

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Grafting of Cellulose with Water-Soluble Monomers by the Xanthate Process

Tomasz Graczyk^a; Vladjmir Hornof^b

^a Department of Chemical, Engineering University of Ottawa, Ottawa, Ontario, Canada

To cite this Article Graczyk, Tomasz and Hornof, Vladjmir(1983) 'Grafting of Cellulose with Water-Soluble Monomers by the Xanthate Process', *Journal of Macromolecular Science, Part A*, 20: 2, 213 – 224

To link to this Article: DOI: 10.1080/00222338308069961

URL: <http://dx.doi.org/10.1080/00222338308069961>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Grafting of Cellulose with Water-Soluble Monomers by the Xanthate Process

TOMASZ GRACZYK and VLADIMIR HORNOF

Department of Chemical Engineering
University of Ottawa
Ottawa, Ontario, Canada

ABSTRACT

Cellulose was grafted with several water-soluble monomers including 2-dimethylaminoethyl methacrylate, 3-dimethylaminopropyl methacrylamide, and 2-acrylamido-2-methylpropyl sulfonic acid. Cellulose xanthate- Fe^{3+} - H_2O_2 redox system was used to initiate the polymerizations. The formation of graft copolymer was investigated as a function of substrate pretreatment, initial pH, and reaction temperature. Although stable graft copolymer was formed in all cases, the grafting efficiency was quite low, ranging from 10 to 30%. The best results were obtained with binary monomer mixtures composed of an acid and a base.

INTRODUCTION

The graft copolymerization of cellulose and other polymers with hydrophilic monomers has received considerable attention during the past decade as a convenient way of introducing ionizable or other polar group into the backbone material. Notably, Lepoutre et al. [1, 2] copolymerized cellulose fibers with 2-dimethylaminoethyl methacrylate and used them to remove color from pulp mill effluents. In their earlier work, Lepoutre, Hui, and Robertson [3] prepared highly ab-

from chloroform. AMPSA (Lubrizol Corp.) was used as received from the manufacturer.

Hydrogen peroxide (Fisher Scientific) was received as 30% solution. It was diluted to 60 g/L of H_2O_2 and the concentration was checked periodically by titration against potassium permanganate.

All the other reagents and materials were used as supplied by their manufacturers.

Copolymerization

The reactions were carried out under nitrogen atmosphere in Pyrex resin kettles. In a typical experiment using DMAEM as the monomer, 4.5 g of xanthated pulp (oven-dry weight), 0.9 g of Tween-40 (surfactant), and 0.06 mol of DMAEM were charged into the reactor and distilled water was added to adjust the volume of the reaction mixture to 450 mL. The monomer was partially neutralized by acid (~70-80% of the amount required to complete neutralization) in order to maintain the pH at 7 or above during the preswelling period. The reaction mixture was stirred for 15 min and then the remainder of acid was added followed by 0.75 g of H_2O_2 to initiate the reaction. The pH of the mixture dropped to about 4 upon adding the second part of the acid.

The system was allowed to react for 2 h whereupon the reaction was stopped by additions of hydroquinone. At the same time, excess H_2O_2 was destroyed by adding a small amount of potassium metabisulfite. The reaction products were quickly filtered off and washed with 2000 mL of distilled water to remove water-soluble homopolymers, then dried under vacuum at 60°C until constant weight.

The AMPSA monomer was completely neutralized to sodium salt prior to the reaction. The initial pH of the reaction was thus 7-7.5. In the case of using cationic-anionic binary monomer mixtures, the homopolymers could not be completely removed from the products by washing with water. To achieve this, the grafted pulp was first brought to pH 10 using NaOH, then to pH 3 using H_2SO_4 , and subsequently washed with water.

Xanthation

Xanthate groups were introduced into the cellulose by an emulsion process. Never-dry pulp was employed. The details of pulp preparation are shown in Table 1.

The degree of xanthation was determined by iodometric xanthation. It was found to be $\gamma = 10.6 \pm 1$ (i.e., approximately 10-11 xanthate groups per 100 glucose units).

TABLE 1. Preparation of Pulp for Grafting

Stage of preparation	Quantity ^a of reagent (mL)	Duration (min)
Xanthation (1 M NaOH, 0.05% surfactant (dodecylbenzene sulfonate))	150	60
Washing (1 M NaCl)	600	2-5
Washing (distilled water, pH = 5.5)	600	5-10
Ion exchange with 0.004% solution of Mohr salt	150	2
Washing (distilled water, pH = 5.5)	300	2-5

^aThe amounts shown refer to 4.5 g pulp samples (oven-dry weight after a correction for pulp losses during the process, due mainly to pulp solubility in NaOH).

