

Graft Copolymerization of Methacrylonitrile on Caesarweed Fibers by Ceric Ion/Isopropanol Redox Pair

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ABSTRACT: The graft copolymerization of methacrylonitrile to caesarweed fiber and its sodium derivative by ceric ions in the presence of isopropanol was investigated in aqueous media. The percentage graft yield decreased initially and then increased with the concentration of isopropanol, but the graft levels of sodium caesarweed fibers were much lower. The graft reaction in the presence of isopropanol was characterized by the high frequency of grafting, up to $2.81 \times 10^2 N_g/10^4$ anhydroglucose units, and the low molecular weight of the grafted polymer, not higher than 0.94×10^3 . The molecular weight of the grafted polymer showed a negative dependence on the concentration of isopropanol, suggesting the involvement of the latter in the transfer reactions with growing grafted

polymer chains, which permitted calculation of the transfer constant, k_A/k_p , for the process: 7.91×10^{-2} . The graft yield percent was found to be negatively dependent on the concentration of ceric ions for grafting of methacrylonitrile on sodium caesarweed fibers, but the molecular weight of the grafted polymer showed no clear-cut trend with ceric ion concentration. The graft yield percent increased with temperature in the range of 30°C–50°C and decreased markedly at 70°C. The calculated activation energy of the graft reaction was 10.5 kcal/mol. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 353–358, 2006

Key words: graft copolymers; biofibers; radical polymerization; activation energy

INTRODUCTION

The caesarweed plant, *Urena lobata*, is a member of the mallow family, malvacea, one of the most important fiber plant families. The plant is cultivated in warm regions of several countries including those of West Africa, and it often grows wild in abundance. It possesses cellulosic bast fibers, which closely resemble jute, although shorter and coarser. Commercial utilization of the fiber in the textile industry is limited, but in some applications, it is used as a substitute for jute fiber, notably for production of twines and sacks. Studies of the physical properties of the bast fibers of plants that grow in the wild showed an initial modulus and breaking extension for caesarweed fibers of 5.25 Ntex^{-1} and 3.7%, respectively.^{1,2}

Grafting as a tool for achieving desired properties of polymeric substrates has continued to attract considerable attention.³ In previous reports,^{4–7} it was demonstrated that vinyl monomers can be grafted to caesarweed fibers by oxidants, namely, ceric ions and permanganate, in a redox pair with readily oxidizable organic compounds, resulting in varying yields of grafted copolymers that depend, in part, on the reac-

tivity of the monomer and the initiating species derivable from the redox pairs.

For the graft copolymerization of methyl methacrylate to modified plantain pulp initiated by ceric ions, the presence of isopropanol resulted in an increased rate of grafting and reduced molecular weight of the graft copolymer. The latter was attributed to the terminating effect of the isopropanol radical species on the growing graft polymer chain.

The present report is on a study of graft copolymerization of methacrylonitrile onto caesarweed fibers initiated by ceric ions in the presence of isopropanol. Grafting characteristics, graft copolymer molecular weight, and graft frequency are discussed.

EXPERIMENTAL

Materials

Methacrylonitrile (MA; Aldrich Corp., Germany) was washed with 5% aqueous sodium hydroxide and then distilled. It was dried over anhydrous calcium chloride and fractionally distilled. Other reagents, ceric ammonium nitrate, glacial acetic acid, nitric acid, and isopropanol (ISP), were used without further purification. Caesarweed plants were obtained locally in Abeokuta, Nigeria.

