

Graft Copolymerization of Acrylonitrile onto Allylated Caesarweed Fibres by Ceric Ion in the Presence of 2-Mercaptoethanol

C. O. Eromosele, Q. O. Afolabi, I. C. Eromosele

Department of Chemistry, University of Agriculture, P.M.B.2240, Abeokuta, Ogun State, Nigeria

Received 25 June 2007; accepted 14 January 2008

DOI 10.1002/app.28183

Published online 27 August 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Polyacrylonitrile was grafted onto caesarweed fibers and on the allyl derivative in aqueous media by ceric ion-2-mercaptoethanol redox pair. The allylfibre was obtained by treatment of caesarweed fibers with sodium hydroxide followed by allylchloride in diisopropylether to yield an average degree of substitution of 3.24 allyl moieties per anhydroglucose unit (AGU). The graft yield dependence on 2-mercaptoethanol concentration, in the range, $10.7\text{--}64.0 \times 10^{-4}M$ was characterized by a minimum followed by an enhanced yield. This suggested the existence of two initiating species, a thioglycol radical and mercaptoethoxyl radical. A fivefold increase in the concentration of 2-mercaptoethanol was accompanied by reduction in the frequency of graft, F_g from $75.6\text{--}0.79 \text{ Ng}/10^4 \text{ AGU}$ and a concomitant increase, by two orders of magni-

tude, in the average molecular weight of grafted polymer M_v , with values of up to 11.78×10^5 . Infrared spectroscopy of allylfibre-g-polyacrylonitrile copolymer showed evidence of radical coupling reaction involving thioglycol radical species and allylic macroradicals of the allylfibre. The unmodified fiber was more reactive than the allylfibre by as much as a factor of 2, and was ascribed to resonance stabilization of allylic macro radicals derived from the latter. For the allyl fiber, a 150% increase in monomer concentration resulted in nominal increase in graft yield, not higher than 7%. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2796–2801, 2008

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

INTRODUCTION

Graft copolymerization reactions are effective for imparting desired properties on polymeric substrates.^{1–3} The use of oxidants in a redox pair with readily oxidizable organic compounds have been reported.^{4–10} The yields of graft copolymer, and overall grafting characteristics are dependent, in part, on the reactivities of the monomer and of the initiating species derivable from the redox pairs. For the graft copolymerization of acrylonitrile on kenaf fibers by ceric ion-*p*-xylene redox pair in aqueous medium, the observance of two kinetically-controlled reactions was associated with the presence of two precursor initiating species, a *p*-xylyl radical and a diradical.¹¹ Similarly, chemical modification of cellulose substrates prior to grafting can influence the course of reaction.^{12–15} For grafting of methyl methacrylate onto plantain pulp, allylation of the latter markedly enhanced the extent of graft polymer formation¹⁴ in contrast to lower graft yield observed for the thiolated derivative.¹⁵

Caesarweed, *Urena lobata*, is of the mallow family, Malvaceae, 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 closely resemble jute, but somewhat shorter and coarser.

This study is on grafting of acrylonitrile onto allylated caesarweed fibers initiated by ceric ion-2-mercaptoethanol redox pairs. The grafting characteristics, molecular weight of grafted polymer and frequency of graft are presented and discussed.

EXPERIMENTAL

Material

Ceric ammonium nitrate, glacial acetic acid, nitric acid, and 2-mercaptoethanol (MET) were used without further purification. Acrylonitrile (AN; Aldrich Corp) was washed successively with 5% aqueous sodium hydroxide and 5% sodium chloride. It was dried over anhydrous calcium chloride and fractionally distilled. Caesarweed plants were obtained locally in Abeokuta, Nigeria.

Methods

The bast fibers from caesarweed plant were air dried and beaten in a mortar. The fibers were treated with

Correspondence to: I. C. Eromosele (iceromosele@yahoo.com).