Determination of Stability of Xanthated Pulp

A sample of pulp (4.5 g) was subjected to the same treatment as that preceding a copolymerization. It was then dispersed in distilled water to give a total volume of 450 mL. The pH of the dispersion was adjusted to 4 by adding 2 N sulfuric acid, and a magnetic stirrer was employed to speed up reaching an equilibrium. After a desired period of time, the residual γ -number of the pulp was determined by iodometric titration.

Dialysis

The filtrate obtained after removing the insoluble products contained soluble homopolymer which was isolated by dialysis. The solution was first reduced in volume to about 200 mL by evaporation under vacuum and then put into dialysis tubes (Spectrapor No. 1) for 3-4 d. The dialyzed solution of the homopolymer was once again reduced in volume to about 50 mL by vacuum evaporation and in the final step the homopolymer was isolated by freeze-drying.

Characterization of Products

The following grafting parameters are used:

$$\text{Copolymer loading (\%)} = \frac{A - B}{B} \times 100$$

$$\text{Grafting efficiency (\%)} = \frac{A - B}{D - B} \times 100$$

where A = weight of products after filtration and washing (homopolymer-free products)

B = weight of pulp charged (corrected for losses due to pulp solubility)

C = weight of monomer charged

D = combined weight of all products (copolymer + homopolymer)

RESULTS AND DISCUSSION

Copolymerization with DMAEM

Effect of Pulp Preswelling

The DMAEM monomer is a base and it can be polymerized only in the form of a salt. Since its $pK = 4.25$ [3], it can be polymerized at $pH \leq 4.25$. Figure 1 shows the titration curve of DMAEM with sulfuric acid.

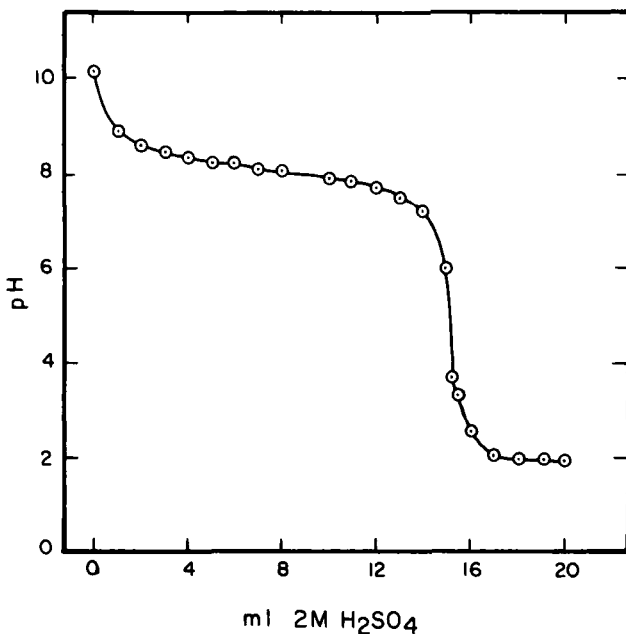


FIG. 1. Titration curve of DMAEM by 2-M sulfuric acid.

Fanta et al. [4] and Lepoutre et al. [3] grafted DMAEM to starch and cellulose, respectively, at pH = 2. However, the present work employs partially xanthated cellulose and it is known that the xanthate bond is only stable in alkaline media. Swelling xanthated cellulose at pH = 2 would lead to a rapid decrease in the number of xanthate groups bound to cellulose (i.e., the γ -number), thus affecting reaction kinetics and polymer yield.

Prior to starting the copolymerization experiments, it was thus important to find out how rapid the decrease in γ -number would be. With this goal in mind, a series of experiments was carried out to determine the γ -number as a function of time. For this, a sample of xanthated pulp was prepared in the same manner as for a copolymerization experiment. The sample was then dispersed in water and the pH was adjusted to 4.0 (just below the pK of DMAEM). Figure 2 shows the dependence of γ -number on time. It is seen that 15 min at pH = 4 is sufficient to reduce the γ -number to one-half of its original value, while almost no xanthate groups are present after 60 min.