Methods

Bast fibers were obtained from the stem of the caesarweed plant, air-dried, and beaten in a mortar. Holo-

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TABLE I
Effect of Isopropanol Concentration on Grafting of Methacrylonitrile on Caesarweed and Sodium Caesarweed Fibers in Aqueous Media by Ceric Ions

[ISP] × 10 ² (M)	P _g ^o (%)	Efficiency (%)	Caesarweed			Na Caesarweed P _g (%)
			M _v × 10 ⁻³	F _g × 10 ⁻² (Ng/10 ⁴ AGU)	P _g (% H ₂ O/acetone)	
0	57.7	5.8	0.30	5.72	0.3	62
5.6	110.9	11.1	—	—	6.7	66
16.7	59.6	5.9	0.94	1.32	0.2	67
27.8	55.1	5.5	0.47	2.62	—	36.2
44.4	64.6	6.5	0.42	2.81	11.1	—
55.6	75.3	7.5	0.41	2.56	—	45.6

[H⁺] = 0.62M; [AcOH] = 1.1M; fiber = 0.1 g; [Ce⁺⁴] = 3.3 × 10⁻³ M; [MA] = 0.49M; POT = 10 min; time = 3 h; temperature = 30°C.

cellulose was obtained from the fibers by a method previously reported.⁴ It was bleached by treatment with aqueous sodium hypochlorite solution and air-dried. A certain proportion of the holocellulose was modified by treatment with 12M sodium hydroxide solution at ambient temperature for 1 h to yield sodium caesarweed fiber,⁹ which was washed with copious amounts of distilled water and air-dried.

The experimental procedure for the graft copolymerization reaction was based on the method described by Lepoutre and Hui¹⁰ as reported previously.⁴ In a typical reaction, a redox interaction of the ceric ions and the isopropanol was allowed to occur for a given time, the preoxidation time (POT), before the addition of the monomer to the reaction mixture, which marked the onset of the graft reaction. The reaction was stopped by the addition of excess distilled water, and the product was immediately filtered, dried, and weighed. The ungrafted polymethacrylonitrile (PMA) homopolymer was extracted with acetone, and the caesarweed graft copolymer residue was air-dried and reweighed. Graft percent and graft efficiency were calculated from the relations:

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

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

where W₁, W₂, and W₃ 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.¹¹ The resulting hydrolysate was filtered hot on a Buchner funnel and washed with distilled water and dried at 40°C. The grafted polymer was extracted with acetone, and the average molecular weight was determined from the viscosity of the acetone solution at 20°C using the Mark-Houwink equation¹²: $[\eta] = 95.5 \times 10^{-3} M_v^{0.56}$. Graft frequency, F_g, defined as moles of grafted PMA (N_g) per 10⁴ anhydroglucose units (AGU), was determined from the relation⁸ $F_g = N_g M_o \times 10^4$, where N_g is the weight of

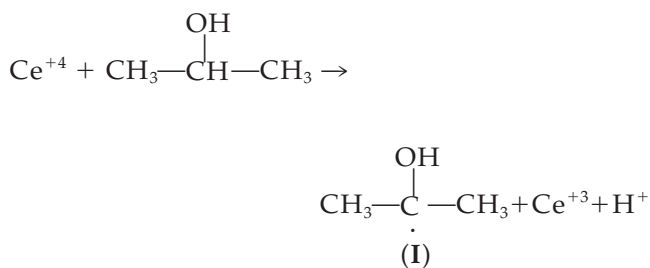
the grafted polymer per gram of fiber divided by the molecular weight of the polymer and M_o is the molecular weight of 1 AGU.

The kinetic parameters were determined gravimetrically, and the rate constants for the graft reactions were obtained from the slope of the plots of the reciprocal of monomer concentration versus reaction time.¹³ The solubility of the graft copolymer in sulfuric acid was determined by a standard method.¹⁴

RESULTS AND DISCUSSION

Effect of isopropanol concentration on graft yield, molecular weight, and graft frequency

The effect of isopropanol (ISP) concentration on graft copolymerization of methacrylonitrile (MA) on caesarweed fiber (unmodified) and on its sodium derivative by ceric ions in aqueous media is shown in Table I. For the unmodified fiber, the percent graft yield, P_g, decreased initially and then increased with increases in concentration of ISP in the range of 5.6–55.6 × 10⁻² M. The percent graft yield ratio, P_g/P_g^o, where P_g^o is the graft yield in the absence of ISP, was in the range of 0.95–1.92. A similar trend was evident for graft copolymerization of MA onto the sodium derivative of the fiber with P_g/P_g^o in the range of 0.58–1.08 but with generally lower graft yields at the corresponding concentrations of ISP. As proposed previously,^{8,16} in a redox pair with ceric ions, an isopropanol radical species (I) could be obtained as follows.