10% sodium sulfite to obtain a holocellulose as previously reported.¹⁶ It was bleached with aqueous sodium hypochlorite solution and air-dried. A portion of the bleached holocellulose was allylated. Specifically, 7 g of the fiber was reacted with 150 mL 20 wt %, aqueous sodium hydroxide solution at 0°C for 20 min, filtered and dried. It was then refluxed for 3 h with 50 wt % solution of allylchloride in 80 mL diisopropyl ether.¹⁴ The allylcellulose was washed several times with diisopropyl ether to remove excess allylchloride and air-dried. The amount of allyl moiety in the fiber was determined by reacting 0.5 g of the latter with 25 mL of 0.1M iodine solution for an hour followed by back titration with 0.05M thiosulphate solution.¹⁴ The titration was replicated and the average titer was used to determine the allyl content of the fiber by the equation

$$N = \frac{(V_o - V_t) \times M_t \times 162}{W_s \times 127}$$

where N is the number of moles of allylchloride per anhydroglucose unit (AGU) of the fiber, V_o and V_t the blank and sample titer values, respectively, M_t , the molarity of the thiosulphate solution and W_s is the weight of the allylfibre. From eq. (1), the number of allyl moiety per anhydroglucose unit was 3.24.

Graft copolymerization reaction was conducted by the method described by Lepoutre and Hui¹⁷ as reported previously.¹⁶ Specifically, a redox interaction of the ceric ions and 2-mercaptoethanol was allowed to occur in the reaction medium for a given time, the preoxidation time (POT), before 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, followed by immediate filtration of the product. The ungrafted polyacrylonitrate (PAN) homopolymer was extracted from the product with N,N' -dimethylformamide and the graft copolymer residue air-dried and weighed. 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 W_1 , W_2 and W_3 are the weights of the fiber, the grafted fiber, and the monomer, respectively.

Isolation of the grafted polymer from the fiber was conducted by hydrolysis of the graft copolymer in 30% sodium hydroxide for 2 h. The hydrolysate was filtered hot on a Buchner funnel, washed several times with distilled water and dried at 40°C. The grafted polymer was extracted with N,N' -dimethylformamide and the average molecular weight determined from the viscosity of the N,N' -dimethylforma-

mid solution at 30°C using the Mark-Houwink equation,¹⁸ $[\eta] = 2.09 \times 10^{-4} M_v^{0.75}$

The frequency of graft, F_g defined as moles of grafted PAN per 10^4 anhydroglucose unit (AGU), was determined from the relation $F_g = N_g M_o \times 10^4$, 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 one AGU.¹⁴

Infrared spectroscopy

The infrared spectroscopy of allylfiber and graft copolymer was conducted on Infrared Spectrophotometer model FTIR Niconet Appata Series 330 using potassium bromide (KBr) pellet.

RESULTS AND DISCUSSION

Infrared spectroscopy of unmodified and modified fibers

The infrared spectra for unmodified fibers, the allyl-derivative, and allylfiber-g-polyacrylonitrile copolymer are represented in Figures 1–3. In Figure 1, the peak at 3446.34 cm^{-1} is associated with unbounded hydroxyl groups of the anhydroglucose unit. In Figure 2, the peak at 1646.18 cm^{-1} is associated with C=C stretching vibration.¹⁹ Together with the C—O—C stretch at 1155.65 cm^{-1} and allylic C—H bending vibrations at 898.92 and 849.70 cm^{-1} , the presence of an allylic moiety on the fiber is confirmed. From the number of moles of allyl moiety per anhydroglucose unit, that is 3.24, the three hydroxyl groups of the latter are fully substituted. This is corroborated by the absence of a sharp peak at 3446.34 cm^{-1} in Figure 2.

For Figure 3, the C=C stretching vibration and C—O—C stretch occurred, with a slight shift, at 1635.93 cm^{-1} and 1203.08 cm^{-1} , respectively. Similarly, the allylic C—H bending vibration is shifted slightly to 897.32 cm^{-1} . The C≡N stretching vibration from acrylonitrile repeat unit in the graft copolymer occurred at 2360.46 cm^{-1} . The peak at 1428.37 cm^{-1} is associated with C—S—C stretching vibration and suggests radical termination by coupling between the allylic radical of the fibers and thioglycol radical species.

