

# Graft Copolymerization of Acrylamide onto Carboxymethylcellulose with the Xanthate Method

Bothaina Abd El-Hady,<sup>1</sup> Maha M. Ibrahim<sup>2</sup>

<sup>1</sup>Polymer and Pigment Department, National Research Center, El-Tahrir Street, Dokki, Cairo, Egypt

<sup>2</sup>Cellulose and Paper Department, National Research Center, El-Tahrir Street, Dokki, Cairo, Egypt

Received 5 May 2003; accepted 19 December 2003

DOI 10.1002/app.20393

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

**ABSTRACT:** Acrylamide was grafted to an xanthate mixture of carboxymethylcellulose with a sodium bisulfate/ammonium persulfate redox initiator system in water, sodium hydroxide, potassium hydroxide, and dioxane at 40, 50, 60, 70, and 80°C during a reaction period of 2 h. The grafted polymer and homopolymer were isolated with diethyl ether from the reaction mixture, dried, and weighed. The grafted polymer was characterized with IR and mass spectrometry methods, and the microscopic morphology was detected with electron scanning microscopy. The graft

level percentage distinctly increased with the use of sodium hydroxide, potassium hydroxide, and dioxane over that of a reaction carried out completely in an aqueous medium. Also, the graft level decreased as the reaction temperature increased. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 271–278, 2004

**Key words:** initiators; infrared spectroscopy; mass spectrometry; electron microscopy

## INTRODUCTION

The chemical modification of natural polymers by grafting has received considerable attention in recent years because of the wide variety of monomers available.<sup>1</sup> Cellulose is a naturally occurring complex polysaccharide and the most abundant renewable raw organic material in the world. Graft polymerization has gained importance in the modification of the chemical and physical properties of pure cellulose and has been investigated in the last few decades.<sup>2</sup>

Cellulose has been demonstrated to be particularly useful for large beads (>300  $\mu\text{m}$  in diameter) and beads with low solid contents and high mechanical strength, without the need for crosslinking.<sup>3</sup> Unmodified cellulose, however, is useful neither for selective binding nor for dissolution in the usual solvents.<sup>4</sup> This is why cellulose derivatives [i.e., chemically modified cellulose with (active) functional groups installed before bead formation] would offer advantages for the formation of preactivated separation materials with a uniform distribution

of active sites and with simpler solvent systems.<sup>5</sup>

A lot of work has been reported on the grafting of various vinyl monomers onto cellulosic materials with different types of initiators.<sup>6–20</sup> The xanthate method of grafting is one of the most promising for industrial applications.<sup>21</sup> Takahashi and Takahashi<sup>22</sup> studied the graft copolymerization of acrylamide (AM) and AM/acrylic acid onto carboxymethylcellulose (CMC) in homogeneous and heterogeneous media with ammonium persulfate and ceric ammonium sulfate as initiators, respectively. They stated that the graft copolymerization on CMC proceeded by a radical mechanism.

In this work, the effects of the reaction temperature and different media on the graft copolymerization of AM onto CMC xanthate with a redox pair initiator (sodium bisulfate/ammonium persulfate) were investigated.

## EXPERIMENTAL

### Materials

All the reagents—AM (Merck, Schuchardt, Germany), CMC in its sodium salt form (CMCNa; degree of substitution = 0.7–0.85; Fluka, Buchs, Switzerland), carbon disulfide (Panreac, Egypt), sodium hydroxide

Correspondence to: M. M. Ibrahim (mwakleed@hotmail.com).

