

Radiation Grafting of Acrylic and Methacrylic Acid to Cellulose Fibers to Impart High Water Sorbency

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Synopsis

Acrylic and methacrylic acids have been directly grafted to rayon and cotton using the preirradiation technique with ^{60}Co γ rays. The rate of grafting increased with increasing temperature and monomer concentration, as did the final degree of grafting. The amount and rate of grafting also increased with the total irradiation dose but tended to level off at higher doses, in agreement with the leveling off of the radical content reported previously. Methacrylic acid grafted more and faster than acrylic acid to both rayon and cotton. Methacrylic acid grafted more with rayon than cotton, but acrylic acid gave somewhat similar yields with both fibers. The water absorbency of the grafted fibers depended strongly on their posttreatment. Decrystallizing with 70% zinc chloride or with hot sodium hydroxide developed supersorbency. The two treatments in succession, respectively, gave the highest values. Methacrylic acid brought about less sorbency than the corresponding acrylic acid grafts. Useful levels of grafting and supersorbency could be readily and practically achieved by the methods described.

INTRODUCTION

There has been considerable interest in recent years in the development of materials with the capacity for absorbing massive amounts of water. A good discussion of some of these products and their application has been presented in the technical press.¹ A number of these materials have been prepared by grafting acrylonitrile and its copolymers to starch² or cellulose,³⁻⁶ followed by alkaline hydrolysis to the corresponding acrylic acid salts. The present authors have produced similar materials by the direct grafting of acrylic acid or methacrylic acid to cellulose, followed by decrystallizing and the formation of the corresponding salt.^{7,8} The decrystallizing technique was originally developed to produce highly elastic cellulosic products.⁹⁻¹³ Almost any method of grafting can be used.⁷ In this paper, however, the results obtained using ^{60}Co γ radiation to initiate the grafting will be described. Both acrylic and methacrylic acid polymerize extremely rapidly with high-energy radiation, and the direct or mutual method cannot be readily used except in the vapor phase or with the use of substantial amounts of inhibitor. For this reason, the so-called preirradiation technique was employed in this work. A note describing some preliminary studies has been published recently.⁸

Experimental

A continuous-filament semidull rayon and a 30s cotton yarn were used. The acrylic acid, methacrylic acid, and the other reagents used were obtained from the Fisher Scientific Company.

The experimental procedures for the grafting reactions have been described previously.⁸⁻¹² Briefly, the cellulose is irradiated to a given dose in a sealed tube under vacuum, after degassing. The dose rate was fixed at 0.3 Mrad/hr. Previously degassed monomer solution was then introduced through a break seal and the tubes were kept in a thermostatted water bath for a given time. The grafted samples were then washed thoroughly with water and methanol and dried under vacuum. The percent grafting, based on 100 parts of cellulose, was determined by the increase in weight.

The water sorbency, which includes trapped water, was determined by two methods. The centrifuge method involved equilibrating with water for 1 hr in a centrifuge at 600 rpm. The sample tube was equipped with a fine-mesh strainer at the bottom to allow excess water to drain away. The tubes were also capped to prevent any evaporation of water. The increase in weight was recorded as the water absorption value.

The second method used was the so-called capillary absorbency test described in the technical literature in detail.¹⁴ Briefly, a 1-g pad of the treated cellulose was placed in a fritted-glass filter attached to a burette by Tygon tubing. A 100-g weight was placed over the sample and water was allowed to enter the sample under an increasingly negative head until equilibrium was reached. The water in the burette was initially at the level of the sample. The water absorbency was calculated from the volume of water absorbed and the initial weight of the sample.

