

## Cellulose Graft Copolymers. IV. Graft Copolymerization of Methacrylonitrile with $\gamma$ -Irradiated Cellulose from DMSO-, Acetone-, and Methanol-Water Systems\*

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### Synopsis

Methacrylonitrile was graft-copolymerized from DMSO-, acetone-, and methanol-water systems with  $\gamma$ -irradiated, purified cotton cellulose. The relative extents of scavenging of the free radicals in the irradiated cellulose after immersion in the solvents for 3 min at 25°C, as determined by electron spin resonance spectroscopy, were: methanol (77%) > water (70%)  $\gg$  acetone (5%) > DMSO (0%). After immersion of irradiated cellulose in the solvents for 60 min at 25°C, the relative extents of scavenging of the radicals were: methanol, water (80-85%) > DMSO (80%) > acetone (62%). From these data, it would appear that the overall rates of diffusion of methanol and water into the fibrous macrostructure were greater than the rates of diffusion of DMSO and acetone into the structure. The relative radiochemical yields of the graft copolymerization reactions of methacrylonitrile with irradiated cellulose in the different solvents were: water  $\gg$  DMSO > methanol  $\gg$  acetone. The addition of water to the systems increased the yields of the reactions.

### INTRODUCTION

Avny et al.<sup>1</sup> reported the anionic graft polymerization of acrylonitrile and methacrylonitrile on cellulose acetate from tetrahydrofuran, N,N-dimethyl formamide, and dimethyl sulfoxide (DMSO). When polymerization was initiated by lithium alkoxide derivatives of cellulose acetate in DMSO, no polymerization occurred with methacrylonitrile. In the cases where polymerization of methacrylonitrile was initiated by potassium alkoxide derivatives of cellulose acetate in DMSO, both graft and homopolymerization occurred. However, due to the absence of the  $\alpha$ -acidic hydrogen in methacrylonitrile, less chain transfer occurred when methacrylonitrile was

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the monomer used than when acrylonitrile was used. Consequently, less homopolymerization occurred when methacrylonitrile was used than when acrylonitrile was used. Although there have been numerous reports of graft copolymerization of acrylonitrile onto fibrous cellulose, initiated by both free-radical and nonradical processes, very limited work has been done with methacrylonitrile.<sup>2</sup> Sadovnikova et al.<sup>3</sup> reported graft copolymerization of methacrylonitrile onto cellulose initiated by the ceric ion method. They claimed that the cellulose-poly(methacrylonitrile) copolymer had increased heat and bacterial resistance. Kern and Fernow<sup>4</sup> reported that poly(methacrylonitrile), prepared by free-radical-initiated processes, was tough but not brittle, had a softening point at 115°C, and was soluble in acetone, cyclohexanone, methylene chloride, and benzonitrile.

In this report, the graft copolymerization reactions of methacrylonitrile with irradiated fibrous cotton cellulose from DMSO-, acetone-, and methanol-water systems are reported. Since poly(methacrylonitrile) is soluble in acetone and DMSO and insoluble in water and methanol, the Trommsdorff-type effects of these solvent systems are compared. The extent of scavenging of the free radicals in the irradiated cellulose by the different systems is also reported.

## EXPERIMENTAL

### Materials

Cotton cellulose of Deltapine variety, spun into 7s/3 yarns, was purified in the usual manner.<sup>5</sup> Methacrylonitrile, obtained from a commercial source, was purified by passing the monomer through columns of activated alumina (grade F-20, 80-200 mesh, obtained from Alcoa Chemicals) in order to remove inhibitors of polymerization. Dimethyl sulfoxide (DMSO), acetone, and methanol were reagent grade and were dehydrated prior to use. Distilled water was used to prepare the solutions.

### Methods

Samples of purified cotton cellulose yarns were dried overnight under vacuum at 50°C and then irradiated at ambient temperature in a nitrogen atmosphere to a dosage of  $5.2 \times 10^{19}$  eV/g (1.0 Mrad). The SRRL <sup>60</sup>Co radiation source,<sup>6</sup> which had a dose rate<sup>7</sup> of about  $5.9 \times 10^{19}$  eV/g-hr, was used. Samples of irradiated cellulose were transferred to quartz tubes (3-mm diameter) at 25°C, using a drybox under a nitrogen atmosphere, for examination in the EPR spectrometer. Free radical concentrations in the irradiated celluloses during the postirradiation reactions were determined using a Varian 4502-15 EPR spectrometer system which was equipped with a variable temperature accessory and a dual sample cavity. To minimize the effects of the absorption of microwave power by the solvents, the samples of irradiated cellulose were frozen by immersing them in liquid nitrogen. After warming the samples to -180°C, their ESR spectra were recorded. The free-radical concentrations in the irradiated celluloses were

recorded in arbitrary units by measuring the distance between the peak-to-peak values of the spectra.