The initial decrease in graft yield using the fiber and its sodium derivative may have arisen from competi-

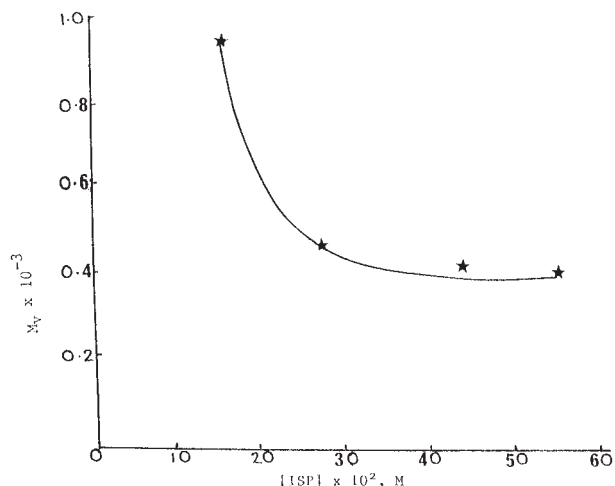


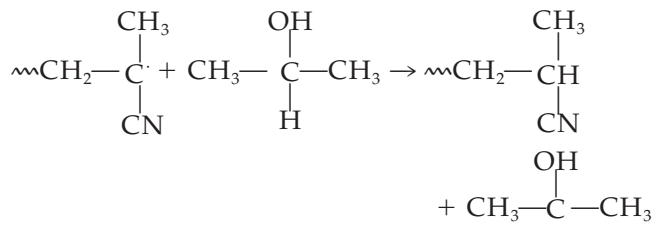
Figure 1 Effect of ISP concentration on M_v for grafting of MA to caesarweed fibers ($[MA] = 0.49M$; $[Ce^{+4}] = 33.3 \times 10^{-3} M$; temperature = $30^\circ C$).

tive reactions of caesarweed fiber and ISP with ceric ions. The subsequent increase in the graft yield at higher concentrations of ISP may then be associated with enhanced activity of isopropanol radical species I in the graft polymerization reactions.

The formation of sodium caesarweed fibers was expected to lead to a reduced number of available hydrogen atoms per anhydroglucose repeat unit. Thus, the lower graft yield for the sodium derivative was prima facie evidence of the mechanism of graft initiation processes by redox initiators, generally believed to occur by abstraction of hydrogen from the substrate.

Graft copolymerization of MA on unmodified caesarweed fiber was conducted in a 50:50 (v/v) water-acetone mixture. As can be seen in Table I, at an ISP concentration of $44.4 \times 10^{-2} M$, the yield was very low, not higher than 11.1%. This may have been a result of a preponderance of the homopolymerization reaction, which was facilitated by enhanced radical diffusion processes.

Figure 1 shows that the viscosity-average molecular weight, M_v , of the graft polymers of the unmodified caesarweed fibers depended on the concentration of ISP. The M_v values of the polymers were generally low, not higher than 0.94×10^3 , which was not surprising judging from the percent efficiency of utilization of the monomer for graft reactions, which was not higher than 11.1% in the presence of ISP (Table I). The M_v decreased with an increasing ISP concentration in the range of 16.7 – $55.6 \times 10^{-2} M$, with a corresponding decrease in the M_v/M_v^0 from 3.13 to 1.37, where M_v^0 is the molecular weight of the grafted polymer in the absence of ISP. This suggests the involvement of ISP in the transfer reactions with the growing graft polymer chains.



