

Radical Formation and Graft Copolymerization on Photo-irradiated Aldehyde Cellulose

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Synopsis

The relationship between the activity to initiate graft copolymerization under photo-irradiation and the photo-induced radicals of periodic acid-oxidized cellulose (aldehyde cellulose) was investigated. Aldehyde cellulose proved to have a high activity to initiate graft copolymerization under photo-irradiation, and the effect was profound, especially for hydrophilic vinyl monomers such as acrylic acid and acrylamide. By studying the ESR spectrum of photo-irradiated aldehyde cellulose, the formation of a radical giving a singlet spectrum with linewidth of 14–15 G and a g value of 2.001 was observed. This was assigned to an acyl radical originating in the aldehyde group of the sample. Employing low molecular weight aldehydes, it was confirmed that an acyl radical formed on aldehyde compounds by photo-irradiation has a function sufficient to initiate the graft copolymerization of vinyl monomers. It was concluded that the high activity needed to induce the graft copolymerization of aldehyde cellulose under photo-irradiation was based on an acyl radical which originated in the aldehyde group of the sample.

INTRODUCTION

The chemical reactivity of cellulose is known to be strongly influenced by its oxidized status. The enhanced thermal initiation of graft copolymerization on hydrogen peroxide- or sodium hypochlorite-oxidized cellulose¹ and poly(vinyl alcohol) fiber² without the use of initiator was reported. Further, the periodic acid-oxidized cellulose^{3,4} or poly(vinyl alcohol) fiber⁵ has sufficient activity to initiate graft copolymerization under photo-irradiation.

The relationship between the oxidized status and the activity to initiate photografting of periodic acid-oxidized cellulose (aldehyde cellulose) was investigated for the purpose of clarifying the real active sites in the photochemistry of cellulose. By analyzing the ESR spectra of photo-irradiated aldehyde cellulose and low molecular weight aldehyde compounds, radical species formed at the aldehyde groups were studied and their ability to initiate the polymerization of vinyl monomers discussed.

EXPERIMENTAL

Materials

Commercial pulps from softwoods were treated with an aqueous periodic acid solution at 45°C for 60 min (ratio of material to liquid, 1:100) to form aldehyde cellulose. After the treatment, the sample was washed with water, dried under reduced pressure, and used for further experiments. It is well-known that periodic acid-oxidation leads to introduction of aldehyde groups on the cellulose

sample.^{6,7} The carbonyl content of aldehyde cellulose was determined according to the hydroxylamine method.⁸

Acrylic acid (AA), N-vinyl-2-pyrrolidone (N-VP), acrylamide (AAm), methyl methacrylate (MMA), acrylonitrile (AN), and vinyl acetate (VAc) were used as vinyl monomers. All monomers were purified according to the usual methods before being used.

Acetaldehyde, propylaldehyde (PA), *n*-butylaldehyde (BA), and glutaraldehyde (GA) were used as low molecular weight models of aldehyde. The model compounds were reagent grade of commercial origin and were used without special purification.

Graft Copolymerization and Photopolymerization

Graft copolymerization was carried out in a system consisting of 0.50 g aldehyde cellulose (oven dry), 2 ml monomer (2.0 g AAm), and 20 ml water under nitrogen in a Pyrex glass tube at 40°C with light irradiation for a given time. Polymer products were washed with water and extracted with acetone, N,N-dimethylformamide, or hot water to remove homopolymers. The percent grafting and the graft efficiency were calculated.⁹

Photopolymerization of vinyl monomers was carried out in a system consisting of 20 ml aqueous solution of aldehyde model compound and 2 ml monomer (2.0 g AAm) under nitrogen in a Pyrex glass tube at 40°C for a given time.

The photo-induced graft copolymerization and the photopolymerization were carried out in a Riko rotary photochemical reactor RH400-10W, around which Pyrex glass tubes were set to rotate.

Measurement of ESR Spectrum

A quartz glass tube (3- or 5-mm diam) filled with a sample and flushed with nitrogen was exposed at -196°C (liquid nitrogen temperature) or room temperature for a given time under irradiation with a Toshiba high-pressure mercury lamp (H400-P) or a Ushio superhigh-pressure mercury lamp HB-251A (250 W). The distance between the sample and the light source was set at approximately 10 cm. ESR measurement was made at -196°C or room temperature with a Japan Electron Optics Laboratory JES-ME-X instrument. Resonance spectra were observed with the x-band and 100 kcps field modulation.

