

## NMR Study of Water Adsorbed on Methyl Methacrylate-Grafted Cellulose

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### Synopsis

Graft cellulose samples were prepared by three different initiation methods, and the widths of the NMR absorption spectra of samples were measured at various water contents. Samples prepared by both hydrogen peroxide and adsorbed ceric ion methods exhibited maximum widths of NMR absorption spectra at about 10% grafting, whereas the corresponding values for the sample prepared by the conventional ceric ion method were about 30%. Even a minimum value was found on the sample prepared by the latter method. The reason for such different water-binding behaviors of samples is discussed from the viewpoint of difference in the composition of graft celluloses.

### INTRODUCTION

Several methods are well known to initiate graft copolymerization of vinyl monomer onto cellulose and its derivatives, and the characterizations<sup>1-10</sup> of these graft copolymers produced have been examined. However, it seems that there are many aspects which have not yet been clarified about the structure of the graft copolymer. The state of water contained in cellulose fibers has been investigated by means of the width of the NMR absorption spectrum in our previous papers,<sup>11,12</sup> and the water-binding characteristics peculiar to each cellulose sample were indicated. If similar experiments were applied to a graft copolymer, novel information could be expected on the structure of this copolymer.

In the present study, graft celluloses containing poly(methyl methacrylate) were prepared by three initiation methods, and widths of their NMR absorption spectra were examined in order to study the relation between water-binding characteristics and the nature of the grafts in the copolymers.

### EXPERIMENTAL

Methyl methacrylate was graft copolymerized on commercial dissolving sulfite pulp by means of the following three polymerization methods: (1) conventional ceric ion method<sup>13,14</sup>; (2) adsorbed ceric ion method<sup>15</sup>; and (3) hydrogen peroxide method.<sup>16</sup> The products were extracted with acetone to exclude homopolymer, and the per cent grafting of the graft

TABLE I  
Conditions of Graft Copolymerization<sup>a</sup>

Polym. method	Cellulose sample	Concn. of initiator, mmole/l.	Polym. temp., °C	Polym. time, min
Conventional ceric ion method	SP	ceric ion, 10	45	120
Adsorbed ceric ion method	SP <sup>b</sup>	—	45	120
Hydrogen peroxide method	SP <sup>c</sup>	hydrogen peroxide, 5	60	120

<sup>a</sup> Liquor ratio, 80; SP = commercial sulfite pulp.

<sup>b</sup> Pretreated with 10 mmole/l. aqueous solution of ceric ammonium nitrate at 45°C for 60 min.

<sup>c</sup> Pretreated with 5 mmole/l. aqueous ferrous sulfate at 45°C for 60 min.

TABLE II  
Descriptions of Samples

Polym. method	Amount of monomer, ml	Grafting, %	$\bar{M}_w$ of grafts <sup>a</sup> × 10 <sup>-4</sup>	No. of grafts, mmoles per 100 g cell
Conventional ceric ion method	3.0	8.6	7.7	0.112
	9.0	32.0	20.0	0.160
	14.4	50.0	30.3	0.164
Adsorbed ceric ion method	12.8	6.3	20.0	0.031
	14.4	15.8	34.9	0.045
	30.0	67.7	140	0.048
Hydrogen peroxide method	3.0	8.0	12.5	0.064
	9.0	28.8	32.0	0.090
	15.0	49.6	50.5	0.098

<sup>a</sup> Weight-average molecular weight of grafts, determined from the viscosity<sup>18</sup> of their acetone solutions at 25°C.

copolymer was directly determined by the sulfuric acid method.<sup>17</sup> In each method, graft copolymerizations were controlled by varying the amount of monomer employed to attain various levels of per cent grafting up to 50%. The conditions and the description of the copolymers are shown in Tables I and II, respectively.

From Table II, it is seen that the average molecular weight of grafts increases in the order adsorbed ceric ion method > hydrogen peroxide method > conventional ceric ion method, while the number of grafts increases in the opposite order. Thus, the composition of the copolymers reflects each initiation method to a large extent.

Samples containing 5% to 30% water were prepared for each graft copolymer and packed closely in sample tubes. By measuring the high-resolution NMR absorption spectrum, the width at half-value of the absorption curve for each sample was obtained. A JEOL NMR spectrometer Model TNM-C-60HL was used under the following conditions:

resonance frequency, 60 Mc; sweep rate, 90 ppm/2.5 min; RF level, 40 db; sample temperature, 20°C.

