Free-Radical Grafting of Cellulose in *N*-Methylmorpholine Oxide: Water-Soluble Pam-*g*-Cellulose Copolymers

EDWARD C. NELSON, *Texaco Research Center, P.O. Box 509, Beacon, New York 12508*

Synopsis

The homogeneous graft copolymerization of acrylamide (AM) onto cellulose initiated by *t*-butylperoxy-2-ethylhexanoate in a cellulose solvent, *N*-methylmorpholine oxide (NMMO), was investigated. The method afforded water-soluble PAM-*g*-cellulose copolymers in fair yields. The copolymers produced are of low molecular weight (50,000–100,000 $\overline{M}_w$). Little apparent homopolymerization was observed.

INTRODUCTION

Stannet[1] has pointed to the need for more effective ways of grafting cellulose with various monomers. Although heterogeneous grafting is a classical way of carrying out these transformations, the products generated by this method generally contain less than one branch per cellulose chain and the chain lengths of the grafts tends to be quite large (ca. 500,000 $\overline{M}_w$). The low "frequency of grafting" has been attributed to the inaccessability of the crystalline regions of cellulose to the grafting reagents, while the high molecular weight of the graft chains reflects the inability of the growing chain to undergo chain transfer, i.e., the "gel effect." Both effects are characteristic of heterogeneous processes which graft cellulose that is dispersed in a nonsolvent.

Recently some work[2–4] has been done in preparing grafted cellulosic copolymers in a homogeneous solution. The advantages of this approach are (1) ready access of the grafting reagents to the cellulose backbone favors a greater grafting frequency than that observed in a heterogeneous reaction and (2) some lowering of graft chain molecular weight is expected because of the absence of a gel effect. Tsuzuki et al.[2,3] have demonstrated these two advantages in the radiation-induced grafting of cellulose with styrene in a ternary solvent system consisting of diethylamine, sulfur dioxide, and dimethyl sulfoxide. They found the number of branches per cellulose molecule ranged from 2.6 to 10.6 and the $\overline{M}_n$ of the side chain to range from 3300 to 3700. However, practical applications of this system would be hindered by difficult solvent recovery and separation. In addition, interaction of the sulfur dioxide in the solvent with the growing polymer chain produces some sulfone linkages in the graft chain which may not be desirable. In light of some of these problems, we investigated *N*-methylmorpholine oxide (NMMO)[5,6] as a possible medium for homogeneous cellulose grafting. We

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report a preliminary study on the grafting of cellulose with acrylamide in NMMO and the production of a water soluble PAM-*g*-cellulose copolymer.

EXPERIMENTAL

Materials. Commercial α-cellulose (Alpha Cellulose Fiber, 99.5%) was used as obtained from Sigma Chemical Co. A 60% aqueous solution of *N*-methylmorpholine oxide (NMMO),* obtained from Texaco Chemical Co., was saturated with nitrogen before use. Acrylamide (97%) was obtained from Aldrich Chemical and used without further purification. The initiator, *t*-butylperoxy-2-ethylhexanoate, was used as a 50% solution in odorless mineral spirits (Lupersol PMS, Pennwalt).

Grafting Reaction. 10 g of α-cellulose powder was immersed in 60 mL of distilled water and heated to 90°C for 1 h. The reaction vessel was flushed with N_2, 200 mL of a 60% aqueous solution of NMMO was added, and water (ca. 130 mL) was distilled from the suspension under reduced pressure (15 mm Hg) until dissolution† had occurred. The solution was quickly cooled to 65°C, 0.2 mL (0.7 mol %, based on moles of anhydroglucose units) of *t*-butylperoxy-2-ethyl-hexanoate was added immediately, and the reaction mixture was warmed to 95°C. After 20 min,‡ 8.8 g of acrylamide was added in portions over 1 h, the reaction mixture was stirred and heated (95–100°C) overnight and then poured into 1 L of methanol to precipitate a white, stringy solid. Trituration in methanol (3 × 50 mL) and drying in a vacuum oven (120°C, 15 mm, 3 h) afforded 19.5 g of a fibrous yellow solid. Continuous extraction of the solid with water provided 5.7 g of a fibrous yellow, water-insoluble solid (fraction I). Concentration of the aqueous fraction by toluene-azeotrope under reduced pressure produced 11.8 g of a water-soluble (fraction II) brown syrup. The syrup was taken up in water, dialyzed (Spectra/Por 2, 12,000-14,000 MWCO, Fisher Scientific), concentrated and dried to afford 5.9 g of a brown, flaky, water-soluble solid.