RESULTS AND DISCUSSION

Photo-induced Graft Copolymerization

Photo-induced graft copolymerization on aldehyde cellulose with hydrophilic and hydrophobic vinyl monomers was investigated. The percent grafting-carbonyl content relation for hydrophilic monomers is given in Figure 1. The percent grafting rose with increasing carbonyl content of the cellulose sample, which exceeded 200% with irradiation of 20 min for AA and AAm. No photo-induced grafting was observed for an unoxidized sample under the same conditions. Thus, a close relationship was shown between the percent grafting and the carbonyl content of aldehyde cellulose, which contributes to effective grafting of hydrophilic monomers under photo-irradiation. A higher graft efficiency for

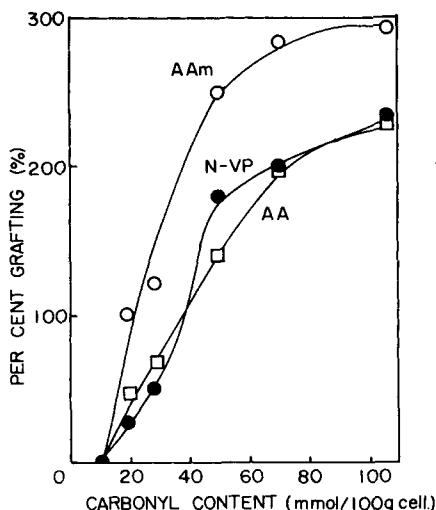


Fig. 1. Photografting of hydrophilic monomers on aldehyde cellulose. Irradiation time: AA and AAm, 20 min; N-VP, 120 min.

each monomer obtained with aldehyde cellulose of higher carbonyl content (Fig. 2).

Figures 3 and 4 show the results for hydrophobic monomers. The percent grafting of VAc increased with increasing carbonyl content of the cellulose sample; however, that of MMA gave a maximum value, and that of AN leveled off in the range beyond a certain carbonyl content. Thus, the grafting of hydrophobic monomers was shown to vary with the type of monomer, although these values were generally low compared with those of hydrophilic monomers. It was also true for the graft efficiency. This difference in graft copolymerization is based on the differences in water solubility, affinity to cellulose substrate, etc., among monomers.

Aldehyde cellulose generally has a high activity to initiate graft copolymerization under photo-irradiation, and the effect is marked especially for hydrophilic vinyl monomers. In the reaction, the carbonyl group in the cellulose

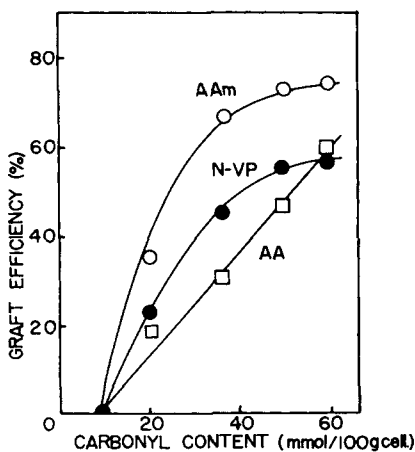


Fig. 2. Photografting of hydrophilic monomers on aldehyde cellulose. Irradiation time: AA and AAm, 20 min; N-VP, 120 min.

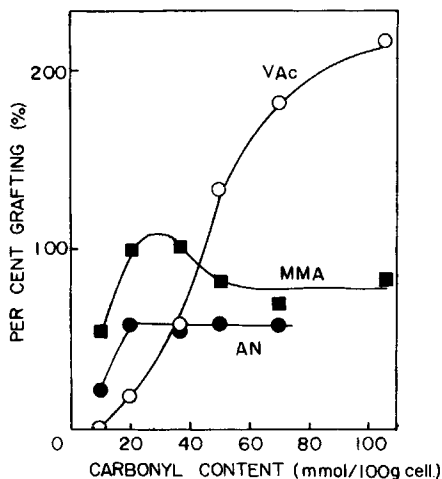


Fig. 3. Photografting of hydrophobic monomers on aldehyde cellulose. Irradiation time, 60 min.