One can envisage two methods of avoiding such a dramatic decrease in γ -number:

1. To eliminate the preswelling period altogether
2. To preswell the substrate in the presence of partly neutralized monomer at pH > 7 and to add more acid just before initiation

Several experiments were conducted to test both methods. The results displayed in Table 2 show that the latter method yields the highest co-

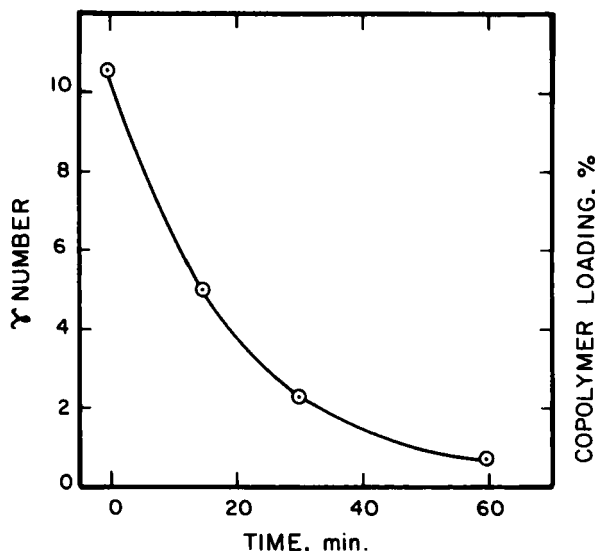


FIG. 2. Dependence of γ -number on time at pH 4.0.

TABLE 2. Effect of Preswelling on the Copolymer Loading of DMAEM

Preswelling conditions			Copolymerization pH		Copolymer loading (%)
pH	Duration (min)	Monomer form	Initial	Final	
8.2	~1 ^a	-	2.5	2.1	0
7.3	~1 ^a	-	4.8	-	7.5
2.0	15	Salt	2.0	2.0	3.1
4.1	15	Salt	4.1	3.2	9.8
10.0	15	Free base	2.3	1.7	9.1
10.2	15	Free base	3.7	2.7	10.2
6.5	15	Partly salt	4.0	3.2	14.9

^aTime required to add acid and initiator (H₂O₂).

polymer loading and, as a consequence, it was employed in all further experiments discussed in this work.

Effect of Initial pH

Figure 3 shows the influence of initial pH on copolymer loading. The curve has a maximum at pH \cong 5.5 (17.4% copolymer loading). A sharp drop in copolymer formation is observed at pH > 6; the corresponding drop is much smaller when going to a pH lower than the optimum. This behavior is similar to that observed by Hornof et al. [9] using acrylonitrile as a monomer. Nevertheless, pH = 4.25 was used for most reactions involving DMAEM, mainly because this was easier to adjust and control than the optimum pH, which is above the pK of the monomer.

The type of counterion used was also found to affect copolymer loading. Preliminary experiments have shown that sulfate ion gave the best combination of copolymer formation and stability, and consequently sulfuric acid was used in all further experiments for the acidification of the reaction mixture.

Effect of Temperature

It was discovered in the course of this work that grafting of DMAEM onto xanthated pulp is strongly dependent of the number of revolutions of the agitator [10]. The dependence on temperature was therefore studied at 60 and 320 rpm, corresponding to high and low reaction rate regions, respectively. The reactions at 60 rpm were conducted at two initial pH values: 2.0 and 4.0. The results are summarized in Fig. 4.

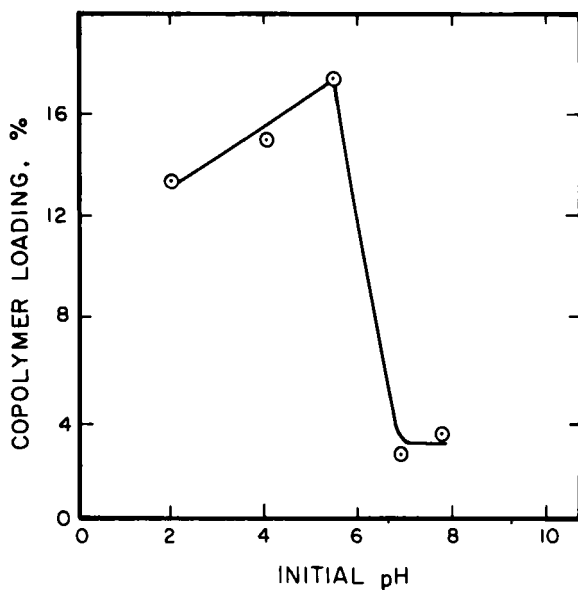


FIG. 3. Effect of initial pH on DMAEM copolymer loading.