Effect of 2-mercaptoethanol concentration on grafting of acrylonitrile on caesarweed fibers and allyl derivative by ceric ion

Figure 4 shows the effect of 2-mercaptoethanol (MET) concentration on the graft copolymerization of acrylonitrile on caesarweed fibers and allyl derivative by ceric ions in aqueous media. Percentage graft (P_g) decreases initially to a minimum and then increases to a maximum over MET concentration range, $10.7\text{--}64.0 \times 10^{-4} \text{ M}$ for both the unmodified

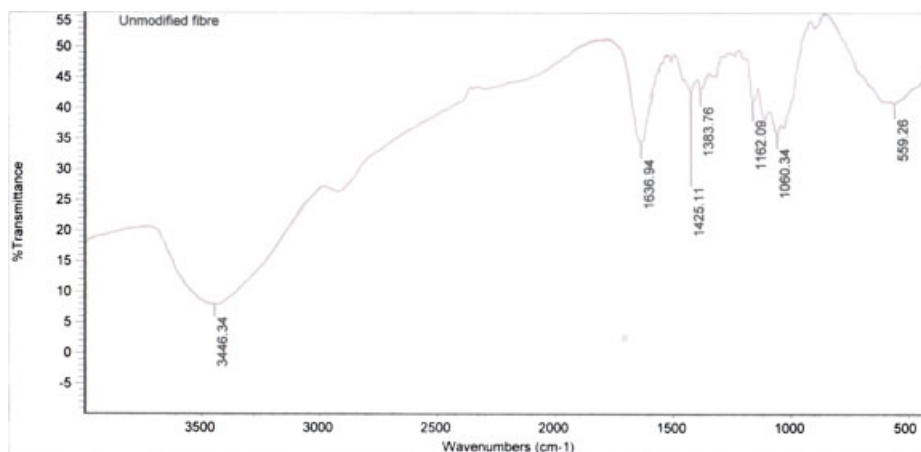
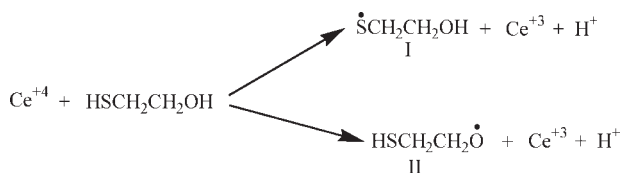


Figure 1 Infrared spectrum for unmodified caesarweed fibers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and allyl-modified fibers. It is evident from Figure 4 that for both fibers, the minimum graft yields occurred at MET concentration of $32.0 \times 10^{-4}M$. For ceric ion-MET redox pair, two initiating radical species may be formed as follows:



Since the redox reaction is by hydrogen abstraction, kinetically, the thioglycol radical species (I) is more readily formed than the 2-mercaptoethoxyl radical species II. Thus, the observed minima and maxima graft yields suggest that the two species are involved in the graft reactions. The initial decrease in graft yield with increase in MET concentration

may arise from two possible termination reactions namely, (i) chain transfer to MET by ceric ion – initiated allylic macroradicals via hydrogen abstraction (ii) termination of allylic macroradicals on the fiber by coupling reactions of the latter with thioglycol radical species (I). The former would lead to low graft yield, homopolymer formation and reduction in the average molecular weight of grafted polymer. It is therefore inconsistent with the observed effect of MET on molecular weight and frequency of graft of grafted polymer as shown in Table I. In the latter Table, it is evident that for a fivefold increase in MET concentration, there is reduction in frequency of graft, F_g by two orders of magnitude i.e., $75.6\text{--}0.79 \text{ Ng}/10^4 \text{ AGU}$, and a concomitant increase, by the same order of magnitude, in the average molecular weight of grafted polymer, i.e., $0.14\text{--}11.78 \times 10^5$. Thus, the second mode of termination as mentioned above is plausible and is consistent with the observations in Table I. This is corroborated by the presence of C—S—C stretching vibration at 1428.37 cm^{-1} in