For the graft copolymerization of methyl methacrylate onto plantain pulp by ceric ions in the presence of ISP, the former was involved in transfer reactions with the growing graft polymer chain, resulting in M_v values that were negatively dependent on the concentration of ceric ions.⁸ The Mayo equation¹⁵— $1/N = 1/N_0 + k_A/k_p [Ce^{+4}]/[M]$ [eq. (1)], where N and N_0 are the degrees of graft copolymerization in the presence and the absence of ceric ions, respectively, and k_A and k_p are the rate constants for chain transfer and for propagation, respectively—was thus applicable to calculation of the transfer constant, k_A/k_p , for the graft reaction. In light of the negative dependence of the M_v of grafted polymethacrylonitrile (PMA) on the concentration of ISP, eq. (1) is also applicable as $1/N = 1/N_0 + k_A/k_p [ISP]/[M]$ [eq. (2)].

Thus, from the plot of $1/N$ versus $[ISP]$, as shown in Figure 2, the value of k_A/k_p , obtained from the slope was 7.91×10^{-2} for the graft reaction. This k_A/k_p was about 4 times higher, a significant difference, than the corresponding k_A/k_p , 2.25×10^{-2} , reported for ceric ions for the graft copolymerization of methyl methacrylate to unmodified plantain pulps and was much higher than the k_A/k_p of 1.82×10^{-4} for transfer reactions by isopropanol.⁸ The latter was only 0.23% of the k_A/k_p for grafting PMA in the presence of isopropanol and reflects that methacrylonitrile had a greater propensity to undergo transfer reactions with isopropanol than did methyl methacrylate. The frequency of graft,

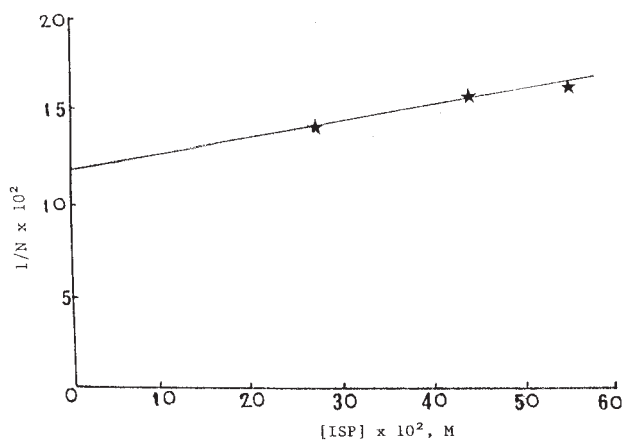


Figure 2 Relationship between $1/N$ and ISP for grafting of MA to caesarweed fibers.

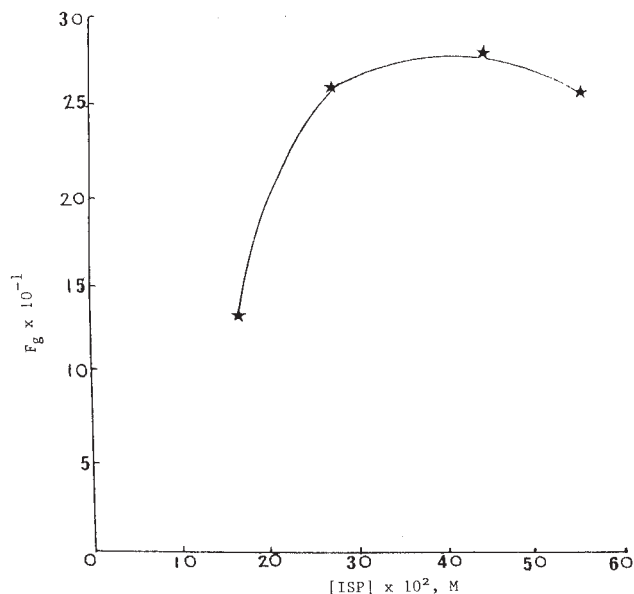


Figure 3 Effect of ISP concentration on F_g for grafting of MA to caesarweed fibers.