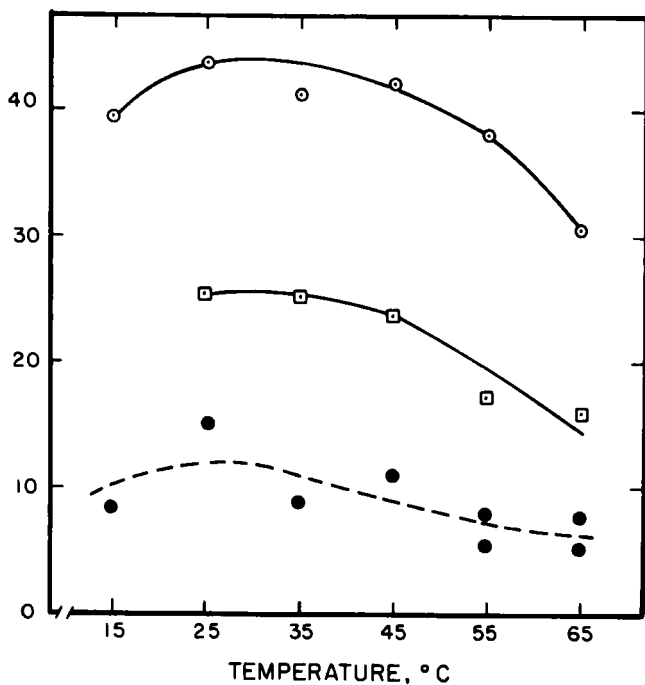


FIG. 4. Dependence of DMAEM copolymer loading on reaction temperature, initial pH of the reaction, and agitator speed. (○) pH = 4.0, 60 rpm. (●) pH = 4.0, 320 rpm. (□) pH = 2.0, 60 rpm.

It is evident that all three curves possess a maximum at about 25°C, although the level of copolymer loading is different for each curve. It can be concluded, at least in a qualitative sense, that the effect of temperature on copolymer loading is independent of pH and agitator speed.

Copolymerization with DMAPMA and AMPSA

DMAPMA is also a base so the copolymerization was carried out under reaction conditions similar to DMAEM. Pulp preswelling was conducted in the presence of partly neutralized monomer during 15 min; then the pH was adjusted to 4.0 and the reaction was started by adding hydrogen peroxide. Figure 5 shows the copolymer loading obtained as a function of temperature. At 60 rpm, maximum copolymer loading was observed at 45°C. The curve obtained at 320 rpm was nearly flat with only a small apparent maximum in the 45-55°C range.

AMPSA being a strong acid, it was copolymerized in the form of

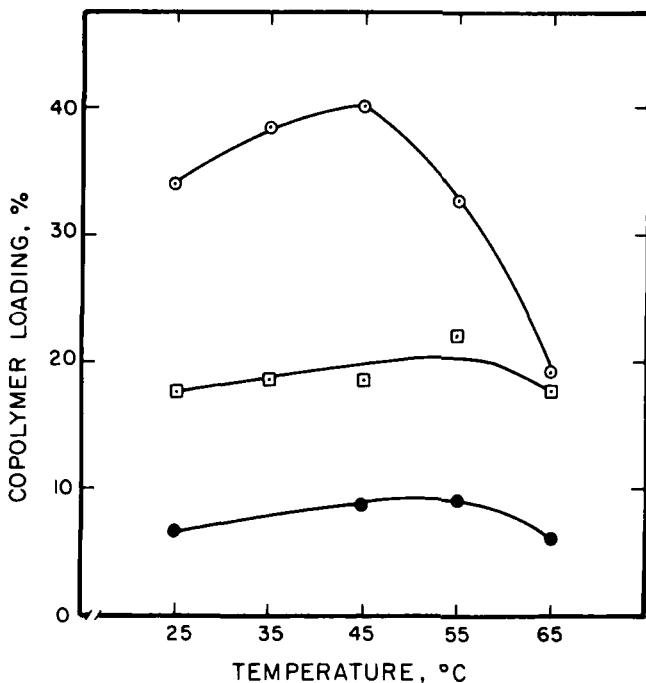


FIG. 5. Copolymer loading of DMAPMA and AMPSA as a function of reaction temperature and agitator speed. (○) DMAPMA, 60 rpm. (●) DMAPMA, 320 rpm. (□) AMPSA, 60 rpm.

sodium salt at an initial pH of 7.0-7.5. The corresponding copolymer loading vs temperature dependence is also shown in Fig. 5. The curve shows that copolymer formation in this case was almost independent of temperature.

