Grafting of Acrylonitrile onto Allylated Caesarweed Fibers by Potassium Permanganate – N,N'-Dimethylacetamide Redox Pair

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ABSTRACT: Caesarweed fiber, *Urena lobata*, was modified by successive treatment with sodium hydroxide and allylchloride in diethylether to yield an average degree of substitution of 2.73 allyl moieties per anhydroglucose unit. The presence of allyl moieties on the fiber was confirmed by infrared spectroscopy. Graft copolymerization of acrylonitrile onto the unmodified and allyl-modified fibers was initiated by potassium permanganate $-N,N'$-dimethylacetamide redox pair in aqueous medium. The allyl fiber was markedly less reactive than the unmodified fiber with graft yields for the latter a factor of 2.3 higher than those of the former. This was attributed to resonance stabilization of allylic macroradicals of the fiber. The graft yield showed positive dependence on N,N'-dimethylacetamide concentration in the range, $9.0–45.0 \times 10^{-4}M$ with P_g/P_{go} of up to 1.39 at the highest concentration. The conversion in graft yield was however characterized by a plateau at the latter concentration and was ascribed to termination of grafted polymer chains by methylacetylaminomethyl radical initiating species. Spectroscopic evidence in support of the latter was the absorption peak at 1680 cm^{-1} for the graft copolymers, characteristic of C=O stretching vibration for tertiary amide. Acetic acid, at concentrations in the range $0.28–2.22M$, was inimical to grafting of acrylonitrile onto allylfibre with P_g/P_{go}, of less than one. Grafting onto allylfiber showed positive temperature dependence in the range, $30–50°C$ with calculated activation energy of 12.3 kcal mol^{-1} for the graft polymerization reaction. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2671–2675, 2008

Key words: graft copolymers; allylfibres; infrared spectroscopy; radical polymerization; activation energy

INTRODUCTION

Potassium permanganate is an effective oxidant of cellulosic materials for initiation of graft copolymerization reaction.[1,2] The latter process can be facilitated or retarded by combination of potassium permanganate with oxidizable organic compounds as redox initiators.[3–5]

Derivatization of cellulose by the introduction of active functional groups onto it can influence the grafting of a number of vinyl monomers.[6–9] Thus, for the graft copolymerization of acrylonitrile, methylmethacrylate, and acrylamide onto partially carboxymethylated cottons by ceric ions, the graft yields increased with the degree of substitution of the cellulose.[6] Furthermore, ceric ion initiated graft copolymerization of methylmethacrylate onto allylated plantain pulp gave an increase in graft yield compared with the values for the unmodified fibers.[8] Conversely, for grafting of methylmethacrylate on thiolated holocellulose by ceric ions, the graft yield decreased with increase in the degree of substitution of the cellulose.[7]

A previous report has shown that N,N'-dimethylaniline in a redox pair with cupric ion was effective for grafting methylmethacrylate onto natural rubber at 70°C and attributed the primary initiating species to methylanilinomethyl radical.[10] For the present work, the acetyl analogue, N,N'-dimethylacetamide was used in combination with potassium permanganate for initiation of graft copolymerization of acrylonitrile onto allylated caesarweed, *Urena lobata*, cellulosic fibers. Caesarweed plant belongs to the mallow family, Malvacea, which is one of the most important of all fiber plant families. The plant is cultivated in warm regions of several countries including West Africa, and it often grows wild in abundance. The bast fibers are cellulosic materials closely resembling jute, but somewhat shorter and coarser. The fibers are used as substitutes for jute and find application in the production of twines and sacks. The grafting characteristics and infrared spectroscopy of the graft copolymer obtained by grafting of acrylonitrile onto allylated caesarweed fibers are reported and discussed.

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EXPERIMENTAL

Materials

Acrylonitrile (AN; Aldrich Corp.) was washed successively with 5% aqueous sodium hydroxide and 5% aqueous sodium chloride solutions. It was then washed with distilled water and fractionally distilled. The middle fraction was collected for the reactions.