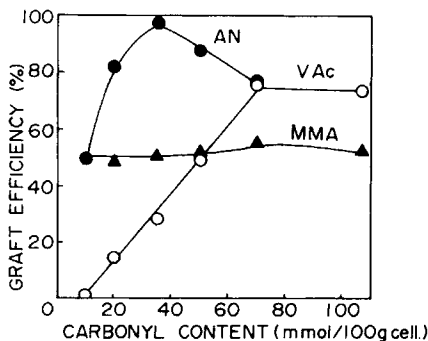


Fig. 4. Photografting of hydrophobic monomers on aldehyde cellulose. Irradiation time, 60 min.

sample is very active toward light, which provides effective radicals for the initiation of graft copolymerization.

Photo-induced Radicals

As the carbonyl content of the cellulose sample increased, the ESR signal intensity of the irradiated sample tended to increase. However, no change in line shape was observed. The spectra of aldehyde cellulose irradiated with a light of $\lambda > 220$ nm in quartz glass system at -196°C are shown in Figure 5. The irradiated samples were warmed to -95° , -57° , and -29°C , respectively, for 1 min. The higher the warming temperature was, the lower the signal intensity. Some changes in the line shape occurred on heating. The maximum peak at the center of the spectrum separated into two peaks, especially in the area of the low field when heated to -95° and -57°C . This maximum of the spectrum changed into almost one line type segment when heated to -29°C . This fact suggests that the central peak includes at least two types of singlet components; one was analyzed to be a singlet with a linewidth of 17–18 G and a g value of 2.003; the other was estimated to be a singlet with a linewidth of 14–15 G and a g value of

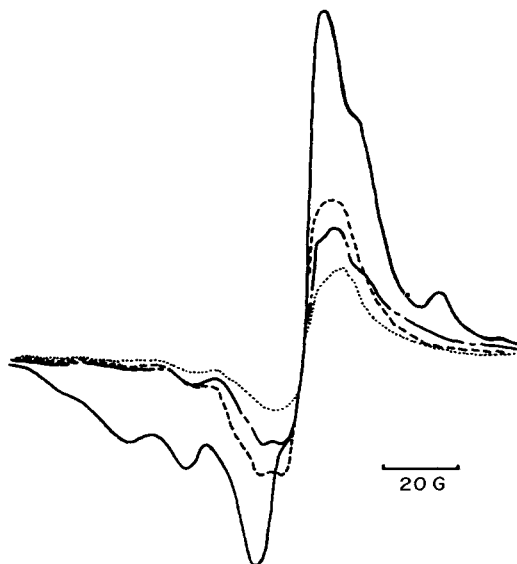


Fig. 5. ESR spectra of aldehyde cellulose irradiated with superhigh-pressure mercury lamp for 120 min at -196°C : (—) observed at -196°C immediately after irradiation; (---), (- - -), and (· · ·) observed at -196°C after heating for 1 min to -95° , -57° , and -29°C , respectively.

2.001. In the spectrum of the irradiated unoxidized sample, the latter singlet component was not included after heating.

The authors^{10,11} found that radicals formed on the photo-irradiated cellulose gave ESR spectra consisting of a superposition of singlet and triplet. The singlet spectrum with a g value of 2.003 was assigned to an alkoxy radical, which is formed at the position of C^{-1} or C^{-4} of the glucose unit which resulted by the cleavage of a cellulose chain. On the other hand, Tsuji¹² reported the formation of an acyl radical on the photo-irradiated ethylene-acrolein copolymer, which gave a singlet spectrum with a g value of 2.001. Accordingly, the two singlet components recorded for the irradiated aldehyde cellulose could be attributed to an alkoxy radical due to the cleavage of the cellulose chain and an acyl radical based on the aldehyde group.

ESR spectra of aldehyde cellulose irradiated with lights of different wavelengths are compared in Figure 6. The spectrum obtained with the irradiation of a light through Pyrex glass (curve a, $\lambda > 300$ nm) was considerably weaker in signal intensity than that given for the sample in a quartz glass system (curve b, $\lambda > 220$ nm). However, the spectrum shape of curve a was found to be very similar to that of curve c, which was observed for the heated sample after irradiation in a quartz glass system. Therefore, the radicals formed in the Pyrex glass system appeared to be the same as those formed in the quartz glass system.

