnO_4] = 4 \times 10^{-3}$ mol/L, [TAS] = 1.6×10^{-3} mol/L, [AN] = 0.37 mol/L, cotton = 0.50 g, time = 6 h, temperature = 35°C.

15.4%, methanol, 1,4-dioxane, and acetic acid appear to depress the graft yield in the order methanol > acetic acid > 1,4-dioxane.

The addition of carbon tetrachloride and acetone, in contrast, appears to increase the graft yield in the order acetone > carbon tetrachloride.

In some systems already studied, the effect of solvents on graft yield is often associated with a number of factors, which include:

1. the ability of the solvent to swell the polymeric substrate.
2. the degree of miscibility with monomer.
3. the formation of solvent radicals and facilitation of chain transfer reactions.

For this system, it seems that the depression of the graft yield is predominantly associated with the formation of solvent radicals from methanol, acetic acid and 1,4-dioxane, by reaction with permanganate. This would lead to reduced equilibrium concentration of the initiating thiol radicals.

The increase in graft yield, in the presence of acetone and carbon tetrachloride, may be associated with the ability of the solvents to swell the cotton and consequently to enhance the diffusion of the monomer molecules in the reaction medium.

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