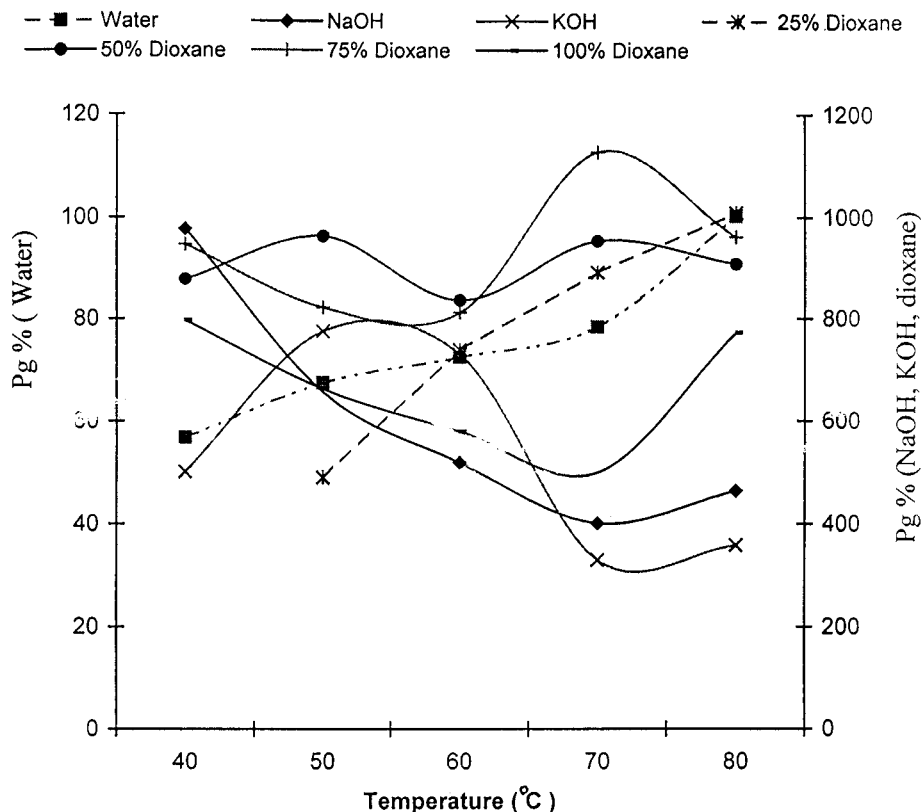


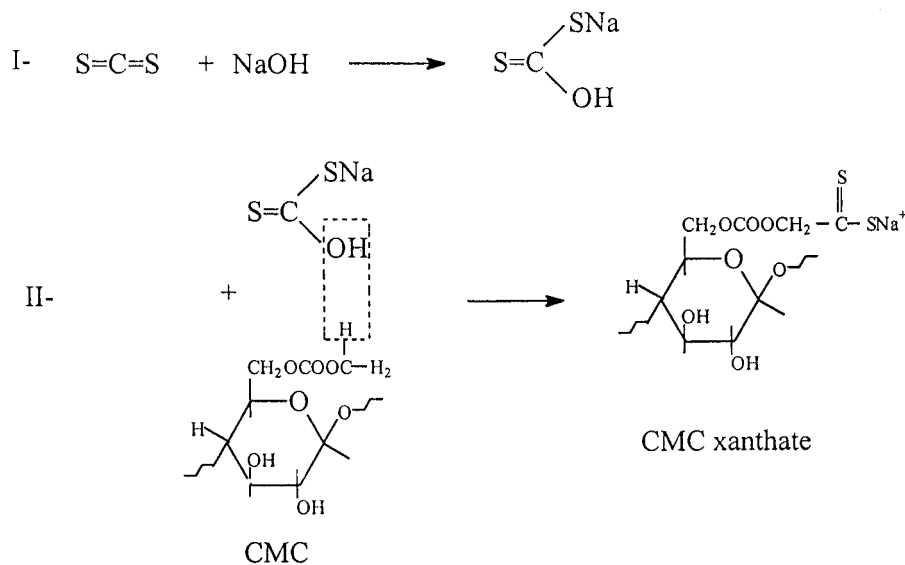
Figure 1 Effect of the reaction temperature on the grafting level (0.5% redox pair initiator, 2-h reaction time).

TABLE I  
Elemental Analysis of the Polymer Products

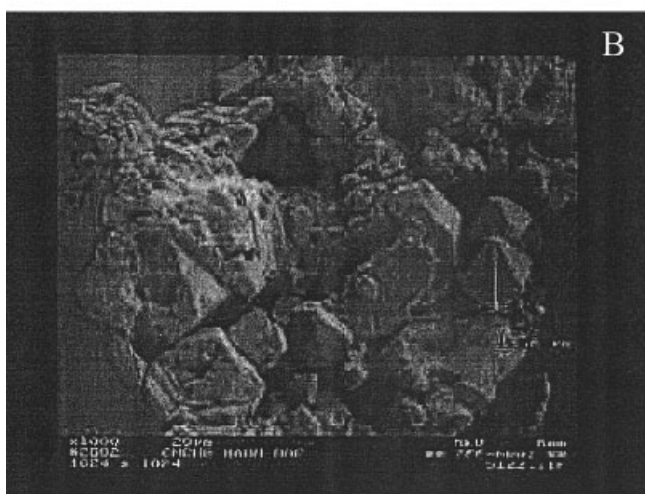
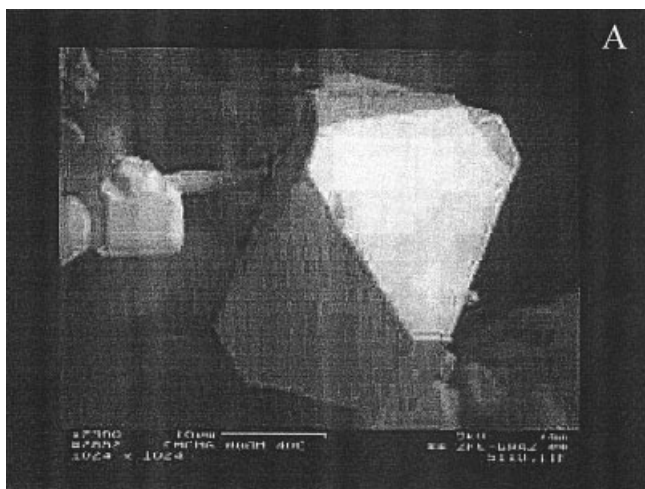
Medium	$P_g$ (%)	$N$ (%) <sup>a</sup>
Water	100.28	4.76
NaOH	464.52	5.71
KOH	358.28	5.31
25%	1009.34	5.81
50% dioxane	909.3	5.64
75%	962.18	5.78
100%	772.78	4.66

<sup>a</sup> From elemental analysis.

(NaOH; Fluka), sulfuric acid (Haby Chemicals, Egypt), hydrochloric acid (BDH, UK), potassium hydroxide (KOH; Merck), potassium dichromate (Aldrich, Gillingham, Dorset, UK), and dioxane (Fluka)—were used as received. Sodium bisulfate and ammonium persulfate (S.D. Fine Chemical, Ltd., Mumbai, India) were used as initiators. Diethyl ether (El Nasr



Scheme 1



**Figure 2** SEM micrographs of the grafted polymer at (A) 40 and (B) 80°C in NaOH.

Pharmaceutical Chemicals, Egypt) was used for precipitation.