Figure 7 shows the ESR spectra for aldehyde cellulose which were irradiated at room temperature. The two spectra showed a difference in linewidth, although they were both singlet. The observed linewidths were 23 and 15 G for samples in the quartz glass system and in the Pyrex one, respectively. Accordingly, it is conceivable that alkoxy and acyl radicals are formed in a quartz glass system and the acyl radical is the main product in a Pyrex glass system.

The relationship between the relative signal intensity and the carbonyl content

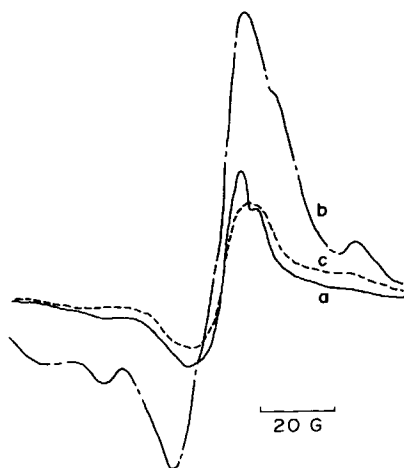


Fig. 6. Comparison of ESR spectra of aldehyde cellulose irradiated with super-high-pressure mercury lamp for 120 min at -196°C : curve a, Pyrex glass system; curve b, quartz glass system; curve c, spectrum after heating (b) to -29°C for 1 min.

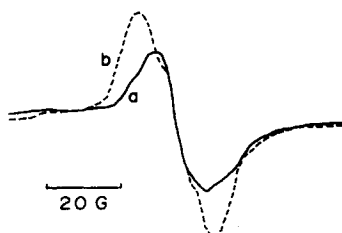


Fig. 7. ESR spectra of aldehyde cellulose irradiated with high-pressure mercury lamp for 60 min and observed at room temperature: curve a, Pyrex glass system; curve b, quartz glass system.

of samples in the quartz glass system is shown in Figure 8. A stronger intensity was observed with the increasing carbonyl content of the sample, which resembles the relationship between percent grafting and carbonyl content (Fig. 1). Thus, aldehyde cellulose easily forms radicals which initiate graft copolymerization under photo-irradiation.

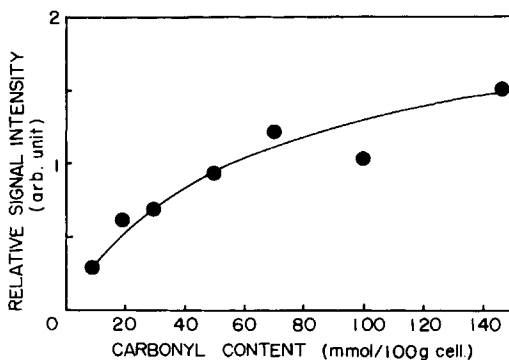


Fig. 8. Relationship between ESR signal intensity and carbonyl content of aldehyde cellulose. Irradiation: high-pressure mercury lamp, 60 min, room temperature.

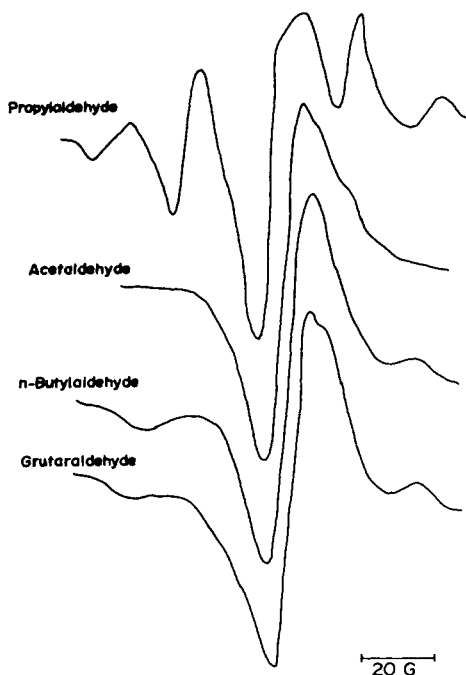


Fig. 9. ESR spectra of low molecular weight aldehydes irradiated with superhigh-pressure mercury lamp for 60 min at -196°C in quartz glass system.