N,N'-dimethylacetamide was purified by fractional distillation. The other reagents, namely, allylchloride, glacial acetic acid, potassium permanganate, and sulfuric acid were used without further purification. Caesarweed plant was collected in the wild in Abeokuta, Nigeria. Details of the bast fiber characteristics of caesarweed plant have been reported previously.[4]

Methods

Caesarweed fibers were obtained from the stem of the plant, air-dried, and beaten in a mortar. Holocellulose was obtained from the fiber by treatment with 10% sodium sulfite solution as previously reported.[4] The fiber was bleached by treatment with aqueous sodium hypochlorite solution and air-dried. A certain portion of the bleached holocellulose was allylated.[8] Specifically, 15 g of the fiber was reacted with 150 mL of a 20 wt % aqueous sodium hydroxide solution at 0°C for 15 min after which, it was filtered dry. It was then refluxed for 3 h in 50 vol % solution of allylchloride in 80 mL of diethyl ether. The resultant allylcellulose was washed several times with diethylether and air-dried. The allyl moiety content of the fiber was determined by reacting 0.5 g of the allyl fiber with 25 mL of $0.1M$ iodine solution for 1 h and the unreacted iodine was determined by back-titration with $0.05M$ sodium thiosulfate solution. The number of moles (N) of allyl moiety per anhydroglucose unit (AGU) was obtained from the equation[8]

$$N = \frac{(V_o - V_t)Mt \times 162}{Ws \times 127} \tag{1}$$

where, V_o and V_t are the titration values for the blank and sample, respectively; M_t is the molarity of the thiosulfate solution and W_s the weight of the allyllated fiber. N was found to be 2.73 mol of allyl-moiety per anhydroglucose unit.

The graft copolymerization reaction was conducted according to the experimental procedure of Lepoutre and Hui[11] as previously reported.[4] Typically, the required amount of the reagents, that is, sulfuric acid, glacial acetic acid, N,N'-dimethylacetamide were introduced into the flask containing an appropriate amount of distilled water. 0.1 g of the fiber was dispersed in the mixture and allowed to stay for 10 min while the flask was kept in a thermostated water bath, regulated to within ± 0.05°C. A

required amount of potassium permanganate was added and allowed redox interaction with N,N'-dimethylacetamide for a given time, the preoxidation time (POT) before addition of acrylonitrile to the reaction mixture which marked the onset of the graft reaction. The reaction was stopped by addition of excess distilled water and immediately filtered, dried, and weighed. The ungrafted polyacrylonitrile was extracted with N,N'-dimethylacetamide and the graft copolymer residue air-dried and re-weighed. The percentage graft level and efficiency of graft were calculated from the equations:

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

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

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

The spectra of the allylated fibers and of the allyl-fiber-g-polyacrylonitrile graft copolymer were recorded on Buck Scientific Spectrophotometer M500 using the potassium bromide disk technique.

RESULTS AND DISCUSSION

Infrared spectroscopy of allylfibers and allylfiber-g-polyacrylonitrile copolymer

Figure 1 shows the infrared spectra for allylated caesarweed fibers. The peak at 3429.8 cm^{-1} is ascribed to residual OH stretching vibration, the degree of substitution of the fibers being 2.73 allylmoieties per anhydroglucose unit. C=C and C—O—C stretching vibrations occur at 1648.3 and 1156 cm^{-1} respectively, and confirm the presence of allyl moiety on the fibers. Figure 2 shows the spectra for allylfiber-g-polyacrylonitrile copolymer. The absorption by residual OH occurred at 3448 cm^{-1} while those for C=C and C—O—C occurred with slight shift at 1703 and 1119.4 cm^{-1}, respectively
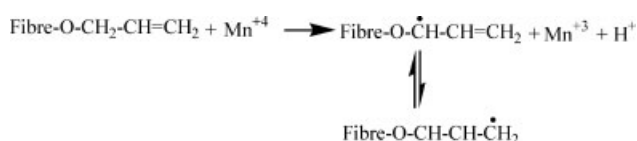
Confirmation of grafting of acrylonitrile onto the allyl fibers is provided by C≡N stretching vibration at around 2200 cm^{-1}. The absorption peak at about 1680 cm^{-1} characteristics of C=O stretching vibration for tertiary amide is an evidence for termination of graft polymerization reaction by N,N'-dimethylacetamide initiating radical species i.e.
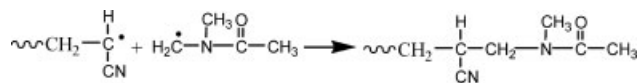
Effect of potassium permanganate on grafting acrylonitrile on caesarweed fibers and on the allyl derivative