About 24 hr after irradiation, samples of cotton yarn were immersed in DMSO-water, acetone-water, or methanol-water solutions containing methacrylonitrile at 25°C. The solutions were evacuated several times and flushed with nitrogen each time. The copolymerization reaction which was initiated was allowed to proceed at 25°C for 60 min. Then the grafted yarns were washed several times with methanol to remove unreacted monomer. The grafted yarns were further extracted at 25°C for 16 hr with a solution of cyclohexane (90 vol-%)-benzene (10 vol-%) to remove any homopolymer. The extracted yarns were then washed in distilled water, dried overnight under vacuum at 50°C, and equilibrated at 25°C and 50% R.H. to constant weight. The extent of graft copolymerization of methacrylonitrile with cotton cellulose was determined as the increase in weight of the grafted yarn over that of a control yarn similarly treated except for the omission of methacrylonitrile. The millimoles of methacrylonitrile grafted per gram of cellulose were calculated from these data. The radiochemical yields,<sup>8</sup> after copolymerization at 25°C for 60 min, were calculated as monomer units of methacrylonitrile grafted per 100 eV/g.

## RESULTS AND DISCUSSIONS

### Effects of Solvents on Free-Radical Concentration

The effects of the composition of the solutions on the extent of scavenging of free radicals in irradiated cotton cellulose are shown in Tables I and II. After immersion of irradiated cellulose in the solvents at 25°C for 3 min, the relative extents of scavenging of the free radicals were: methanol (77%) > water (70%) >> acetone (5%) > DMSO (0%). After immersion of irradiated cellulose in the solvents at 25°C for 60 min, the relative extents of scavenging of the free radicals were: methanol, water (80-85%)<sup>9</sup> > DMSO(80%) > acetone(62%).<sup>10</sup> The maximum extent of scavenging of

TABLE I  
Effects of Immersion of Irradiated Cotton Cellulose in DMSO-Water  
Solutions on the Stability of the Free Radicals<sup>a</sup>

Composition of solutions, vol-%		Free-radical concentration, arbitrary units		
DMSO	Water	30 sec	3 min	1 hr
Control <sup>b</sup>		21	21	21
100	0	21	21	4.3
75	25	17	7.9	3.8
50	50	6.7	6.8	3.8
25	75	5.1	4.7	3.0
0	100	6.2	5.5	3.4

<sup>a</sup> Immersion at 25°C for indicated time periods.

<sup>b</sup> Dried, purified cotton cellulose irradiated in nitrogen atmosphere at 25°C to  $5.2 \times 10^{19}$  eV/g with <sup>60</sup>Co  $\gamma$ -radiation.

TABLE II  
Comparison of the Extent of Scavenging<sup>a</sup> of Free Radicals in Irradiated  
Cellulose by the Solutions and Radiochemical Yield<sup>b</sup> of  
Grafted Poly(methacrylonitrile) from the Solutions

Composition of solutions, vol-%		Solvent in solutions					
		DMSO		Acetone		Methanol	
Solvent	Water	Radicals scavenged, %	Radiochemical yield	Radicals scavenged, %	Radiochemical yield	Radicals scavenged, %	Radiochemical yield
100	0	0	1400	5	0	77	900
75	25	62	3700	70	1800	74	2100
50	50	72	6300	72	2600	79	3500
25	75	78	6700	77	4400	79	5100
0	100	70	5400	70	5400	70	5400

<sup>a</sup> Decrease in free-radical concentration after immersion of irradiated cellulose in solution for 3 min at 25°C.

<sup>b</sup> Monomer units grafted/100 eV/g.

the free radicals occurred when irradiated cellulose was immersed in solvent-water solution that had a composition of about 25/75 vol-% (see Table II). In the case of methanol-water solutions, the extent of scavenging of the free radicals was about the same for solutions containing 25 to 50 vol-% methanol. From these data, it would appear that the overall rates of diffusion of methanol and water into the cellulosic structure were greater than the rates of diffusion of DMSO and acetone into the structure. However, after immersion of the irradiated cellulose in the solvents at 25°C for 60 min, the extent of diffusion of DMSO into the cellulosic structure was about the same as methanol and water; the extent of diffusion of acetone into the structure was less than that of the other solvents.