TABLE I
Photopolymerization of Vinyl Monomers in the Presence of Low Molecular Weight Aldehydes^a

Monomer	Conversion, %			
	None	Propyl- aldehyde	<i>n</i> -Butyl- aldehyde	Glutaral- dehyde
Acrylamide	0	42.3	37.5	10.1
N-Vinyl-2-pyrrolidone	0	29.4	33.8	16.9
Acrylonitrile	0	17.6	13.2	6.2
Vinyl acetate	0	58.1	54.7	25.2
Methyl methacrylate	5.4	35.5	27.3	39.6

^a Concentration of aldehyde, 10 mmole/l.; polymerization temperature, 40°C ; polymerization time, N-vinyl-2-pyrrolidone, acrylonitrile, and methyl methacrylate, 60 min; vinyl acetate, 30 min; acrylamide, 10 min.

ESR spectra of irradiated low molecular weight aldehydes included a common spectrum component with a linewidth of 14–15 G and a g value of 2.001 at the center, although each spectrum differed in shape according to the kind of molecule (Fig. 9). This singlet spectrum can be attributed to an acyl radical, which agreed completely with the singlet observed for the irradiated sample of aldehyde cellulose with a g value of 2.001. Accordingly, it is believed that an acyl radical can easily be formed in the aldehyde group of aldehyde cellulose by photodegradation.

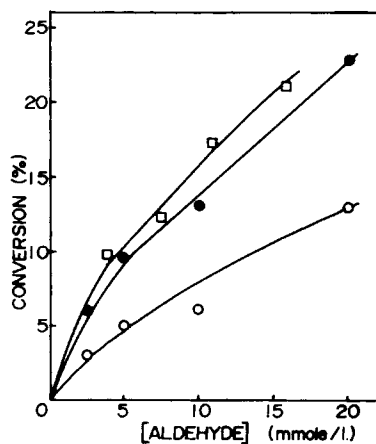


Fig. 10. Photopolymerization of AN in the presence of low molecular weight aldehydes. Polymerization: 60 min, 40°C; (○) glutaraldehyde; (●) *n*-butylaldehyde; (□) propylaldehyde.

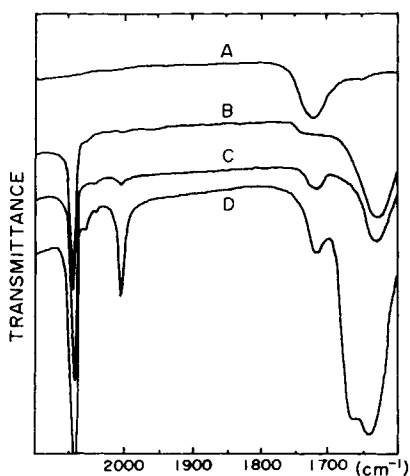


Fig. 11. IR spectra of propylaldehyde (PA) and polyacrylonitrile (PAN): A, PA; B, PAN prepared by thermal polymerization of AN in the presence of ceric salt as initiator; C and D, PAN prepared by photopolymerization of AN in the presences of PA and *n*-butylaldehyde (BA), respectively.

Polymerization by Photo-irradiated Aldehyde

The photo-induced polymerization of vinyl monomers was examined in the presence of low molecular weight aldehydes to check the initiating function of the acyl radical. The polymerization took place in the system with the existence of aldehyde, whereas it was hardly observed in the system without aldehyde (Table I). Further, the increase of monomer conversion of AN is proportional to the concentration of aldehyde (Fig. 10). Such results clearly suggest the function of radicals in initiating vinyl polymerization.

IR spectra of PA and polyacrylonitrile are shown in Figure 11. Samples C and D were prepared from AN by a photo-induced polymerization in the presence of aldehyde. They have absorption characteristics similar to the carbonyl group at 1720 cm^{-1} of the spectra. On the other hand, sample B was polymerized using a ceric salt as initiator, which indicates no carbonyl absorption. The absorption at 1720 cm^{-1} represents an aldehyde group of the initiator, and polymerization is initiated by an acyl radical.

An acyl radical is easily formed on aldehyde compounds by photo-irradiation, which initiates the polymerization of vinyl monomers. Accordingly, it is believed that an acyl radical is also formed on the photo-irradiated aldehyde cellulose, which promotes photo-induced graft copolymerization on aldehyde cellulose.

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