Figure 3 shows the effect of potassium permanganate on graft copolymerization of acrylonitrile onto

unmodified and allyl modified caesarweed fibers in the absence of N,N'-dimethylacetamide (DMAc). In both cases, the graft yields are high but higher for the unmodified fibers. At $66.7 \times 10^{-3}M$ concentration of permanganate, the graft yield for the unmodified fibers is a factor of 2.3 higher than the corresponding value for the allyl derivatized fiber. The allylic hydrogen atom of the fiber is intrinsically labile and is expected, *a priori*, to be susceptible to oxidative abstraction by permanganate to yield an allylic radical species. The latter is resonance-stabilized in contrast to an alkoxyl radical species derivable from the unmodified fiber i.e.

$$\text{Fibre-O-CH}_2\text{-CH=CH}_2 + \text{Mn}^{+4} \longrightarrow \text{Fibre-O-}\overset{\bullet}{\text{C}}\text{H-CH=CH}_2 + \text{Mn}^{+3} + \text{H}^+$$

$$\text{Fibre-O-CH-CH-}\overset{\bullet}{\text{C}}\text{H}_2$$

The resultant effects of resonance stabilization of allylic radical species are the ready formation of the latter and its lower reactivity for graft copolymerization reaction. The latter explains the observed lower graft yields for the allyl fibers. For the graft copolymerization of methylmethacrylate onto allyl-modified plantain pulp initiated by ceric ions, the presence of allylmoiety on the fibers enhanced the graft yields, albeit nominally. For the unmodified fiber in Figure 3, permanganate concentrations higher than 66.7×10^{-3} are inimical to grafting and suggests termination of the reactive alkoxyl macroradicals of the fiber by permanganate.

Effect of N,N'-dimethylacetamide on graft yield

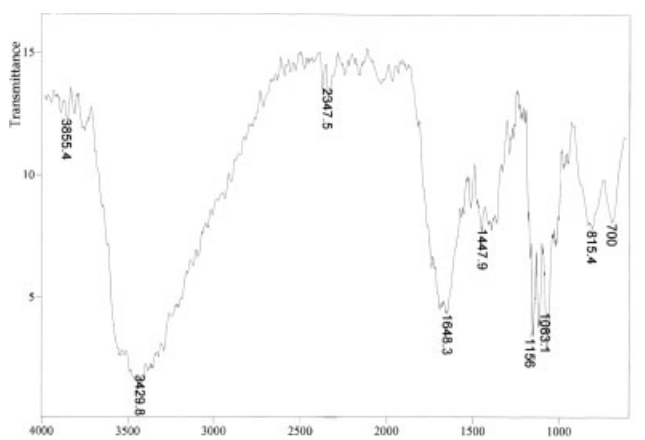The effect of N,N'-dimethylacetamide (DMAc) on grafting acrylonitrile onto allylfiber is shown in Fig-

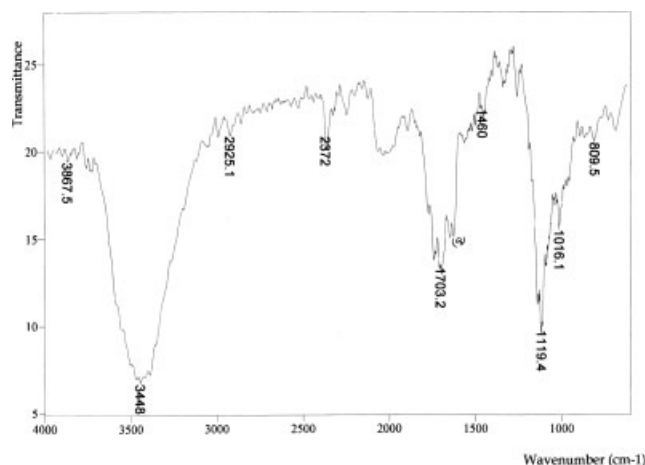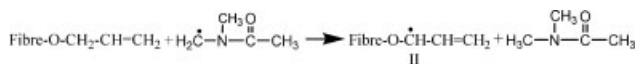**Figure 1**   Infrared spectrum for allylfiber.