The addition of methacrylonitrile to the solutions probably changes their rates of diffusion into the cellulosic structure slightly. It would appear that for these solutions the maximum extent of copolymerization of methacrylonitrile with irradiated cellulose should occur from DMSO solutions, since the extent of diffusion of DMSO solution into the cellulosic structure after reaction times of 60 min or more appears to be equal to or greater than the other solutions and/or a smaller fraction of cellulosic free radicals is scavenged by DMSO solutions than by the other solutions. This would, of course, leave a higher fraction of the cellulosic free radicals available for initiating copolymerization reactions with methacrylonitrile.

### Graft Copolymerization

**DMSO-Water-Methacrylonitrile System.** The effects of composition of DMSO-water solution and concentration of methacrylonitrile on extent of graft copolymerization with irradiated cotton cellulose are shown in Figure 1. From 0 to about 10 vol-% DMSO in water, the extent of copolymerization of methacrylonitrile with irradiated cellulose was relatively in-

dependent of the apparent concentration of monomer. Since the monomer has a low degree of solubility in water (less than 3 wt-% at 25°C), the concentration of methacrylonitrile in these aqueous solutions was constant, that is, about 3 wt-%, and relatively independent of the amount of mono-

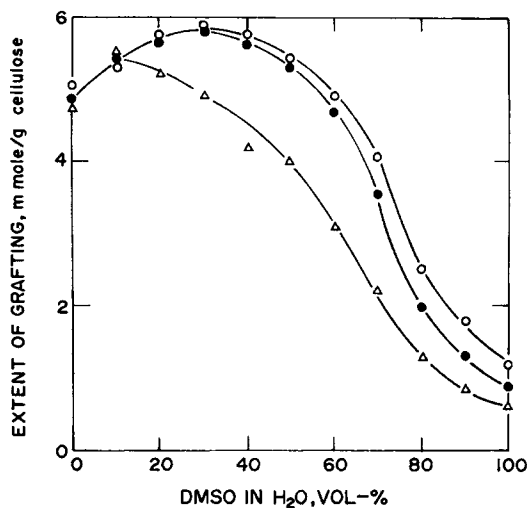


Fig. 1. Effect of composition of DMSO-water solution and concentration of methacrylonitrile on extent of graft copolymerization with irradiated cellulose at 25°C and 60 min: ( $\Delta$ ) 4 vol-% methacrylonitrile; ( $\bullet$ ) 8 vol-%; ( $\circ$ ) 17 vol-%. Dosage,  $5.2 \times 10^{19}$  eV/g; cellulose solution ratio, 1/80.

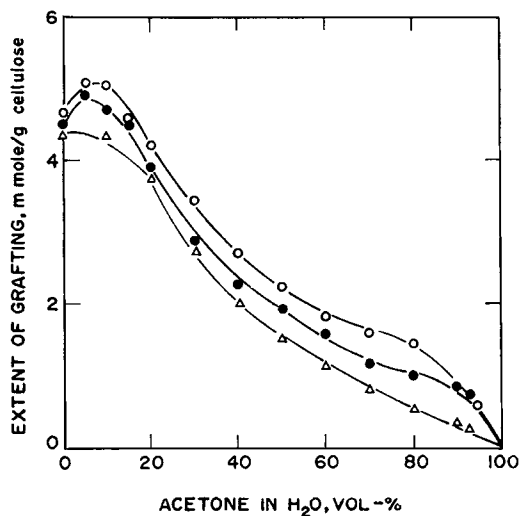


Fig. 2. Effect of composition of acetone-water solution and concentration of methacrylonitrile on extent of graft copolymerization with irradiated cellulose at 25°C and 60 min: ( $\Delta$ ) 4 vol-% methacrylonitrile; ( $\bullet$ ) 8 vol-%; ( $\circ$ ) 17 vol-%. Dosage,  $5.2 \times 10^{19}$  eV/g; cellulose solution ratio, 1/80.

mer mixed with the system.<sup>11</sup> Graft copolymerization of methacrylonitrile with irradiated cellulose probably only occurred from these monomer-saturated aqueous solutions. As the amount of DMSO in water was increased, the solubility of monomer in the system increased, and the extent of copolymerization became more dependent on the amount of monomer added to the system. As DMSO was added to the water-methacrylonitrile system, the extent of copolymerization increased to a maximum and then decreased, particularly at the higher amounts of DMSO added to the system. This was probably due to the Trommsdorff-type<sup>12</sup> accelerative effect of water, since poly(methacrylonitrile) is soluble in DMSO and insoluble in water.<sup>11</sup>