## Methods

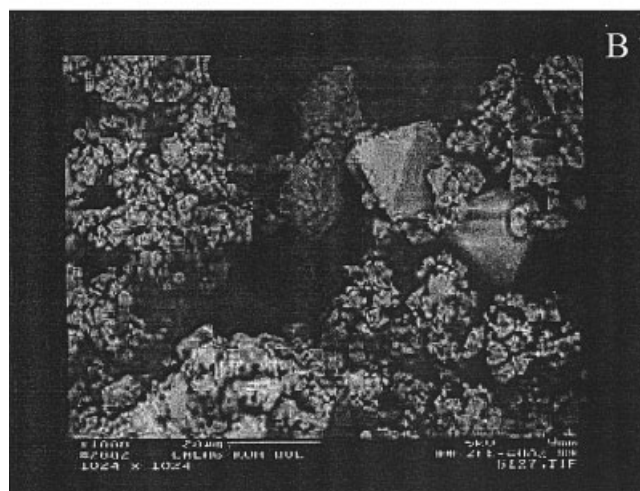
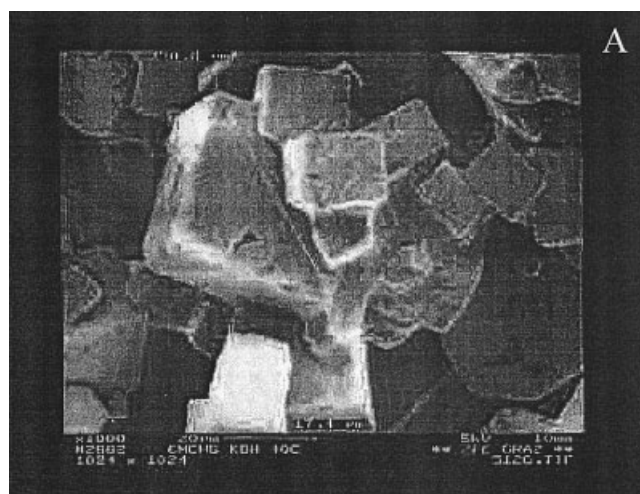
### Xanthation

CMCNa (1 g) was soaked in carbon disulfide (1.5 mL) for 10 min with constant shaking and was treated with an aqueous NaOH (12% w/v) solution for 4 h at 20°C with occasional shaking; a liquor ratio of 30:1 was maintained. The treated sample was then diluted with distilled water to 200 mL and centrifuged for 3 min; 10 mL of the solution was transferred to a 100-mL flask and neutralized with 5% sulfuric acid. The mixture was heated until fuming; then, 68% sulfuric acid (20 mL) was added, and the mixture was allowed to stand for 1 h with constant shaking. The treated mixture was refluxed with 1N potassium dichromate (10 mL) until

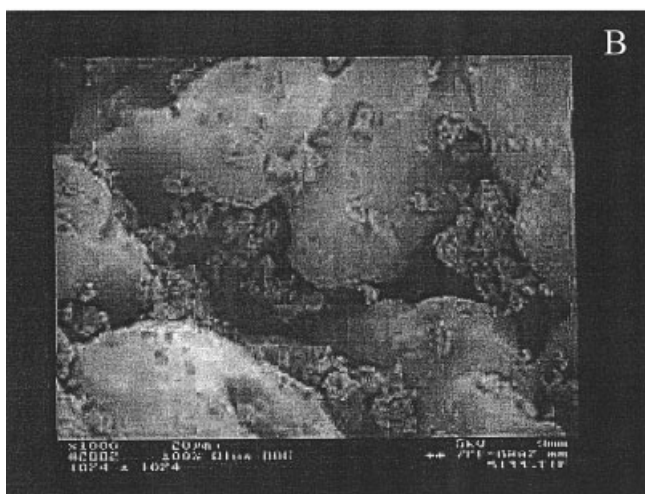
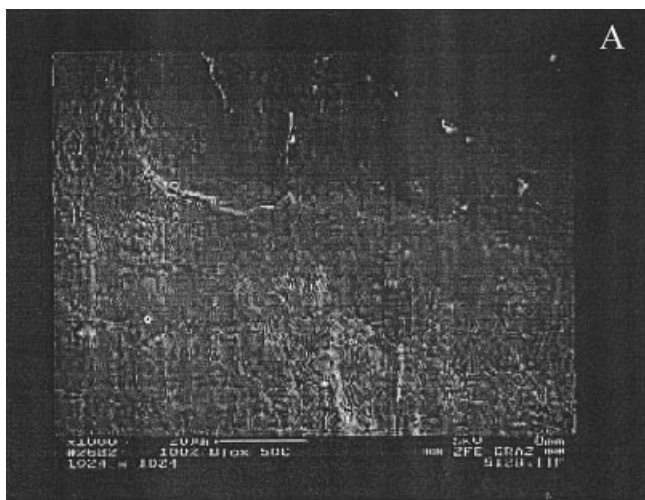
a clear solution was obtained. The xanthate solution was then allowed to cool to room temperature.