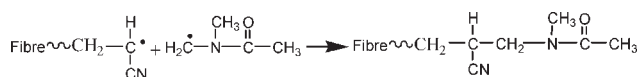**Figure 2**   Infrared spectrum for allylfiber-g-polyacrylonitrile copolymer.

ure 4. The yield increases with DMAc concentration in the range, $9.0–45.0 \times 10^{-4}M$ at 30°C. The ratio of percentage graft, P_g/P_{go} in the presence and absence of DMAc, respectively, is greater than unity with values of up to 1.39 at the highest concentration of DMAc. Of interest is the apparent reactivity of DMAc in combination with permanganate for grafting of acrylonitrile on allyl fibers under ambient temperature conditions. This is in contrast to N,N'-dimethylaniline, which in redox pair with cupric ion, was inactive for grafting methylmethacrylate onto natural rubber under ambient temperature conditions.[10] In a redox pair with permanganate, a methylacetylamino methyl initiating radical species (I) may be formed from DMAc as follows:

$$\text{CH}_3\overset{\overset{O}{\|}}{\text{C}}-\overset{\overset{CH_3}{|}}{\text{N}}-\text{CH}_3 + \text{Mn}^{+4} \longrightarrow \text{CH}_3-\overset{\overset{O}{\|}}{\text{C}}-\overset{\overset{CH_3}{|}}{\text{N}}-\overset{\bullet}{\text{C}}\text{H}_2 + \text{Mn}^{+3} + \text{H}^+$$
$$\text{I}$$

Interaction of species I with allyl fiber leads to formation of allyl fiber macro radicals (II) i.e.,

$$\text{Fibre-O-CH}_2\text{-CH=CH}_2 + \text{H}_2\overset{\bullet}{\text{C}}-\overset{\overset{CH_3}{|}}{\text{N}}-\overset{\overset{O}{\|}}{\text{C}}-\text{CH}_3 \longrightarrow \text{Fibre-O-}\overset{\bullet}{\text{C}}\text{H-CH=CH}_2 + \text{H}_3\text{C}-\overset{\overset{CH_3}{|}}{\text{N}}-\overset{\overset{O}{\|}}{\text{C}}-\text{CH}_3$$
$$\text{II}$$

From the conversion in graft yield in Figure 4, it can be seen that it approaches a plateau at the highest concentration of DMAc. This is attributable to possible termination of graft polymer chains by species I i.e.,
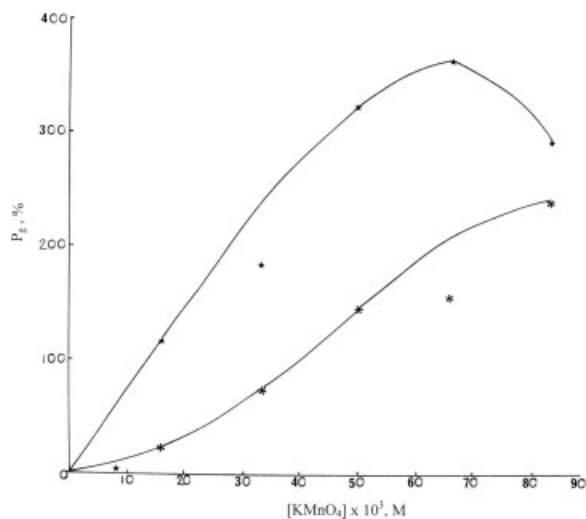
$$\text{Fibre}\sim\sim\text{CH}_2-\overset{\overset{H}{|}}{\underset{\underset{CN}{|}}{\text{C}}}{}^{\bullet} + \text{H}_2\overset{\bullet}{\text{C}}-\overset{\overset{CH_3}{|}}{\text{N}}-\overset{\overset{O}{\|}}{\text{C}}-\text{CH}_3 \longrightarrow \text{Fibre}\sim\sim\text{CH}_2-\overset{\overset{H}{|}}{\underset{\underset{CN}{|}}{\text{C}}}-\text{CH}_2-\overset{\overset{CH_3}{|}}{\text{N}}-\overset{\overset{O}{\|}}{\text{C}}-\text{CH}_3$$

Figure 3 Effect of permanganate concentration on graft yield $[H^+] = 0.61M$; $[AcOH] = 0.56M$; $[AN]$ 0.31M; fiber = 0.1 g; POT = 10 min; temperature = 30°C; time = 3 h; (☆☆) unmodified fiber; (*) allylfiber.