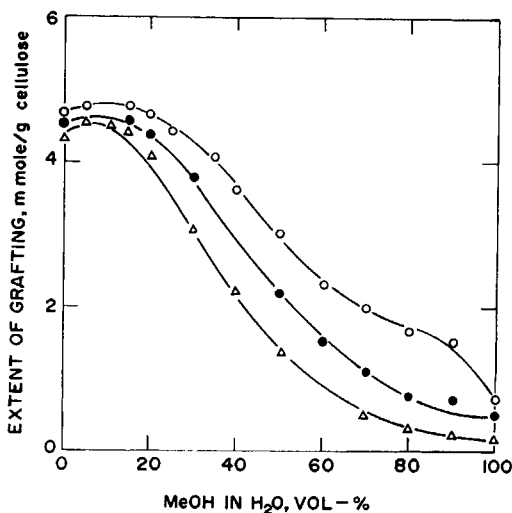


Fig. 3. Effect of composition of methanol-water solution and concentration of methacrylonitrile on extent of graft copolymerization with irradiated cellulose at 25°C and 60 min: ( $\Delta$ ) 4 vol-% methacrylonitrile; ( $\bullet$ ) 8 vol-%; ( $\circ$ ) 17 vol-%. Dosage,  $5.2 \times 10^{19}$  eV/g; cellulose solution ratio, 1/80.

**Acetone-Water-Methacrylonitrile System.** The effects of composition of acetone-water solution and concentration of methacrylonitrile on extent of graft copolymerization with irradiated cotton cellulose are shown in Figure 2. The extent of copolymerization of methacrylonitrile with irradiated cellulose was dependent on the amount of monomer added to the system and decreased as the concentration of acetone in the system increased. In solutions of about 10 vol-% acetone-90 vol-% water, a maximum extent of copolymerization was obtained. This maximum could be attributed to a Trommsdorff-type<sup>12</sup> effect of water. This maximum extended over a smaller range of solvent-water composition than in the case

of the DMSO–water system and may indicate a higher degree of solubility of poly(methacrylonitrile) in acetone–water solutions than in DMSO–water solutions.

**Methanol–Water–Methacrylonitrile System.** The effects of composition of methanol–water solution and concentration of methacrylonitrile on extent of graft copolymerization with irradiated cotton cellulose are shown in Figure 3. As in the case of the acetone–water system, the extent of copolymerization of methacrylonitrile with irradiated cellulose was dependent on the amount of monomer added to the system and decreased as the concentration of methanol in the system increased. In water and in solutions containing up to about 20 vol-% methanol, a maximum extent of copolymerization was obtained. Poly(methacrylonitrile) is insoluble in both water and methanol.<sup>11</sup>

**Radiochemical Yields.** Comparisons of the radiochemicals yields of grafted poly(methacrylonitrile) from different solutions on irradiated cellulose are made in Table II. In each case, the cellulose was preirradiated to the same dosage, so that the initial concentration of cellulosic free radicals was constant. The radiochemical yields of grafted polymer depended primarily on (1) the competition between the monomer and the solvent for the free radicals; (2) the effects of the interaction of the solution with the fibrous macrostructure, so that monomer was brought into contact with the free radicals and in sufficient concentration to maintain a chain reaction; (3) the use of solutions in which a minimum of chain transfer reactions occur that would probably lead to homopolymerization rather than to graft copolymerization.

DMSO, methanol, and water apparently interacted with the fibrous macrostructure in such a way that the monomer could compete with the solvent for the cellulosic free radicals. As discussed earlier, DMSO and acetone interacted with the fibrous macrostructure at a slower rate than methanol and water; however, after immersion of irradiated cellulose in the solvents for 60 min at 25°C, the extent of interaction of DMSO, methanol, and water with the fibrous macrostructure was about the same, as shown by the extent of scavenging of the free radicals. As reported previously, only a small fraction of the initial concentration of free radicals in irradiated cellulose initiate copolymerization reactions, and a large fraction of the initial radicals is terminated by scavenging by the solution.<sup>13</sup>

The relative radiochemical yields in the different solvents are water  $\gg$  DMSO  $\gg$  methanol  $\gg$  acetone. The addition of water to DMSO, acetone, and methanol increased the radiochemical yields of the reactions from each of the solutions. Poly(methacrylonitrile) is insoluble in water and methanol, so that part of this yield could be attributed to the Trommsdorff-type effect.<sup>12</sup>

Trade names are given as part of the exact experimental conditions and not as an endorsement of the products over those of other manufacturers.

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