## RESULTS AND DISCUSSION

Figure 1 shows the relationship between the width at half-value and the water content of samples prepared by the hydrogen peroxide method. Though the width at half-value tended to decrease along with the water content in each sample, it was noticed that different curves were obtained for samples with different per cent grafting. If one were to suppose that a hydrophobic polymer part coexists with a cellulosic part in the sample without any influence on the original water-binding character of the cellulose, and also without any water being adsorbed by itself, any series of graft copolymers ought to be included in a single common curve in such a figure with an abscissa of water content based on just the cellulose content in graft celluloses. Contrary to expectations, a relationship almost similar to that of Figure 1 was obtained even after the abscissa was converted. This seems to indicate that graft copolymerization positively affects the water-binding characteristics of the original cellulose.

The position of the curves in the figure cannot be said to vary simply with the per cent grafting of the samples. Here, we must consider the width of the absorption spectrum as an index of the water-binding power of the sample. The fact that the water-binding power does not relate linearly with the per cent grafting of the samples seems to shed somewhat important light on the structure of the graft cellulose.

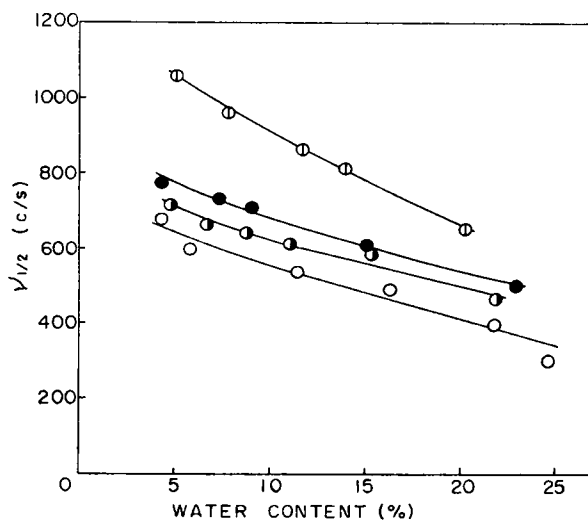


Fig. 1. Relationship between width at half-value and water content of copolymers prepared by hydrogen peroxide method. Per cent grafting: (○) 0%; (⊙) 8.0%; (●) 28.8%; (●) 49.6%.

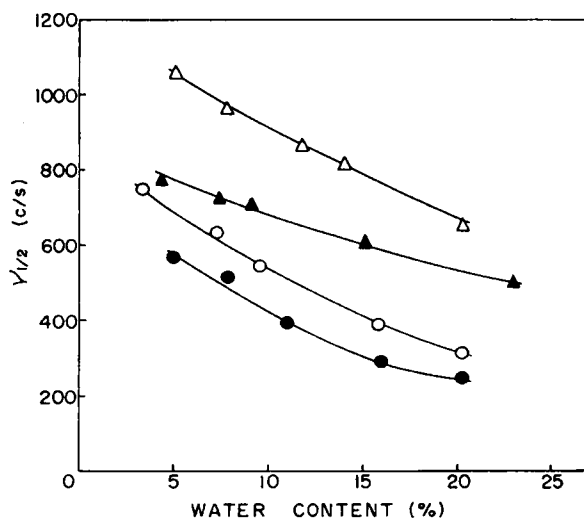


Fig. 2. Comparison of width at half-value vs. water content among copolymers prepared by hydrogen peroxide or conventional ceric ion method. Per cent grafting, conventional ceric ion method: (O) 8.6%; (●) 50.0%; hydrogen peroxide method: (Δ) 8.0%; (▲) 49.6%.

Figure 2 shows the relationship between the width at half-value and the water content of the samples with about 8% and 50% grafting prepared by two different initiation methods. If compared at the same water content, samples prepared by the hydrogen peroxide method have water-binding powers always higher than those prepared by the conventional ceric ion method. Therefore, it can be safely said that the initiation method as well as the per cent grafting positively contribute to the water-binding power of samples.

The relationship between the width at half-value and the per cent grafting of samples prepared by the hydrogen peroxide method is shown in Figure 3. The values of the width at each water content were taken from the curves in Figure 1. It is noticed that the maximum values appeared at about 10% grafting in all three curves. Thus, the water-binding power first increases and then decreases with the per cent grafting. It is hard to explain this phenomenon clearly; however, it is conceivable that the covering effect of grafted polymer over the cellulose fiber surface is a major factor. That is, it might be said that the rough structure of cellulose fibers, which does not have power enough to restrict the motion of neighboring water molecules, is preferentially attacked by grafting. In such a manner, the water-binding power at the first stage of grafting perhaps undergoes an increase due to the covering effect. Such an effect conceivably develops markedly within the range of low per cent grafting. However, with progress of the polymerization reaction, the location of the grafting site is not always limited to the surface of the fibers, but also proceeds on the inside of the fibers, the amorphous part, which originally has a rather high water-