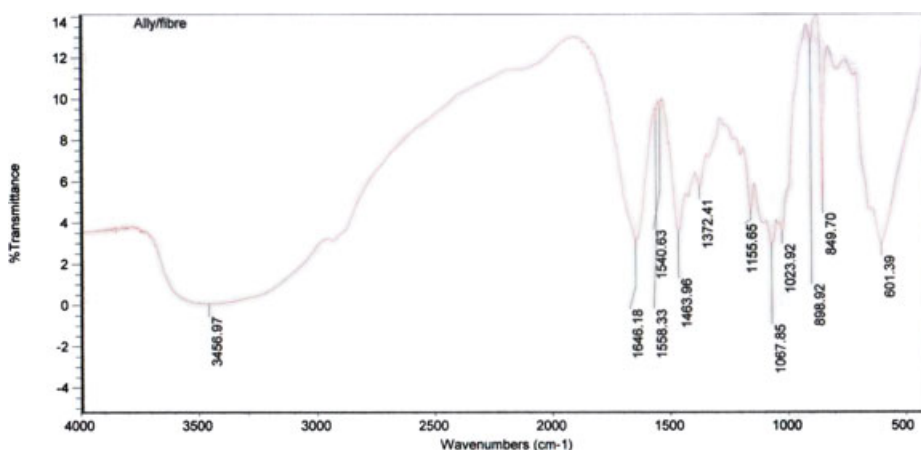


Figure 2 Infrared spectrum for allylfibers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

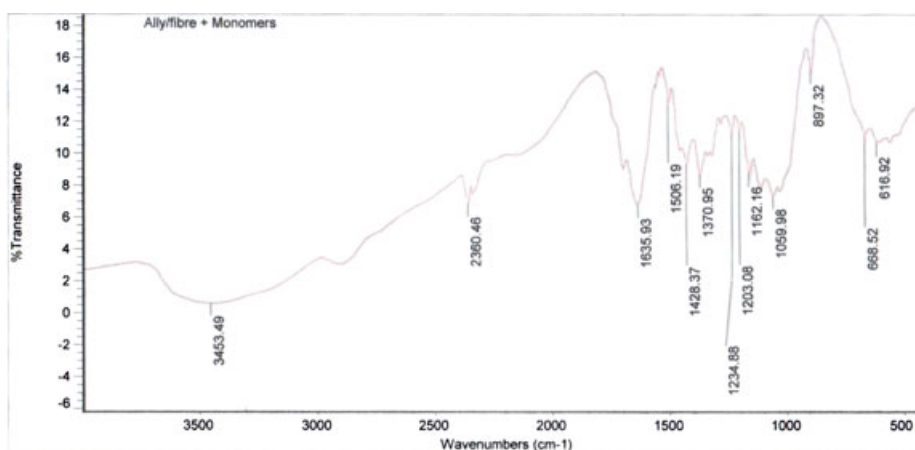


Figure 3 Infrared spectrum for allylfibres-g-polyacrylonitrile copolymer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 3 earlier associated with coupling reactions of thioglycol radical species (I) with allylic radicals of the fiber derivative. The preponderant effect of the latter reaction is reflected by the ratios of percentage graft, P_g/P_{g0} , in the presence and absence of MET, respectively, which are less than unity and the corresponding M_v/M_{v0} ratios of up to 4.31.

The greater reactivity of the unmodified fibers is evident in Figure 4 from the higher graft yields compared with the corresponding ones for the allyl derivative. Lower reactivity of the latter is to be expected since allylic radical compounds are resonance-stabilized with consequent reduction in their reactivities with monomers for graft reaction i.e.



At 32.0×10^{-4} M MET concentration, the graft yield for the unmodified fiber (81.3%) is about a factor of 2 higher than the corresponding value (44.5%) for the allyl derivative.