F_g as a function of ISP was high, up to $2.81 \times 10^2 N_g/10^4$ AGU at an ISP concentration of $44.4 \times 10^{-2} M$, as shown in Figure 3. The high graft frequency suggests that the combined rates of initiation of the graft reactions on the polymeric backbone of caesarweed fiber by ceric ions and an isopropanol radical species were comparable to the rate of transfer reactions with growing copolymer chains by the latter species.

Effect of ceric ion concentration on grafting of methacrylonitrile on caesarweed fibers

Figure 4 shows the effect of ceric ion concentration on the grafting of MA on sodium caesarweed fibers. It

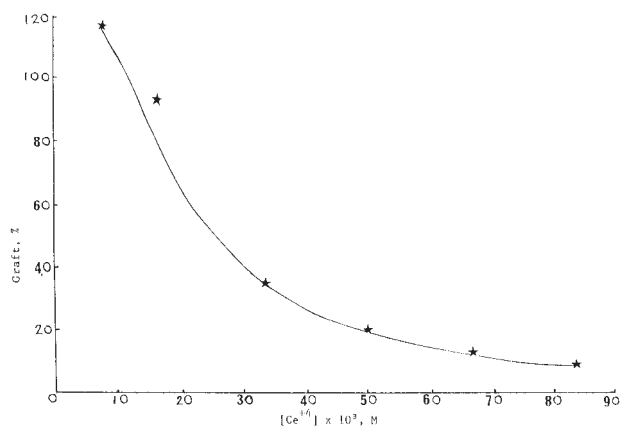


Figure 4 Effect of ceric ion concentration on graft yield for grafting of MA to sodium caesarweed fibers ($[H^+] = 0.62M$, $[AcOH] = 1.1M$; $[ISP] = 5.6 \times 10^{-2} M$; fiber = 0.1 g; $[MA] = 0.49M$; POT = 10 min; time = 3 h; temperature = $30^\circ C$).

TABLE II
Effect of Ceric Ion Concentration on Grafting of Methacrylonitrile on Sodium Caesarweed Fibers in Aqueous Media

$[Ce^{+4}] \times 10^3 (M)$	$P_g (\%)$	$M_v \times 10^{-3}$
8.3	117	0.13
16.7	72.9	0.43
33.3	34.3	0.08
50.0	19.6	1.11
66.7	13.4	0.14
83.3	8.6	0.16

$[H^+] = 0.62M$; $[AcOH] = 1.1M$; fiber = 0.1 g; $[MA] = 0.49M$; $[ISP] = 5.6 \times 10^{-2} M$; POT = 10 min; time = 3 h; temperature = $30^\circ C$.

can be seen that graft yield decreased with up to a 10-fold increase in ceric concentration. The molecular weight of the graft polymer (Table II), however,