IR Spectra. IR spectra of all samples were determined from KBr pellets using a Perkin-Elmer 710B Spectrophotometer. Samples were dried in an Abderhalden drying apparatus containing P_2O_5 at 100°C for 24 h under high vacuum (0.5 mm Hg).

Size Exclusion Chromatography. SEC chromatograms were recorded on a Waters HPLC system equipped with a Model 401 refractive index detector using an aqueous mobile phase (1 mL/min) containing 0.02% NaN_3 as a preservative. Sample injections ranged from 10 to 25 μL of 1000 ppm polymer solution. Separation was affected by the following columns in se-

* Available from Texaco Chemical Co. Typical assay: 60 wt % NMMO, 1 wt % *N*-methylmorpholine, 100 ppm H_2O_2, remainder H_2O.

† The clear yellow solution had a kinetic viscosity at 100°C of 334.1 cS. The addition of water, methanol or 15% methanol in methyl ethyl ketone resulted in rapid precipitation of the cellulose. If the solution was cooled below 65°C, solid NMMO monohydrate (mp 60°C) began to crystallize from the solution.

‡ Lower yields of the desired water-soluble polymer were obtained without this induction period.

ries: Waters Bondagel High Å, E-Linear; Toyo Soda TSK-60. Columns were calibrated using Pharmacia dextran standards ($\overline{M}_w = 1 \times 10^4 - 2 \times 10^6$; $\overline{M}_w/\overline{M}_n$ 2.0) and Polyscience polyacrylamide standards ($\overline{M}_w = 5 \times 10^5$, 9.5 $\times 10^5$).

Scanning Electron Microscope. Samples were carbon coated with a Hummer V Sputter Coater. A Coates and Welter "CWIKSCAN" Model 100-4 was used for all examinations.

RESULTS AND DISCUSSIONS

Infrared Analysis

Figure 1 shows the infrared spectra of (1) a commercially available polyacrylamide (Polysciences, $\overline{M}_w$ = 950,000); (2) a synthetically-prepared water-soluble PAM-g-cellulose copolymer (Table I, Entry 1), and (3) a commercially available α-cellulose sample (Sigma Chemical). The spectrum of the graft copolymer contains features characteristic of both the celluosic portion and PAM. For instance, the PAM spectrum contains peaks at 3400 and 3200 cm^{-1} of roughly equal intensity characteristic of symmetric and asymmetric carboxamide stretching, while the spectrum of cellulose contains only one strong peak near 3400 cm^{-1} characteristic of hydroxyl O—H bond stretching. In contrast, the cellulose-g-PAM copolymer contains a large peak at 3400 cm^{-1} and a smaller shoulder at 3200 cm^{-1} as expected