Effect of ceric ion concentration on grafting of acrylonitrile on caesarweed fibers and allyl derivative

The graft yield profile is also characterized by the occurrence of minimum and maximum yields in the ceric ion concentration range, $16.7\text{--}58.3 \times 10^{-3}\text{M}$ as shown in Figure 5. The explanation for this phenomenon in Figure 4 is applicable. The minimum and maximum graft yields occur at ceric ion concentrations of 25.0×10^{-3} and $41.7 \times 10^{-3}\text{M}$ respectively, for the unmodified fiber and allyl derivative at 30°C . At the latter concentration of ceric ions, the graft yield for the unmodified fibers, 106.5%, is a factor of 2 higher than the corresponding value, 55.8% for the allyl derivative. The increase in graft yield in the ceric ion concentration range, $25.0\text{--}41.7 \times 10^{-3}\text{M}$, suggests a preponderance of ceric ion-initiated macro radicals on the fibers for the graft reaction processes.

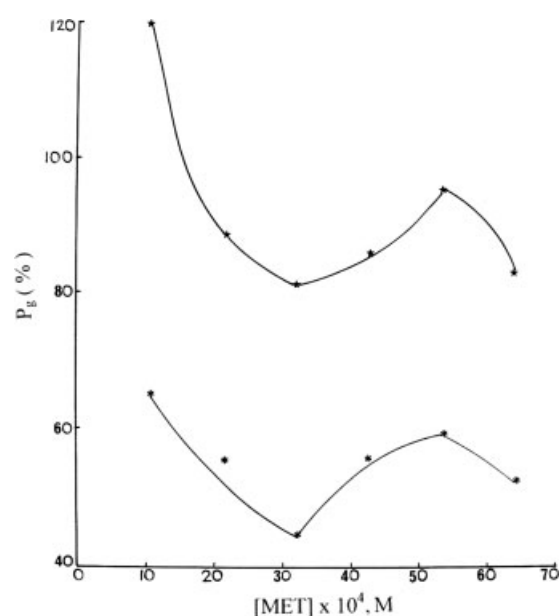


Figure 4 Effect of MET concentration on graft yield for grafting of AN to caesarweed fibers and allyl derivative. $[\text{AcOH}] = 0.56\text{M}$; $[\text{Ce}^{+4}] = 33.3 \times 10^{-3}\text{M}$; $[\text{AN}] = 0.31\text{M}$; $[\text{H}^+] = 0.52\text{M}$; Fiber = 0.1 g; POT = 10 min; time = 3 h; temperature = 30°C ; (\star) unmodified; (\ast) allyl derivative.

TABLE I
Effect of 2-Mercaptoethanol on Graft Yield, Molecular Weight and Frequency of Graft on Allylfibre

[MET] (M)	P_g (%)	P_g/P_{go}	$M_v \times 10^5$	M_v/M_{vo}	F_g ($N_g/10^4$ AGU)
0	74.9	—	2.73	—	4.37
10.7	65.5	0.87	0.14	0.05	75.6
21.3	55.8	0.74	0.23	0.08	39.2
32.0	44.5	0.59	1.01	0.36	7.12
42.7	55.9	0.75	1.90	0.69	4.76
53.3	59.3	0.79	11.78	4.31	0.79

[AcOH] = 0.56M; $[Ce^{+4}] = 33.3 \times 10^{-3}M$; [AN] = 0.31M; $[H^+] = 0.52M$; Fiber = 0.1 g; POT = 10 min; time = 3 h; temperature = 30°C.

Effect of monomer concentration on graft yield

Figure 6 shows the effect of monomer concentration on graft yield. For the unmodified fibers, the graft yield increases with monomer concentration in the range 0.63 – $6.29 \times 10^{-1}M$. At higher concentrations, the graft yield decreases and may be ascribed to an enhanced homopolymer formation. For the allyl derivative, the graft yields are lower than the corresponding values for the unmodified fibers by as much as 41%. Furthermore, the graft yield profile for the allyl derivative shows an initial decrease in yield with increase in monomer concentration in the range, 0.63 – $6.29 \times 10^{-1}M$. This suggests a dominant homopolymerization reaction initiated by thioglycol radical species(I), accentuated by the intrinsically low reactivity of allyl macro radical towards graft reaction. The latter is corroborated by the nominal increase in graft yield, not higher than 7% for a 150% increase in monomer concentration.