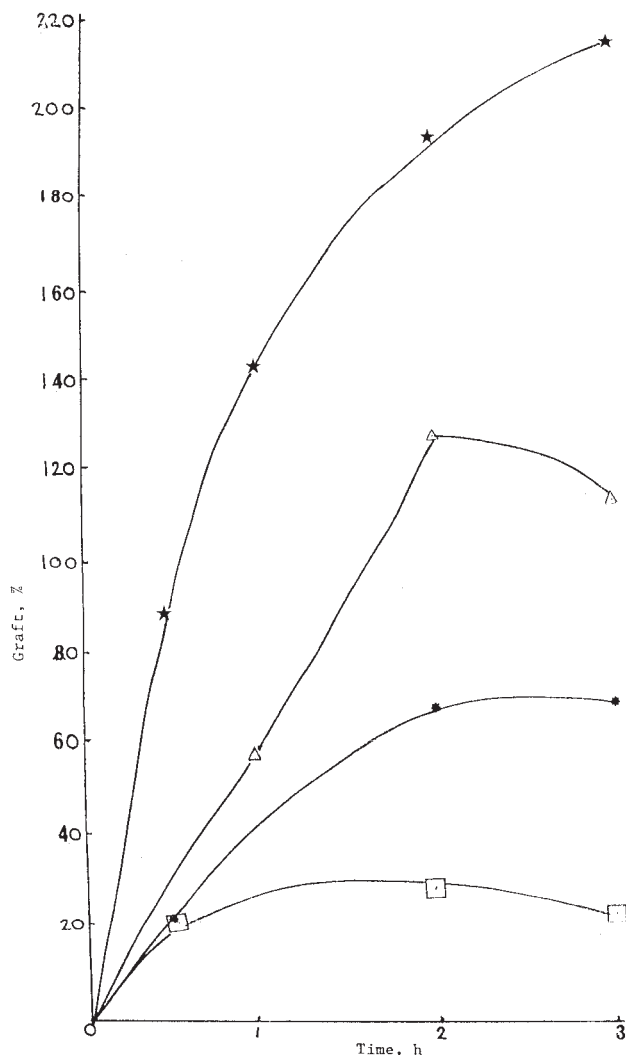


Figure 5 Effect of temperature on graft yield ($[H^+] = 0.62M$; $[AcOH] = 1.1M$; fiber = 0.1 g; $[MA] = 0.49M$; $[ISP] = 5.6 \times 10^{-2} M$; $[Ce^{+4}] = 33.3 \times 10^{-3} M$; (*) $30^\circ C$; (Δ) $40^\circ C$; (\square) $50^\circ C$; (\circ) $70^\circ C$).

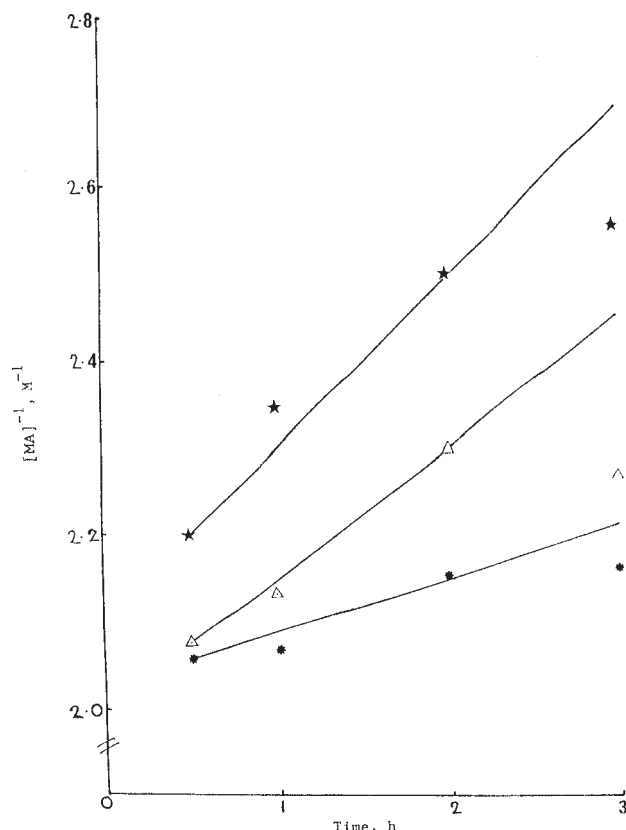


Figure 6 Relationship between $[MA]^{-1}$ and time [(*) 30°C; (Δ) 40°C; (\star) 50°C].

showed no clear-cut trend with ceric ion concentration.