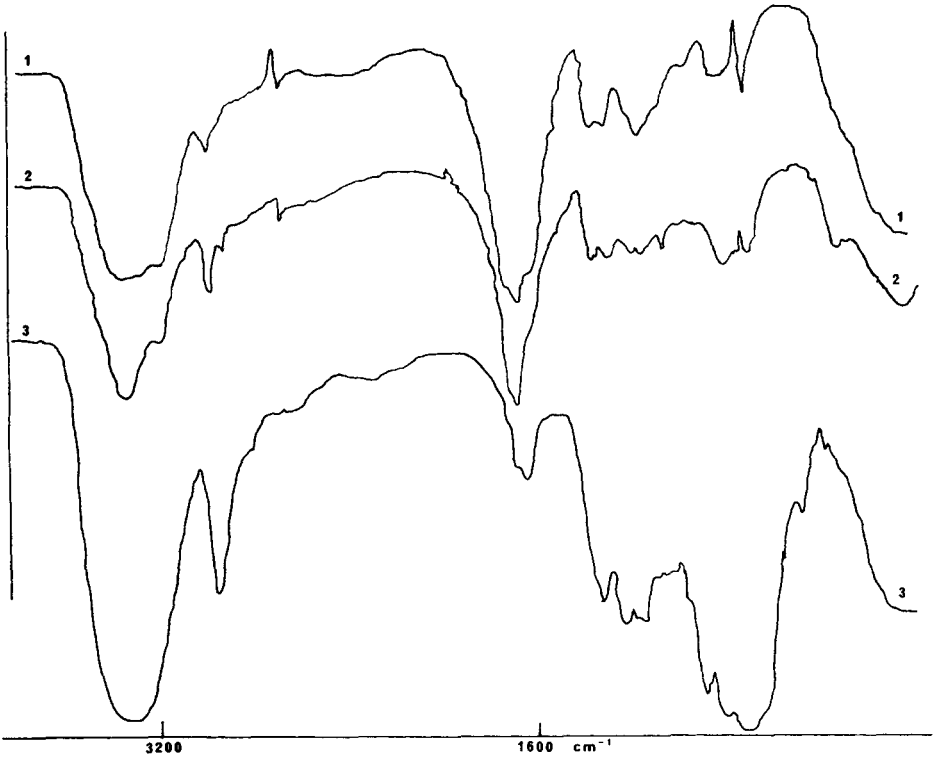


Fig. 1. IR spectra of (1) polyacrylamide, (2) PAM-g-cellulose (2:1), and (3) α-cellulose.

TABLE I
Results and Calculations

Sample	Mol monomer[a]/ mol AHG units	% Recovery	% Recovered[b] cellulose	% Graft copolymer	% N	Graft content
1	2	93	57	46	15.5	3.5
2	4	84	58	37	17.1	6.7
3	1	97	68	19	13.3	2.1
4	2[c]	88	73	18	14.8	3

Calculations

$$\% \text{ Recovery} = \frac{\text{wt precipated solids}}{\text{wt AM charged} + \text{wt cellulose charged}} \times 100$$

$$\% \text{ Recovered cellulose} = \frac{\text{wt water-insoluble fraction}}{\text{wt cellulose charged}} \times 100$$

$$\% \text{ Graft copolymer} = \frac{\text{wt dialysate}^{d}}{\text{wt AM charged} + (\text{wt cellulose charged} - \text{wt water-soluble fraction})} \times 100$$

$$\text{Graft content} = \frac{\text{wt PAM in copolymer}}{\text{wt cellulose charged} - \text{wt water-insoluble fraction}}$$

[a] Based on the initial weight ratio of acrylamide to cellulose at the outset of the reaction.
[b] Typically contained less than 5% PAM by % N analysis.
[c] AM addition was started immediately after initiator was added.
[d] No homopolymer was detected by SEC of the dialysates (Fig. 5).

for a polymer that contains both the hydroxyl stretching and carboxamide NH_2 stretching. While a physical mixture of cellulose and PAM might show similar peaks, one would not expect such a mixture to exhibit the observed water solubility. The graft-copolymer also contains a strong broad peak at 1655 cm^{-1} (carboxamide carbonyl) and a doublet at 1455 cm^{-1} and 1425 cm^{-1} (methylene rocking) both characteristic of a PAM chain and not observed in the spectrum of α-cellulose.

SEM Analysis

Samples of α-cellulose and the water-soluble (fraction II) and insoluble (fraction I) portion of the PAM-*g*-cellulose copolymer (**1**) were examined by scanning electron microscopy (SEM). As can be seen in Figure 2(a), cellulose predominantly consists of short crinkled fibers. After treating a NMMO solution of this cellulose with AM, a sample of the water-insoluble fraction (fraction I, mostly cellulose by % N analysis) shown in Figure 2(c) appears as a matrix of chunky blocks. Some of the fibrous material seen in the starting material is occluded in the matrix, and some long regularly shaped rods are attached to the matrix. We suspect that the fibrous α-cellulose has been transformed during the reaction or isolation procedure to a matrix of chunky blocks. The flexible rods observed [Fig. 2(b)] are probably PAM strands that are occluded in or grafted to the cellulose matrix. Their scarcity in the sample agrees with a nitrogen analysis that shows 5% N by weight. Figure 2(d) is the water-soluble graft copolymer (**1**) and appears as a glassy, amber sheet containing blocks of light colored fragments. Percent nitrogen analysis of this sample indicates that this copolymer is 78% PAM and 22%