It should be emphasized that both methods include trapped water and are highly dependent on the state of the sample. A more thorough and detailed description of the limitations and fundamentals of such methods has been presented by Burgeni and Kapur.¹⁵

RESULTS AND DISCUSSION

Preirradiation Grafting to Cellulose

The influence of acrylic acid concentration in water on the preirradiation grafting of acrylic acid to rayon is shown in Figure 1 and indicates a roughly linear increase in grafting level with solution concentrations within the range investigated. In a separate set of experiments, shown in Figure 2, the effect of irradiation dose on the grafting levels for two monomer concentrations is summarized. The leveling off of the grafting yields at higher doses can be attributed to the approach to a steady-state radical concentration, observed beyond about 6.0 Mrad.¹¹ Typical preirradiation grafting curves at 0, 45, and 70°C for the grafting of 30 and 75% acrylic acid to rayon are given in Figures 3 and 4, respectively. The shape of the grafting-time curves is quite characteristic and has been discussed in detail elsewhere.^{10,11} Examination of the radical buildup curves for rayon¹¹ indicated that the region between zero and 6 Mrad is well within the buildup region, which is further reflected in the grafting-time curves for 1 and 4 Mrad, as can be seen in Figure 5.

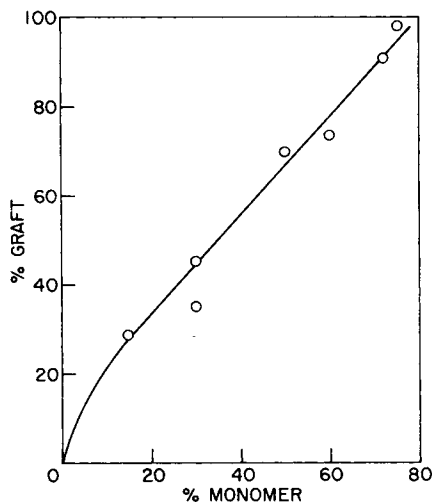


Fig. 1. Effect of monomer concentration on the preirradiation grafting of aqueous acrylic acid to rayon at 45°C: dose, 4.0 Mrad; reaction time, 10 hr.

In a separate series of experiments methacrylic acid was grafted to rayon under otherwise similar conditions as acrylic acid; the results are shown in Figure 6. Again, graft level plateauing with time was observed, but at a much higher level than that found with acrylic acid, as the results taken from Figure 4 show clearly.

Grafting curves for both acrylic acid and methacrylic acid onto cotton are summarized in Figure 7. In a fashion similar to rayon, the methacrylic acid grafts to a higher level for all reaction times, although the ultimate grafting percentage achievable for cotton is far less than the less crystalline rayon. With acrylic acid, however, the grafting yields appear to be similar with both cotton and rayon (see

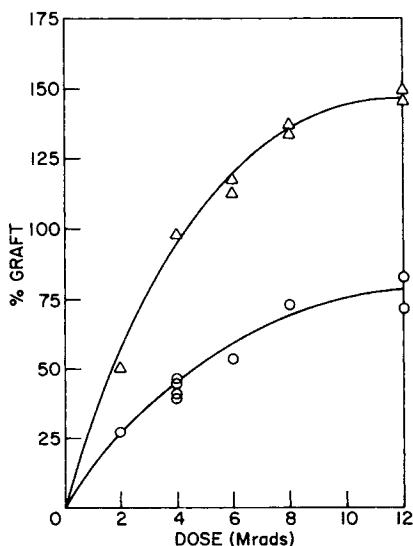


Fig. 2. Effect of total dose on the preirradiation grafting of acrylic acid to rayon at 45°C: reaction time, 10 hr; (O) 30% monomer; (Δ) 75% monomer.

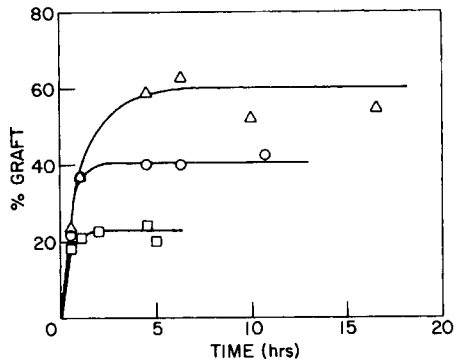


Fig. 3. Preirradiation grafting—time curves for acrylic acid to rayon: dose, 4.0 Mrad; 30% monomer solution; (□) 0°C; (○) 45°C; (△) 70°C.