### Graft copolymerization

A solution of 0.5 g of CMC xanthate was added to a reaction mixture of 3 mL of AM (1.5 g) and a 0.5% redox pair initiator. The reaction was carried out by the flask being placed in a water bath at 40, 50, 60, 70, or 80°C for 2 h with constant shaking. The reaction was also undertaken with different media: 17.5% NaOH, 17.5% KOH, and different concentrations of dioxane (25, 50, 75, and 100%). After the desired reaction time had elapsed, the polymerization was stopped by the addition of hydrochloric acid to the reaction flask. The graft copolymer and homopolymer were separated by the addition of diethyl ether to the reaction mixture. The solution was filtered, the precipitated polymer was washed with diethyl ether, and the precipitate was then dried *in vacuo* at 60°C. The graft



**Figure 3** SEM micrographs of the grafted polymer at (A) 40 and (B) 80°C in KOH.



**Figure 4** SEM micrographs of the grafted polymer at (A) 50 and (B) 80°C in 100% dioxane.

level percentage ( $P_g$ ) is reported as the weight of the graft polymer, divided by the weight of the CMC xanthate used, multiplied by 100.

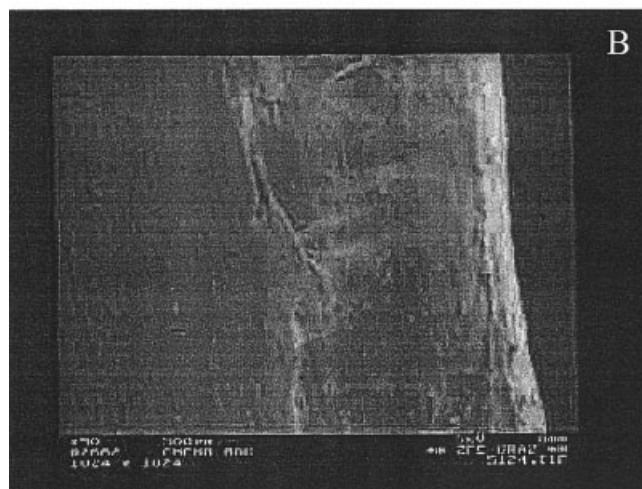
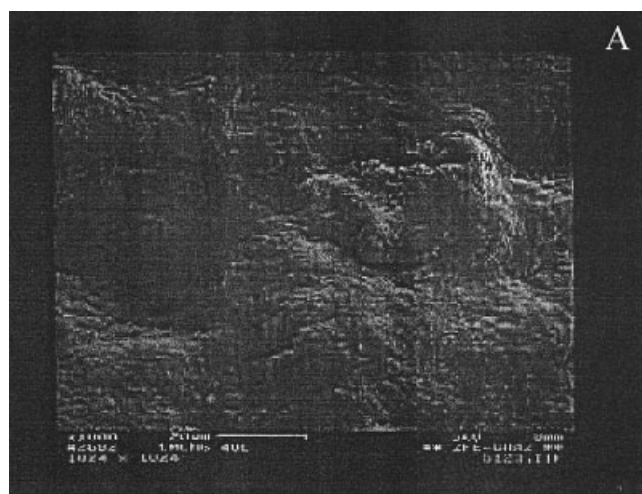
### Characterization

Fourier transform infrared spectroscopy was performed with a Bruker Vector 22 instrument (Germany) for the characterization of the grafted polymer. Mass spectrometry (MS) was performed with a Finnigan SSQ 7000 instrument (UK), and elemental analysis for the grafted polymer products was performed with a Vario El Elementar (Germany). Scanning electron microscopy (SEM) was performed with a Zeiss DSM P82 Gemini, Gemini (Institut für Universität Organischer Stoffe, Graz, Austria), and the hardness of the grafted samples was tested with a Wolpert hardness tester Wolpert hardness tester (Schweiz).

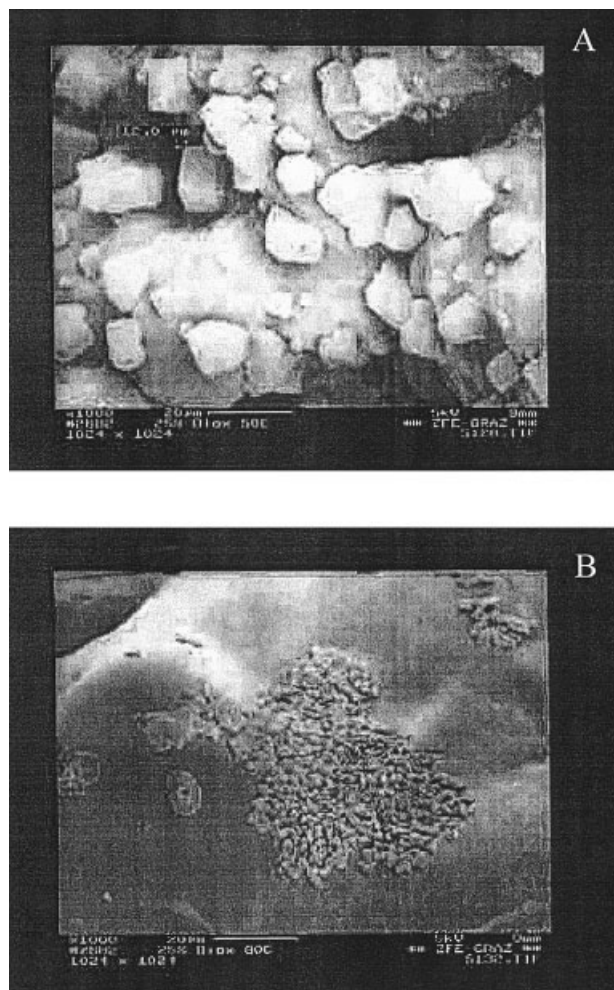
## RESULTS AND DISCUSSION

Numerous methods have been developed for the grafting of vinyl monomers to cellulose. The aim of our work was to provide a comparison of the grafting polymerization of AM onto CMC xanthate at different reaction temperatures in different media. Figure 1 summarizes the effect of the reaction temperature on  $P_g$  in different media. The grafting parameters distinctly increased for the reaction carried out completely in an aqueous medium. This may be attributed to the solubility of the homopolymer in water (i.e., pseudografting).