Evidence in support of this reaction is seen in the absorption peak at 1680 cm^{-1} for the infrared spectra for the graft copolymer (Fig. 2) which is characteristics of C=O stretching vibration for tertiary amide.

Effect of acetic acid on graft yields

Acetic acid was added to the reaction medium to facilitate the solubility of acrylonitrile in aqueous medium. Figure 5 shows the effect of acetic acid on graft yield at 30°C. In the concentration range, 0–1.1M, graft yield is reduced by acetic acid with P_g/P_{go}, of 0.58 at the latter concentration of the acid. The reduction in yield may be attributed to transfer reac-
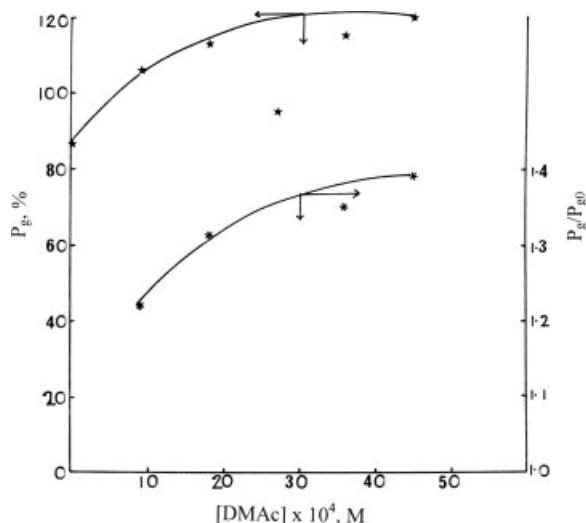

Figure 4 Effect of DMAc concentration on yield for grafting onto allylfiber $[H^+] = 0.61M$; $[AcOH] = 0.56M$; $[AN] = 0.31M$; $[KMnO_4] = 33.3 \times 10^{-3}M$; fiber = 0.1 g; POT = 10 min; temperature = 30°C; time = 3 h.
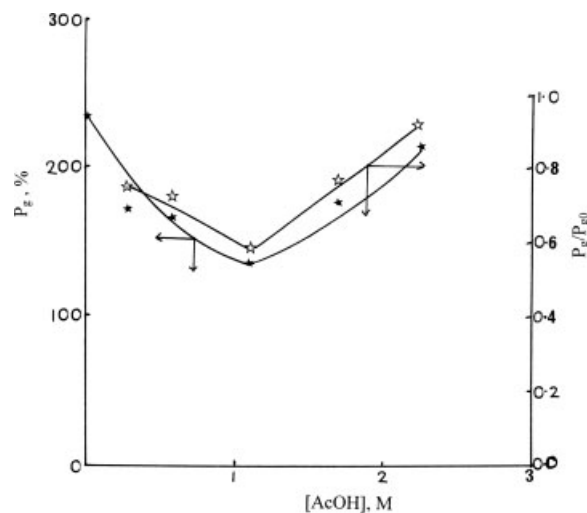
Figure 5 Effect of acetic acid on yield for grafting onto allylfiber. $[H^+] = 0.61M$; $[DMAc] = 18.0 \times 10^{-4}M$; $[KMnO_4] = 33.3 \times 10^{-3}M$; $[AN] = 0.31M$; fiber = 0.1 g; POT = 10 min; temperature = 30°C; time = 3 h.

tions involving acetyl radicals derivable from acetic acid and the attendant homopolymer formation.[12]

However, at higher concentrations of the acid, P_g/P_{go} increases, albeit less than unity and suggests an enhanced lability of abstractable allylic hydrogen atom and increased concentration of fiber macroradicals for graft reaction.

Effect of allylfibre weight on graft yield

Table I shows the effect of allylfiber weight on graft yield. Graft yield decreases with increase in allylfiber weight in the range, 0.1–0.6 g. This is consistent with low reactivity of resonance-stabilized allylfiber radicals, low percentage efficiency in monomer conversion to graft polymer (not higher than 24%) and the disproportionate effect of the increase in fiber weight on graft yield.