Fig. 4, for example). Additional experiments are needed if this conclusion is to be confirmed.

Water Absorbency Measurements

Selected grafted samples were subjected to water absorbency measurements using both the centrifuge and capillary absorbency methods described in the above section. These samples were also subjected to various decrystallization conditions. Typical water absorbency results for various grafting levels of acrylic acid-grafted rayon under a variety of decrystallization conditions are given in Table I. It is clear from these results that grafting of a hydrophilic monomer such as acrylic acid does not substantially increase the water absorption without decrystallization of the grafted sample. For example, a sample containing 96% graft absorbs the same amount of water, 2.5 cm³/g, as the control sample. However, when the sample is subjected to decrystallization with 70% ZnCl₂, followed by 3% NaOH, the samples become highly water absorbent with values in excess of 30 cm³/g. But decrystallizing and leaving the samples in the form of the zinc salt did not result in such large increases.

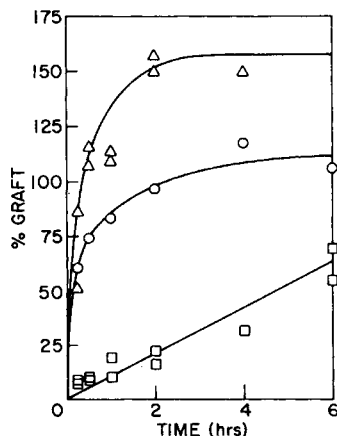


Fig. 4. Preirradiation grafting—time curves for acrylic acid to rayon: dose, 4.0 Mrad; 70% monomer solution; (□) 0°C; (○) 45°C; (△) 70°C.

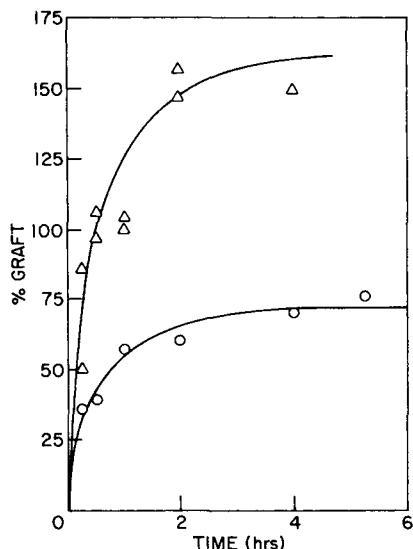


Fig. 5. Preirradiation grafting-time curves for acrylic acid to rayon at 70°C: 75% monomer solution; (O) 1.0 Mrad; (Δ) 4.0 Mrad.

As discussed in a previous communication,⁸ the ability of the decrystallized sample to absorb high percentages of water relative to the nondecrystallized sample is presumably due to the less restrained swelling possible when the crystalline regions are dissolved, i.e., decrystallized.

Although sodium hydroxide is not a pure cellulosic solvent and has only a small effect on the water absorption for ungrafted rayon, it does, under certain conditions, behave as a decrystallization agent for the acrylic acid-grafted rayon, where presumably the presence of the grafted side chain helps to solubilize local

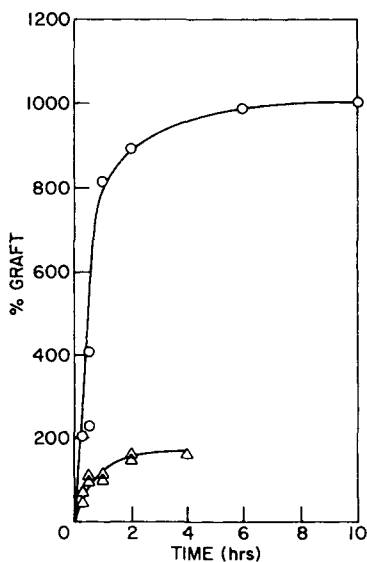


Fig. 6. Preirradiation grafting-time curves for methacrylic acid and acrylic acid to rayon: dose, 4.0 Mrad; 70°C; 75% monomer solution; (O) methacrylic acid; (Δ) acrylic acid.