Grafting with a Mixture of Two Monomers

A series of experiments was carried out in which cellulose was grafted with a mixture of two monomers. The results are compiled in Table 3. It is evident that for mixtures involving AM and the two cationic monomers, the resulting copolymer loading depends strongly on the monomer ratio.

An interesting phenomenon was observed when two monomers were used of which one was an acid and one was a base. Copolymer loadings obtained with DMAEM, DMAPMA, and AMPSA alone (under comparable conditions) were 43.6, 34.0, and 17.6%, respectively. Grafting of monomer pairs (DMAEM + AMPSA) and (DMAPMA + AMPSA) gave copolymer loading values of 123.5 and 101.6%, respectively. This dramatic increase in copolymer formation is in agreement with recent findings of Salamone and co-workers [11].

Analysis for Homopolymers

Large amounts of homopolymers were formed in most of the reactions reported in this work, the only exceptions being the copolymerizations with acid-base monomer mixtures. Attempts to isolate the homopolymers by dialysis (as described in Experimental) were unsuccessful in that the results were not reproducible. This is why no homopolymer data are reported here. However, the description of the dialysis procedure was retained as it may be helpful to other workers.

From the data available, it was estimated that the grafting efficiency (ratio of grafted polymer to total polymer formed) varied from 10 to 30%. It should be noted that low grafting efficiency is not unusual when water-soluble monomers are used. In their study of DMAEM grafting on starch, Fanta et al. [6] recorded grafting efficiencies ranging from 17 to 53%, depending on reaction conditions and on the pretreatment of the starch substrate. Hornof and Puissant [12] grafted methacrylic acid onto cellulose and observed grafting efficiencies well below those obtained with more hydrophobic monomers under comparable conditions. These observations have yet to be explained. An attempt to increase grafting efficiency by using higher concentrations of initiator components (Fe^{2+} , H_2O_2) was unsuccessful.

TABLE 3. Grafting with Binary Monomer Mixtures^b

Monomer ratio ^a					Copolymer loading (%)
DMAEM	DMAPMA	AMPSA	AM	AA	
-	-	-	1	-	30.9
2	-	-	1	-	46.4
1	-	-	1	-	50.8
1	-	-	2	-	18.4
-	2	-	1	-	41.7
-	1	-	1	-	34.8
-	1	-	2	-	23.5
-	-	2	1	-	10.0
-	-	1	1	-	7.7
-	-	1	2	-	11.0
1	-	1	-	-	123.5
-	1	1	-	-	101.6
1	-	-	-	1	35.5

^aRatio by weight; total monomer charged = 4.5 g.

^bAll reactions were conducted at 60 rpm agitator speed.

ACKNOWLEDGMENT

The authors wish to thank the Natural Sciences and Engineering Research Council of Canada for the financial support of this work.

REFERENCES

- [1] P. Lepoutre, S. H. Hui, and A. A. Robertson, "A Novel Process for the Treatment of Pulp Mill Effluents Using the Grafted Pulp Fibres," in *Modified Cellulosics* (R. M. Rowell and R. A. Young, eds.), Academic, New York, 1978.
- [2] S. H. Hui and P. Lepoutre, *J. Appl. Polym. Sci.*, **19**, 1771 (1975).

- [3] P. Lepoutre, S. H. Hui, and A. A. Robertson, *Ibid.*, 17, 3143 (1973).
- [4] G. F. Fanta, R. C. Burr, C. R. Russell, and C. E. Rist, *Ibid.*, 15, 1889 (1971).
- [5] G. F. Fanta, R. C. Burr, C. R. Russell, and C. E. Rist, *Ibid.*, 14, 2601 (1970).
- [6] G. F. Fanta, R. C. Burr, W. M. Doane, and C. R. Russell, *Ibid.*, 16, 2835 (1972).
- [7] G. F. Fanta, R. C. Burr, W. M. Doane, and C. R. Russell, *Ibid.*, 15, 2651 (1971).
- [8] D. A. Jones and W. A. Jordan, *Ibid.*, 15, 2161 (1971).
- [9] V. Hornof, B. V. Kokta, and J. L. Valade, *Ibid.*, 19, 545 (1975).
- [10] T. Graczyk and V. Hornof, *Polym. Prepr.*, 23(2), 124 (September 1982).
- [11] J. C. Salamone, C. C. Tsai, A. P. Polson, and A. C. Watterson, *Adv. Chem.*, 187, 337 (1980).
- [12] V. Hornof and L. Puissant, *Cellul. Chem. Technol.*, 17, 3 (1983).

Accepted by editor December 12, 1982

Received for publication January 12, 1983