Apart from pseudografting, the graft level decreased as the reaction temperature increased with NaOH, KOH, and dioxane, except at a concentration of 25%. The degradative process occurring at higher temperatures may be attributed to an interaction taking place between the solvent and the growing polymer radical.<sup>23</sup> Radical termination may also increase



**Figure 5** SEM micrographs of the grafted polymer at (A) 40 and (B) 80°C in an aqueous medium.



**Figure 6** SEM micrographs of the grafted polymer at (A) 50 and (B) 80°C in 25% dioxane.

with the temperature.<sup>24</sup> Table I shows that an increase in the graft level resulted in an increase in the nitrogen content in the polymers. This may have been due to the higher conversion of the polymer.

SEM images of the grafted polymers at 40, 50, and 80°C (Figs. 2–4) show that degradation occurred at higher temperatures. When water or 25% dioxane was used, no degradation occurred (Figs. 5 and 6). Table II presents the hardness of the produced polymers, and the results can be clarified by the SEM images. The increase in the bonding for the polymers produced with water [Fig. 5(a)] and 100% dioxane [Fig. 4(a)] led to greater hardness than that of the polymers produced with KOH [Fig. 3(a)] and 25% dioxane [Fig. 6(a)].

IR spectroscopy is a valuable tool for identifying graft copolymerization reactions, and it is used to establish evidence of grafting,<sup>25–27</sup> to ensure the complete removal of ungrafted products, and to determine the functional grouping of grafted samples.

Figure 7 presents a typical IR spectrum of grafted CMC. Beside the absorption peaks at 3425, 2370, and

1060–1115  $\text{cm}^{-1}$ , which are characteristic of CMC,<sup>28</sup> additional peaks at 3164 and 3047  $\text{cm}^{-1}$  for amide, at 1655  $\text{cm}^{-1}$  for C=O, at 1406  $\text{cm}^{-1}$  for C–N, and at 1221  $\text{cm}^{-1}$  for C–O can be seen. The O–H stretch for grafted CMC is very broad (3400–2750  $\text{cm}^{-1}$ ) because of the strong hydrogen bonding and often interferes with C–H absorption.

Considering the reaction of carbon disulfide with CMC, we can suggest the mechanism for the formation of CMC xanthate (Scheme 1).

The persulfate ion is known to act as a strong oxidizing agent in aqueous solutions.<sup>29–31</sup> During the redox reaction, free radicals are produced in one stage.<sup>32,33</sup> It has been reported that grafting takes place when persulfate is used as a catalyst to initiate the grafting of vinyl monomers onto polymers carrying oxidizable hydroxyl groups.<sup>34–36</sup> The importance of the presence of persulfate ions to grafting can be suggested with the diagram (Scheme 2).

The absence of a C=S group in the IR spectra leads us to reject path 1b. The mass spectra (Fig. 8) of the grafted CMC xanthate clarify that CMC xanthate is grafted with AM according to path 2b or 2a, in which the presence of ion fragments of  $m/e = 71$  and  $m/e = 220$  represents a fragment of one AM molecule and CMC, respectively. In addition, the  $m/e = 57$  molecular ion is attributed to a carboxymethyl group ( $\text{COOCH}_3$ ), and so path 2a or 2b can be suggested for the grafting mechanism (Scheme 3).

## CONCLUSIONS

In this work, AM-grafted CMC was prepared with the xanthate method. The effects of the polymerization temperature and reaction medium were investigated. The hardness behavior of the grafted polymers was related to their chemical composition. The reduction in the graft level in a completely aqueous medium was due to the solubility of the homopolymer in water. Also, the decrease in the graft level as the reaction temperature increased was attributed either to the interaction taking place between the solvent and the growing polymer radical or to radical termination. The increase in the nitrogen content of the grafted polymers with an increase in the graft level could be due to a higher conversion of the polymer.

**TABLE II**  
Hardness of the Polymer Products

Medium	Hardness (N/m <sup>2</sup> )
Water	160.83
KOH	141.77
25% dioxane	151.84
100% dioxane	159.49