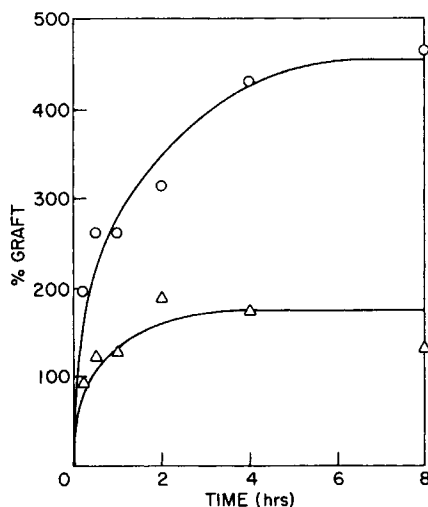


Fig. 7. Preirradiation grafting-time curves for methacrylic acid and acrylic acid to cotton yarn: dose, 4.0 Mrad; 70°C; 75% monomer solution; (O) methacrylic acid; (Δ) acrylic acid.

segments of the cellulosic chain. The results included in Table I also show that as the amount of acrylic graft increases, the extent of "super" absorbency is extended several-fold. For example, the water uptake increases from 11.2 to 38.8 cm^3/g as the grafting level is increased from 77 to 138%, using similar decrystallizing conditions. For comparison, the water absorbency of a rayon sample grafted to 288% with methacrylic acid is included in Table I. Again, under these conditions of decrystallization, the sample is highly absorbent but probably less than with acrylic acid.

TABLE I
Water Absorbency of Acrylic Acid-Grafted Rayon Before and After Decrystallization

% Graft	Decrystallization conditions	Water absorbency, cm^3/g	
		Buret	Centrifuge
0	none	2.86	2.00
64	none	2.26	2.45
72	none	2.72	3.12
100	none	2.35	2.40
138	none	2.39	2.30
64	3% NaOH (cold)	4.30	5.10
77	3% NaOH (hot)	—	11.20
100	3% NaOH (cold)	4.26	6.16
114	3% NaOH (hot)	—	22.10
138	3% NaOH (cold)	6.96	8.89
138	3% NaOH (hot)	—	38.80
138	3% NaOH (hot)	—	35.60
98	70% ZnCl_2 at 40°C for 2 hr	3.8	—
98	70% ZnCl_2 at 40°C for 2 hr, then 3% NaOH (cold)	15.3	31.6
104	70% ZnCl_2 at 40°C for 2 hr	3.1	—
144	70% ZnCl_2 at 40°C for 2 hr	3.8	—
147	70% ZnCl_2 at 50°C for 5 hr, then 3% NaOH, (cold)	—	53.5
82	70% ZnCl_2 at 50°C for 3 hr, then 3% NaOH (cold)	—	36.2
288 ^a	3% NaOH (hot)	—	45.90

^a Methacrylic acid.

TABLE II
Water Absorbency of Acrylic Acid- and Methacrylic Acid-Grafted Cotton Before and After Decrystallization

% Graft	Decrystallization conditions	Water absorbency, cm ³ /g	
		Buret	Centrifuge
Acrylic acid			
0	none	4.02	4.03
96	none	4.26	3.00
191	none	4.07	3.58
96	3% NaOH (cold)	4.84	6.80
191	3% NaOH (cold)	8.89	12.00
191	3% NaOH (hot)	—	26.2
Methacrylic acid			
194	none	2.89	2.69
194	3% NaOH (cold)	4.40	6.30
194	3% NaOH (hot)	—	16.50