Effect of temperature on graft yield

The temperature dependence of the graft reaction, in the range 30°C–70°C, is represented in Figure 5. The graft yield showed a positive dependence on temperature up to 50°C and thereafter a negative dependence. At each temperature, conversion increased with time, approaching a plateau at 50°C, with a maximum percent grafting efficiency of 21.6% after a 3-h reaction. The reduction in graft yield at 70°C was marked by up to 90% of the corresponding value at 50°C. The rate constant, k , values for the graft reactions were obtained from the conversion plots of $[MA]^{-1}$ versus time shown in Figure 6. In accordance with the Arrhenius expression, $k = Ae^{-E/RT}$, the overall activation energy for the graft reaction determined from the slope of $\log k$ versus $1/T$ (Fig. 7) was 10.5 kcal/mol. The activation energy was consistent with the observed low graft yield and low molecular weight of the grafted polymer.

Solubility of caesarweed–polymethacrylonitrile graft copolymer in acid

The solubility of the caesarweed fiber– polymethacrylonitrile graft copolymer in 72% sulfuric acid is shown

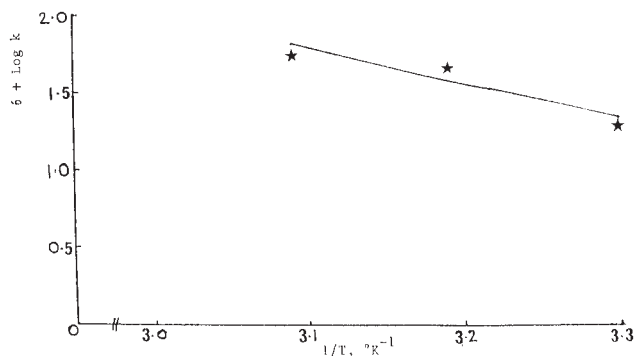


Figure 7 Arrhenius plot of rate of graft versus reciprocal of temperature.

in Figure 8. The improved resistance of the graft copolymer to the action of acid was evident by the decrease in solubility of the copolymer with an increase in percent graft yield. A 10-fold increase in graft yield, from 20.7% to 216.3%, resulted in an 88% reduction in the solubility of the graft copolymer in the acid. This property confirmed an earlier report on the solubility of kenaf fiber–polymethacrylonitrile graft copolymer in 72% sulfuric acid.¹⁶

CONCLUSIONS

Graft copolymerization of methacrylonitrile onto caesarweed fibers and its sodium derivative by ceric ions in the presence of isopropanol produced graft yields that were much lower for the latter fibers. The graft reaction was characterized by a high graft frequency, up to $2.81 \times 10^2 N_g/10^4$ AGU, and a low molecular weight of the grafted polymer, not higher than 0.94×10^3 .

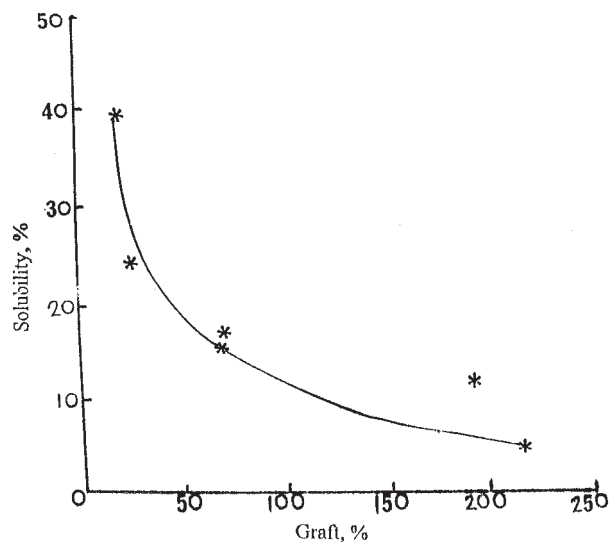


Figure 8 Solubility of caesarweed–polymethacrylonitrile graft copolymer in 72% sulfuric acid.

The molecular weight of the grafted polymer was negatively dependent on the concentration of isopropanol, suggesting the involvement of the latter in transfer reactions with growing graft polymer chains.

The percentage graft yield increased with temperatures in the range of 30°C–50°C and decreased markedly at 70°C, with the overall activation energy of the reaction calculated as 10.5 kcal/mol.

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