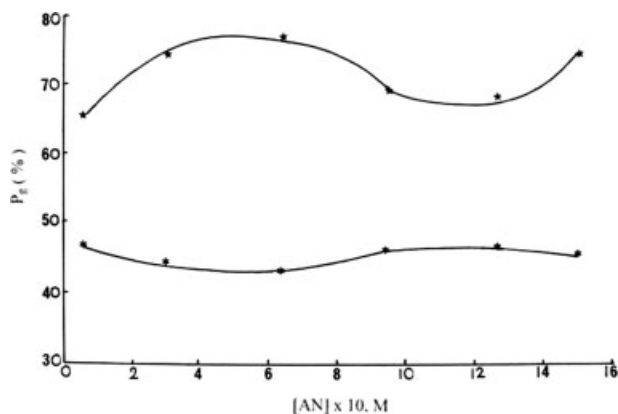


Figure 5 Effect of monomer concentration on graft yield. $[H^+] = 0.52M$; [AcOH] = 0.56M; [MET] = $21.3 \times 10^{-4}M$; $[Ce^{+4}] = 33.3 \times 10^{-3}M$; fiber = 0.1 g; POT = 10 min; time = 3 h; temperature = 30°C; (☆) unmodified; (*) allyl derivative.

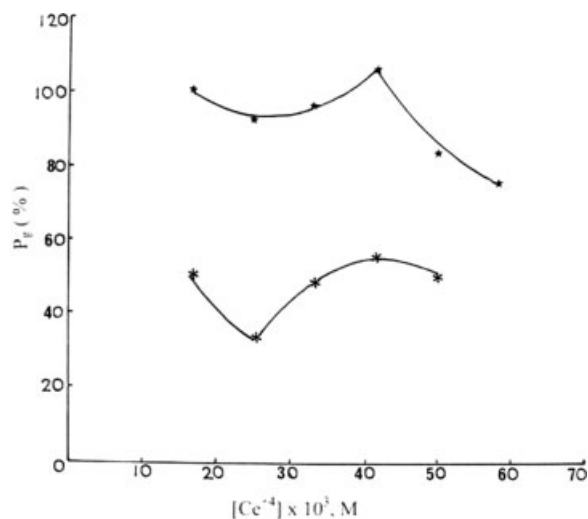


Figure 6 Effect of ceric ion concentration on graft yield for grafting of AN to caesarweed fibers and allyl derivative. $[H^+] = 0.52M$; [AcOH] = 0.56M; [MET] = $10.7 \times 10^{-4}M$; [AN] = 0.31M; fiber = 0.1 g; POT = 10 min; time = 3 h; temperature = 30°C; (☆) unmodified; (*) allyl derivative.

Effect of acetic acid on grafting onto allylfibres

Table II shows the effect of acetic acid on grafting of acrylonitrile on allylfibres. Graft yield increases with acetic acid concentration, albeit nominally, in the range, 0.28–0.83M and thereafter decreases. For up to a fivefold increase in acetic acid concentration, the effect on the graft yield is not higher than $\pm 4\%$ of its value at zero concentration of the acid. The decrease in graft yield at higher concentrations of acetic acid is usually associated with transfer reactions by acetyl radicals.^{20,21}

CONCLUSIONS

Grafting of acrylonitrile onto caesarweed fibers and on its allyl derivative by ceric ion in the presence of 2-mercaptoethanol in aqueous media gave graft yields that were lower for the allylfiber, attributed to resonance stabilization of macro radicals of the latter. The graft yield profiles for both fibers showed a