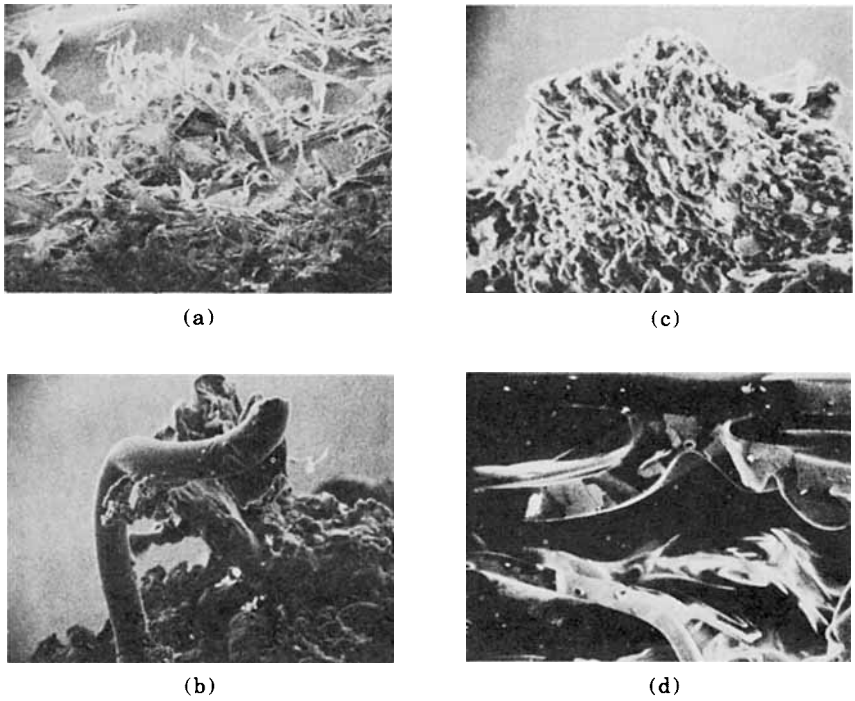


Fig. 2. Scanning electron micrographs: (a)-α-cellulose (100×); (b,c) fraction I (250×, 100×); (d) fraction II, graft copolymer (250×).

cellulose and, in conjunction with the SEM photograph, suggests a solid phase in which cellulose blocks are intimately bonded into a PAM matrix.

Gravimetric Analysis

Acrylamide grafting was carried out under the previously described standard conditions with various *initial ratios* of AM/AHG units; pertinent data and calculations are shown in Table I. The weight of PAM in the copolymer was determined from the %N analysis. Thus, the wt % of PAM based on a maximum %N of 19.7, i.e., pure PAM, was calculated. This was used to afford a "graft content," which is the weight ratio of PAM to cellulose in the copolymer. The graft content of three copolymers synthesized is graphically displayed in Figure 3 and shows a linear dependence of PAM graft content on the initial ratio of mol monomer/mol AGU present at the outset of the grafting reaction. Assuming that the cellulose chains grafted in each of three copolymers are similar in molecular weight, the difference in % PAM incorporation may be due to a difference in the kinetic chain length of the PAM grafts. Such variations could arise by the difference in average monomer concentration during the course of the graft reaction.[7]

By gravimetric analysis of the water-soluble, dialyzed polymers, we also observed that an optimum yield of water-soluble product was obtained when the initial ratio of mol monomer/mol AHG units was 2; a sharp decline was observed when the ratio was changed to one (Fig. 4). In line with the conclusions of Min and Inagaki,[7] we assume that the average number of

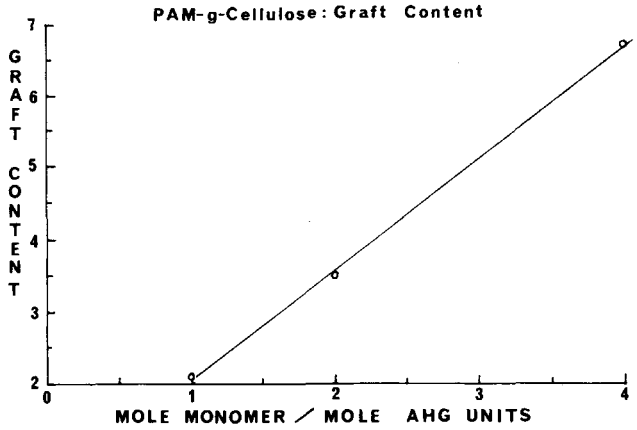


Fig. 3. PAM-*g*-cellulose: graft content.

grafts per cellulose chain is the same for all three copolymers regardless of the amount of monomer used. Therefore, the decline in the percentage of water-soluble polymer collected may be indicative of a minimum DP of the PAM chain required to impart water solubility to the cellulose backbone.

Size Exclusion Chromatography

A molecular weight determination of one of the PAM-*g*-cellulose copolymers (Table I, 1) was made by comparison with some commercially available PAM and dextran standards. On this basis (see Experimental), we estimate this copolymer is in the range of 50,000 to 100,000 in $\overline{M}_w$ (Fig. 5); no contaminating homopolymer was detected.