Effect of temperature on grafting

The time-temperature conversion in the temperature range, 30–50°C for the graft polymerization reaction is shown in Figure 6. It can be seen that the graft yield increases with temperature and from the conversion,

TABLE I
Effect of Fiber Weight on Graft Yield

Allylfibre, g	Graft, %
0.2	72.2
0.3	28.1
0.5	27.6
0.6	9.8

$[H^+] = 0.61M$; $[AcOH] = 0.56M$; $[DMAc] = 18.0 \times 10^{-4}M$; $[KMnO_4] = 33.3 \times 10^{-3}M$; $[An] = 0.31M$; POT = 10 min; temperature = 30°C; time = 3 h.

the initial rates of reaction permit a calculation of the activation energy for the graft polymerization reaction via an Arrhenius plot represented in Figure 7. The calculated activation energy is 12.3 kcal mol^{-1} and is consistent with the observed low reactivity of the allylfiber towards graft polymerization reaction.

CONCLUSIONS

Chemical modification of caesarweed fibers by allyllation yielded value of 2.73 mol of allyl moiety per anhydroglucose unit. The substitution was confirmed by infrared spectroscopy.

Potassium Permanganate – N,N'-dimethylacetamide redox pair was effective for initiation of graft copolymerization of acrylonitrile onto unmodified and allyl-modified fibers. The allylfiber was less reactive than the unmodified fiber for graft polymerization with graft yields for the latter a factor of 2.3 higher than those of the former. This was attributed to resonance stabilization of allylic macroradicals of the allylfiber.

Graft yield showed positive dependence on N,N'-dimethylacetamide concentration in the range, 9.0–4.50 × 10^{-4}M with P_g/P_{go}, of up to 1.39 at the highest concentration. However, at the latter concentration, there was termination of grafted polymer chains by methylacetylaminomethyl radical initiating species. This was corroborated by the absorption
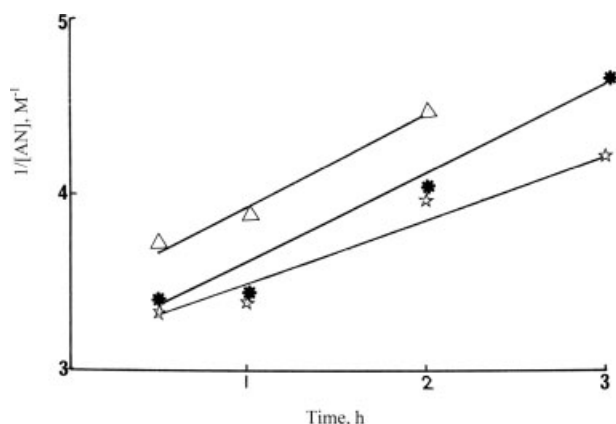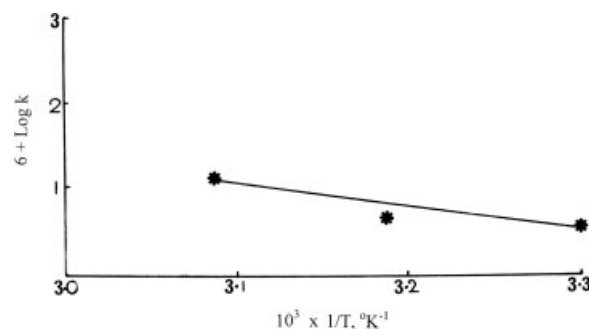

Figure 7 Arrhenius plot of rate of graft versus reciprocal of temperature.

peak at 1680 cm^{-1} of the infrared spectrum for the graft copolymer characteristics of C=O stretching vibration for tertiary amide.

Acetic acid in the concentration range, 0.28–2.22M was inimical to the graft reaction with P_g/P_{go}, less than one and was attributed to transfer reactions by the acid and concomitant homopolymer formation.

Grafting of acrylonitrile onto allylfiber showed positive dependence on temperature in the range, 30–50°C with calculated activation energy of 12.3 kcal mol^{-1} for the graft polymerization reaction.

Figure 6 Effect of temperature on yield for grafting onto allylfiber [H$^+$] = 0.61M; [AcOH] = 0.56M; [DMAc] = 36.0 × 10^{-4}M; [KMnO$_4$] = 33.3 × 10^{-3}M; [AN] = 0.31M; (☆) 30°C; (✳) 40°C; (Δ) 50°C.

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