TABLE II
Effect of Acetic Acid on Grafting Acrylonitrile onto Allylfibre

[AcOH] (M)	P_g (%)	P_g/P_{go}
0	46.5	—
0.28	44.8	0.96
0.56	46.4	0.99
0.83	47.4	1.02
1.11	47.3	1.02
1.39	45.8	0.98

[MET] = $21.3 \times 10^{-4}M$; $[H^+] = 0.52M$; $[Ce^{+4}] = 33.3 \times 10^{-3}M$; [AN] = 0.31M; Fiber = 0.1 g; POT = 10 min; time = 3 h; temperature = 30°C.

characteristic minimum followed by a maximum graft yield at certain concentrations of 2-mercaptoethanol and suggested the presence of two initiating species, a thioglycol radical and 2-mercaptoethoxyl radical.

Infrared spectroscopy showed radical coupling reaction between the thioglycol radical and allylic macro radical of the allylfiber with consequent reduction in the frequency of graft. A fivefold increase in the concentration of 2-mercaptoethanol was accompanied by reduction in the frequency of graft, F_g from 75.6–0.79 $N_g/10^4$ AGU and a corresponding increase, by two orders of magnitude, in the average molecular weight of grafted polymer, M_v with values of up to 11.78×10^5 .

References

1. Hebeish, A.; Guthrie, J. T., Eds. *The Chemistry and Technology of Cellulosic Copolymers*; Springer-Verlag: Berlin, 1981.
2. Arayaprane, W.; Prasassarakich, P.; Rempel, G. L. *J Appl Polym Sci* 2002, 83, 2993.
3. Padma, L. N.; Subasini, L.; Nsrusingha, C. P. *J Polym Sci Polym Chem Ed* 1979, 17, 3425.
4. Mohanty, A. K.; Singh, B. C.; Mishra, M. *J Appl Polym Sci* 1986, 31, 1763.
5. Samal, R. K.; Satrusallya, S. C.; Sahoo, P. K. *J Appl Polym Sci* 1984, 29, 319.
6. Misra, M. *J Appl Polym Sci* 1987, 33, 2809.
7. Eromosele, C. O.; Oloye, M.; Eromosele, I. C. *J Appl Polym Sci* 2006, 101, 353.
8. Eromosele, I. C.; Eromosele, C. O.; Zanna, H. K. *J Appl Polym Sci* 2002, 84, 500.
9. Okieimen, F. E.; Ebhodaghe, J. E. *Macromol Rep A* 1996, 33 (Suppl 7 and 8), 401.
10. Eromosele, C. O.; Omoniyi, O. O.; Awolesi, O. R. *Nig J Polym Sci Technol* 2004, 4, 283.
11. Eromosele, I. C.; Agbo, A. *J Appl Polym Sci* 1999, 73, 1751.
12. Mohanty, A. K.; Tripathy, P. C.; Misra, M.; Parija, S.; Sahoo, S. *J Appl Polym Sci* 2000, 77, 3035.
13. Wang, L.; Xu, Y. *Iranian Polym J* 2006, 15, 467.
14. Okieimen, F. E.; Uroghide, I. N. *Die Angew Makromol Chemie* 1990, 182, 63.
15. Okieimen, F. E.; Idehen, K. I. *J Macromol Sci Chem A* 1987, 24, 1381.
16. Eromosele, I. C.; Hamagadu, T. J. *J Appl Polym Sci* 1993, 50, 645.
17. Lepoutre, P.; Hui, S. H. *J Appl Sci* 1975, 19, 1257.
18. Okieimen, F. E.; Idehen, K. I. *Eur Polym J* 1987, 23, 867.
19. Mu-shih, L.; Chung-Song, H. *J Polym Sci Part A: Polym Chem* 1992, 30, 2303.
20. Eromosele, I. C. *J Appl Polym Sci* 1994, 53, 1709.
21. Singh, B. C.; Misra, B. K.; Rout, A.; Mallick, N.; Rout, M. K. *Makromol Chem* 1979, 185, 953.