Gravimetric analysis suggests that copolymer 1 is composed of approximately 78% PAM; the remainder is attributable to the cellulose backbone. Assuming only one cellulose chain per graft copolymer, the $\overline{M}_w$ of the cellulose chain is probably not larger than 20,000 to 25,000. As the α-

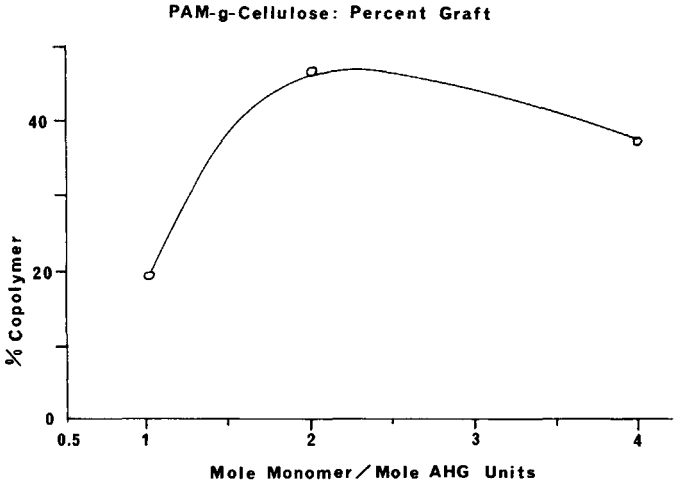


Fig. 4. PAM-*g*-cellulose: percent graft.

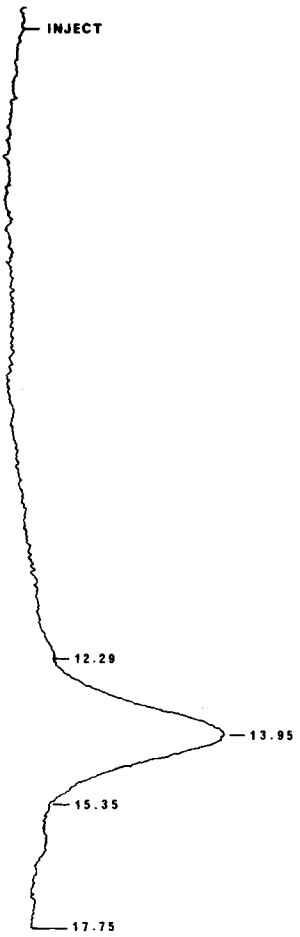
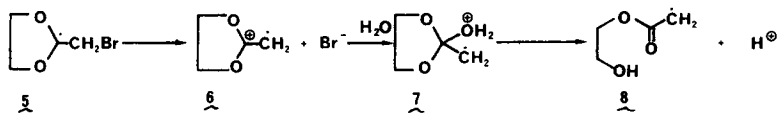


Fig. 5. PAM-g-cellulose 1: SEC chromatogram.

cellulose we started with is typically 10–40 times larger in $\overline{M}_w$ than the cellulosic portion of our graft copolymer **1**, extensive backbone cleavage must have occurred during the reaction. No attempts have been made to elucidate the mechanism of this chain scission. However, Schulte-Frohlinde[8] observed that the radical **5** dissociates very readily in an aqueous solution containing persulfate radical anion at low temperature. Ring scission of **7** leads to the ester **8** (Scheme 1).



5 6 7 8

By a similar mechanism, abstraction of the anomeric proton of an anhydroglucose unit may lead to elimination of protonated C-2 hydroxyl and cleavage of the anomeric linkage.

Viscosity Data

In order to help confirm our conclusions about the low molecular weight of these PAM-*g*-cellulose copolymers, we checked the solution behavior of PAM-*g*-cellulose copolymer (**1**). The copolymer solution (1000 ppm) prepared in distilled water was evaluated in a Brookfield LVT viscometer with UL Adapter at 25°C. Shear rates ranged from 0.37 to 73.4 s^{-1}. The low viscosity enhancement observed, 2.3 cps (at 7.34 s^{-}) is consistent with the expected behavior of a low molecular weight polymer[9] at low shear rates.

SUMMARY

We have been able to graft cellulose under free-radical conditions in a homogeneous solution of NMMO. To our knowledge, this is the first example of the use of NMMO in cellulose grafting reactions. The method afforded low molecular weight PAM-*g*-cellulose copolymers in fair yields and produced minimal amounts of contaminating homopolymer.[§] An obvious disadvantage of this method is the extensive backbone cleavage that occurred to reduce the molecular weight and potential utility of these water-soluble cellulose copolymers.

[§] Table I, Note 1. In addition, polymerization of acrylamide in the absence of cellulose, but otherwise under identical condition, afforded a very low yield of PAM (10%).

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