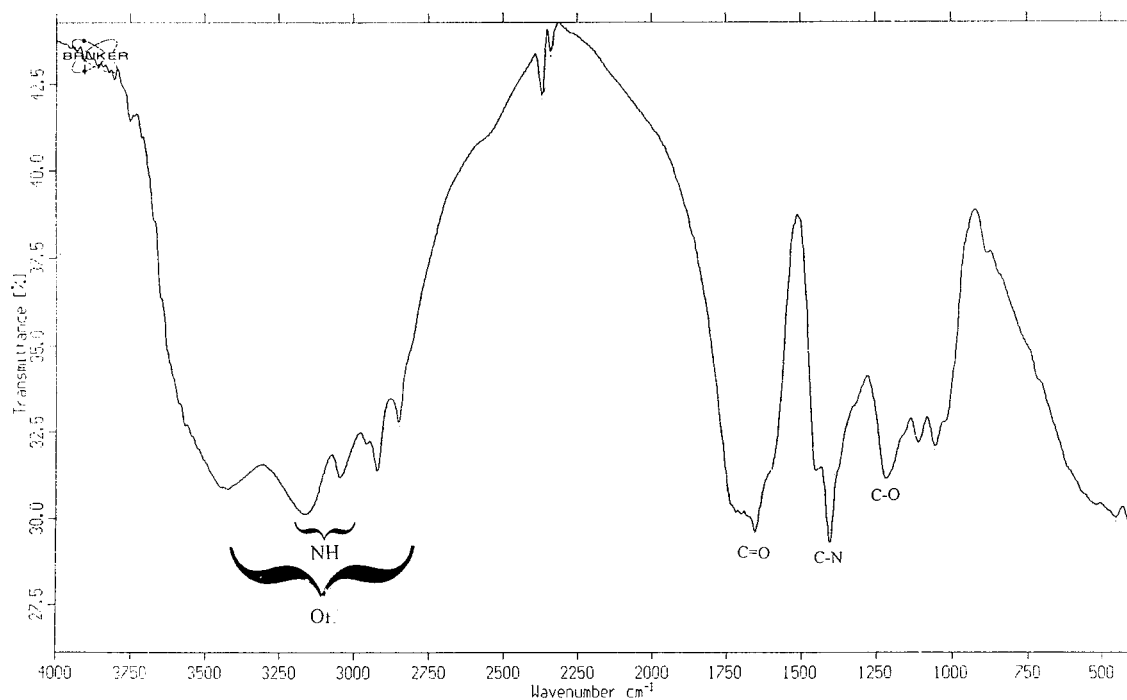
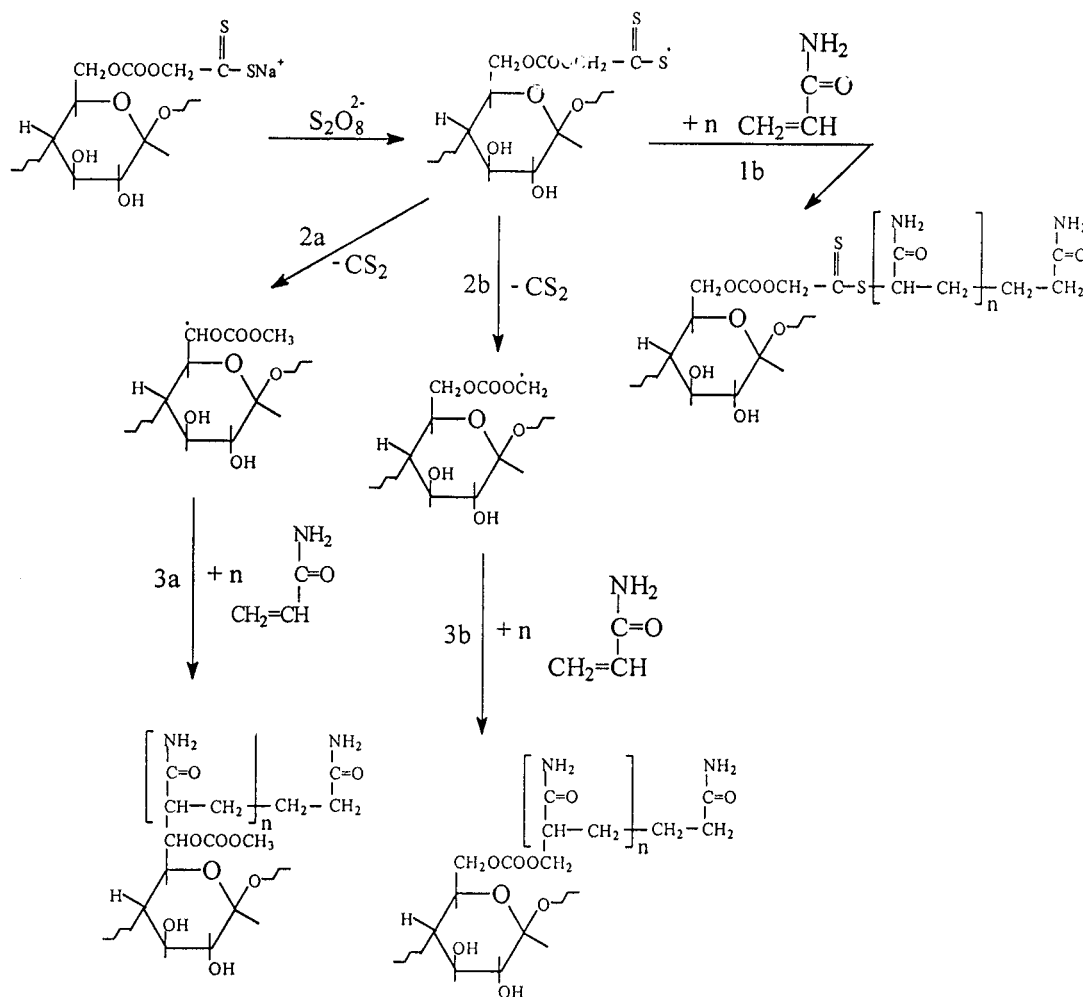


Figure 7 IR spectra of CMC xanthate-graft-AM.