Water absorbency results obtained on acrylic acid- and methacrylic acid-grafted cotton yarn are summarized in Table II. These results demonstrate the same general trend in decrystallization conditions as discussed above in more detail for grafted rayons. For both forms of grafted cellulose, highly absorbent materials can be obtained by the combination of acrylic or methacrylic acid grafting followed by a suitable condition of decrystallization to render the substrate highly absorbent. It is clear in the case of cotton that acrylic acid leads to a considerably higher sorbency than corresponding methacrylic acid grafting. Using the buret method to measure water absorbency, the sorption transients were measured on the grafted rayons for the various conditions. In general, the modified samples reached a plateau level of water absorption after 15–20 min. However, the highly decrystallized sample (zinc chloride followed by sodium hydroxide) continued to slowly absorb water beyond 600 min. The massive increases in water sorbency, brought about by a posttreatment with hot sodium hydroxide, suggests clearly that decrystallization is taking place. This is substantiated by the similar increased absorption achieved with 70% zinc chloride solution, a true cellulose and decrystallizing solvent. However, x ray or other independent evidence is perhaps needed to definitely confirm the decrystallization hypothesis. Transforming the grafted product to the sodium salt is also partially effective, as shown by the improvements brought about by the use of cold 3% NaOH either before or after the zinc chloride treatment. Although work to date has been mainly with radiation grafting techniques, it should be emphasized that other methods of grafting are equally effective, as described in ref. 7. The methods used in this investigation for measuring the water absorption were comparatively simple and only conducted with distilled water. More sophisticated methods such as those described in ref. 15 are more instructive. Also the effect of salts on the water absorption needs to be studied, since many of the applications for these materials are concerned with blood and urine sorption. The methods described are quite practical, however, and adequate degrees of grafting can be achieved with modest doses and reaction times.

References

1. *Chemical Week*, July 24, 1974, pp. 21-22.
2. L. A. Gugliemi, M. U. Weaver, C. R. Russell, and C. E. Rist, *J. Appl. Polym. Sci.* **13**, 207 (1969) and related articles.
3. J. W. Adams and H. W. Hoftiezer, U.S. Pat. 3,256,372 (1966).
4. P. Lepoutre, S. H. Hui, and A. A. Robertson, *J. Appl. Polym. Sci.*, **17**, 1343 (1973).
5. P. Lepoutre, S. H. Hui, and A. A. Robertson, *J. Macromol. Sci. Chem.*, **10** 681 (1976).
6. P. K. Chatterjee and R. F. Schwenker, U.S. Pat. 3,889,678 (1975).
7. J. L. Williams and V. Stannett, U.S. Pat. 4,036,588 (1977).
8. J. L. Williams and V. Stannett, *J. Appl. Polym. Sci.*, **23**, 1265 (1979).
9. J. L. Williams and V. Stannett, *J. Polym. Sci. Polym. Lett. Ed.*, **10**, 665 (1972).
10. J. L. Williams, D. K. Woods, V. T. Stannett, L. G. Roldan, S. B. Sello, and C. V. Stevens, *Text. Res. J.*, **43**, 205 (1973).
11. J. L. Williams, D. K. Woods, V. T. Stannett, S. D. Sello, and C. V. Stevens, *J. Appl. Radiat. Isot.* **26**, 159 (1975).
12. J. L. Williams, D. K. Woods, V. T. Stannett, S. B. Sello, and C. V. Stevens, *J. Appl. Radiat. Isot.* **26**, 169 (1975).
13. J. L. Williams and V. Stannett, U.S. Pat. 3,814,676, (1974).
14. Hercules, Inc., Wilmington, Delaware, Aqualon Data, Bulletin V.C. 494 A; also *Formed Fabrics Industry* April 1976, pp. 17-18.
15. A. A. Burgeni and C. Kapur, *Text. Res. J.*, **37**, 356 (1967).

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