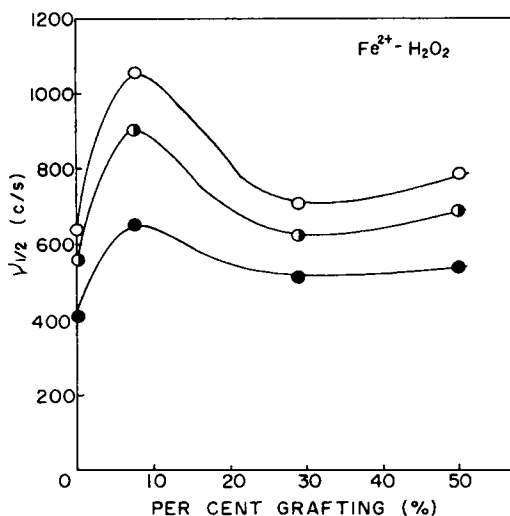


Fig. 3. Relationship between width at half-value and per cent grafting of copolymers prepared by hydrogen peroxide method. Water content: (○) 5%; (◐) 10%; (●) 20%.

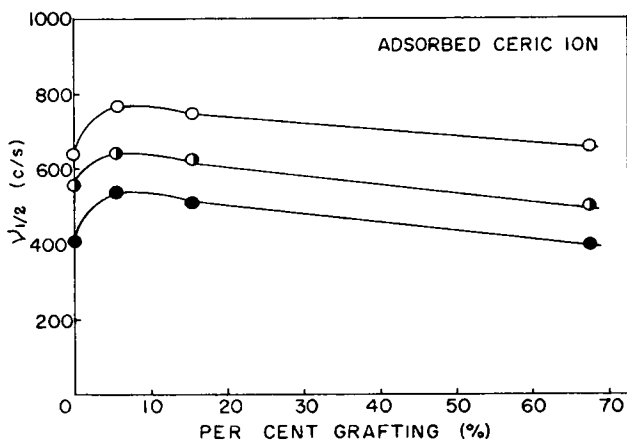


Fig. 4. Relationship between width at half-value and per cent grafting of copolymers prepared by adsorbed ceric ion method. Water content: (○) 5%; (◐) 10%; (●) 20%.

binding power. Thus, the introduction of hydrophobic material in such a manner naturally means a decrease of the water-binding power of the sample resulting in the narrowing of the width of the NMR absorption spectrum.

A similar relationship in graft celluloses initiated by the adsorbed ceric ion method is shown in Figure 4. The tendency of the curves in the figure, i.e., the dependency of width at half-value on per cent grafting, is very much similar to that in Figure 3. However, the widths at half-value are generally narrower than those obtained by the hydrogen peroxide method, indicating the lower water-binding power.

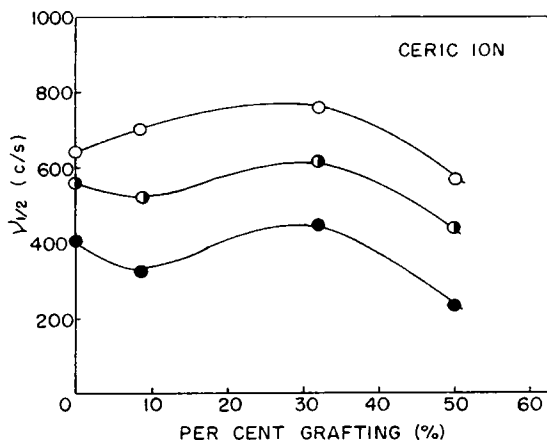


Fig. 5. Relationship between width at half-value and per cent grafting of copolymers prepared by conventional ceric ion method. Water content: (○) 5%; (◐) 10%; (●) 20%.

Figure 5 shows the relationship for samples prepared by the conventional ceric ion method. Curves are characterized by a minimum value at about 10% grafting, though this is not true in the case of 5% water content. This phenomenon seems to indicate, during the first stage of this method, that the effect on the reduction of water-binding power of the sample by the grafted polymer introduced into the rough amorphous parts has an advantage over the covering effect of the fiber surface. In practice, graft celluloses prepared by the conventional ceric ion method have been reported<sup>10</sup> to be far more homogeneous in composition than those prepared by the hydrogen peroxide method. For the above reason, it is almost common to observe a somewhat low maximum value at a higher per cent grafting such as 30%. The dependency of the width at half-value on the per cent grafting in this method is clearly different from that of the other two initiation systems. It is inferred that these facts are caused by the differences in composition of copolymers initiated by the three methods.

As mentioned above, it appears that the location of grafted hydrophobic chains in graft celluloses is markedly affected by the method of initiation. The structure of such graft cellulose can possibly be investigated by the NMR method proposed herein.

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