Scheme 2

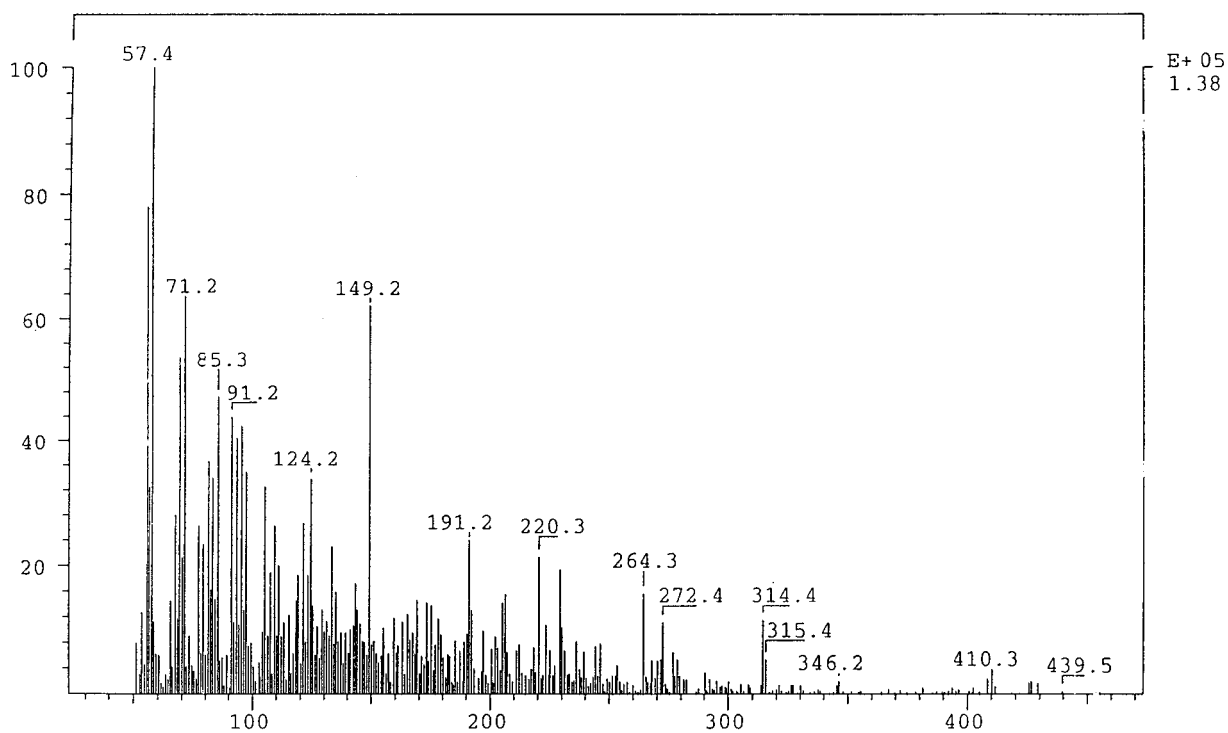
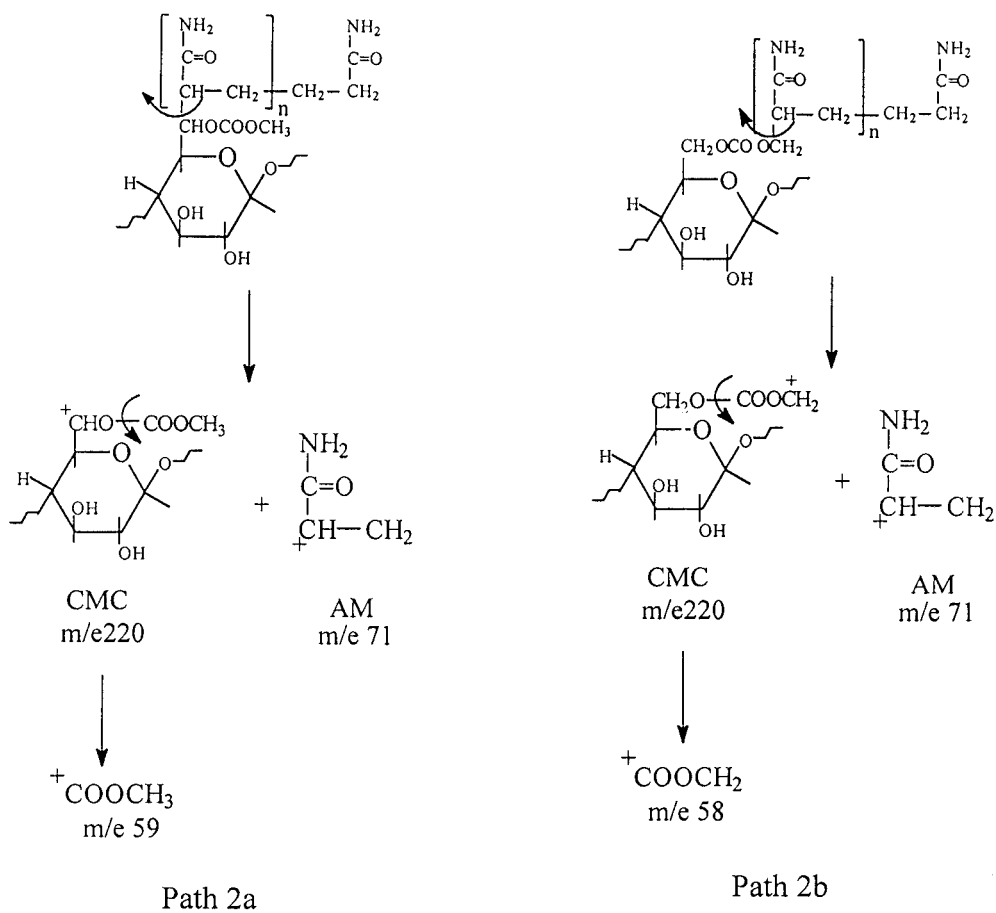


Figure 8 MS spectra of the grafted polymer.



Scheme 3

## References

1. Mohanty, E.; Singh, B. C. *J Appl Polym Sci* 1998, 69, 2569.
2. Gürdağ, G.; Yasar, M.; Gürkaynak, M. A. *J Appl Polym Sci* 1997, 66, 929.
3. de Oliveira, W.; Glasser, W. G. *J Appl Polym Sci* 1996, 60, 63.
4. Turbak, A. F.; Hammer, R. B.; Portnoy, N. A.; Daves, R. E. In *Solvent Spun Rayon, Modified Cellulose Fibers and Derivatives*; Turbak, A. F., Ed.; ACS Symp. Series 58; American Chemical Society: Washington, DC, 1977; p 12.
5. de Oliveira, W.; Glasser, W. G. *J Appl Polym Sci* 1996, 61, 81.
6. Lepoutre, P.; Hui, S. H.; Robertson, A. A. *J Appl Polym Sci* 1973, 17, 3143.
7. Bardhan, K.; Mukhopadhyay, S.; Chatterjee, A. R. *J Polym Sci Polym Chem Ed* 1977, 15, 141.
8. Misra, B. N.; Jassal, J. K.; Pande, C. S. *J Polym Sci Polym Chem Ed* 1978, 16, 295.
9. Misra, B. N.; Dogra, R.; Kaur, I.; Jassal, J. K. *J Polym Sci Polym Chem Ed* 1979, 17, 1861.
10. Misra, B. N.; Dogra, R.; Mehta, J. K. *J Polym Sci Polym Chem Ed* 1980, 18, 749.
11. Fernandez, M. J.; Casinos, I.; Guzman, G. M. *J Polym Sci Part A: Polym Chem* 1990, 28, 2275.
12. Fernandez, M. J.; Casinos, I.; Guzman, G. M. *J Polym Sci Part A: Polym Chem* 1990, 28, 2293.
13. Fernandez, M. J.; Casinos, I.; Guzman, G. M. *Makromol Chem* 1990, 191, 1287.
14. Huang, Y.; Zhao, B.; Zheng, G.; He, S.; Gao, J. *J Appl Polym Sci* 1992, 45, 71.
15. Williams, J. L.; Stannett, V. T. *J Appl Polym Sci* 1979, 23, 1265.
16. Zahran, A. H.; Williams, J. L.; Stannett, V. T. *J Appl Polym Sci* 1980, 25, 535.
17. Okieimen, E. F.; Ebhoaye, J. E. *J Macromol Chem* 1986, 23, 349.
18. Okieimen, E. F.; Ebhoaye, J. E. *J Appl Polym Sci* 1986, 31, 1275.
19. Guthrie, J. T.; Huglin, M. B.; Phillips, G. O. *J Polym Sci* 1972, 37, 205.
20. Flefel, E. M.; Ibrahim, M. M.; El-Zawawy, W. K.; Ali, A. M. *Polym Adv Technol* 2002, 13, 541.
21. Kokta, B. V.; Lo, R. C.; Daneault, C. In *Graft Copolymerization of Lignocellulosic Fibers*; Hon, D. N.-S., Ed.; ACS Symposium Series 187; American Chemical Society: Washington, DC, 1982; p 269.
22. Takahashi, S.; Takahashi, A. *Kogakuin Daiga Ku Kenkyer Hokoku* 1977, 42, 232; *Chem Abstr* 1979, 91, 21184g.
23. Mansour, O. Y.; Nagaty, A. *J Polym Sci Polym Chem Ed* 1974, 12, 1887.
24. McDowall, D. J.; Gupta, B. S.; Stannett, V. In *Graft Copolymerization of Lignocellulosic Fibers*; Hon, D. N.-S., Ed.; ACS Symposium Series 187; American Chemical Society: Washington, DC, 1982; p 45.
25. Mishra, B. N.; Mehta, I. K.; Kheler Pal, R. C. *J Polym Sci Polym Chem Ed* 1984, 22, 2767.
26. Potnis, S. P.; Shethy, S. M.; Prakash, J. *Text Res J* 1970, 40, 389.
27. Koenig, J. L. *Spectroscopy of Polymers*, 2nd ed.; Elsevier Science: New York, 1999.
28. Okieimen, F. E.; Ogbeifun, D. E. *J Appl Polym Sci* 1996, 59, 981.
29. Bartlett, P. D.; Cotman, J. D., Jr. *J Am Chem Soc* 1949, 71, 1419.
30. Levitt, L. S.; Malinowski, E. R. *J Am Chem Soc* 1955, 77, 4517.
31. Ball, D. L.; Crutchfield, M. M.; Edwards, J. O. *J Org Chem* 1960, 25, 1599.
32. Kolthoff, I. M.; Medalin, A. I.; Raaen, H. P. *J Am Chem Soc* 1951, 73, 1733.
33. Merz, J. H.; Waters, W. A. *Discuss Faraday Soc* 1947, 2, 179; *Chem Abstr* 1949, 43, 5269h.
34. Sakurada, I.; Sakaguchi, Y. *Sen-i-Gakkaishi* 1963, 19, 217; *Chem Abstr* 1963, 58, 10512c.
35. Ikada, Y.; Nishitaki, Y.; Sakurada, I. *J Polym Sci Polym Chem Ed* 1974, 12, 1829.
36. Mukhopadhyay, S.; Prasad, J.; Chatterjee, S. R. *Makromol Chem* 1975, 176, 1.