Effect of Water on Vapor Phase Photografting on Cellulose and Its Derivatives

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Synopsis

Effect of water on vapor phase photografting on cellulose was investigated at 60°C. An activated grafting of methyl methacrylate by water contained in the sample was observed in the experiment. The effect of water was commonly recorded irrespective of the type of cellulose derivatives such as cellulose acetate (degree of substitution, DS = 0.18 and 0.33), cellulose nitrate (DS = 0.35 and 0.75), and carboxymethyl cellulose (DS = 0.19 and 0.74). Organic solvents can also be used in place of water, indicating that the percent grafting decreases in the order, water ≫ methanol > acetone > cyclohexane. From ESR studies, water in the sample was found to contribute to the decay of cellulose radicals rather than to the radical formation. The decay was accelerated by organic solvents, and the magnitude of the effect was in the order, water ≈ methanol ≫ acetone > cyclohexane. Based on the above investigations, it was presumed that water contained in the sample cannot contribute directly to the formation of cellulose radicals which may initiate grafting, but mostly promotes the penetration of monomer into cellulose fibers. Such penetration could lead cellulose radicals to an effective initiation of grafting.

INTRODUCTION

In a previous paper[1] it was observed that vapor phase photografting of vinyl monomers on cellulose is markedly influenced by water contained in the sample, and the percent grafting increases with increasing the water content. Such accelerating effect was commonly recorded irrespective of the type of sensitizer and nature of monomer. The purpose of the present study is to make clear the function of water in the vapor phase photografting on cellulose. In this paper the effects of water were examined in terms of the photografting on cellulose derivatives such as cellulose acetate (CA), cellulose nitrate (CN), and carboxymethyl cellulose (CMC), the formation of cellulose radicals by photoirradiation, the radical decay, and the grafting on preirradiated cellulose sample.

EXPERIMENTAL

Samples

Dissolving pulp from softwoods was used as cellulose samples. The cellulose sample (UCEL) was treated with 20 mmol/L aqueous solution of periodic acid at 45°C for 60 min (ratio of material to liquid, 1 : 100) to prepare aldehyde cellulose (ACEL). Fibrous cellulose derivatives, CA, CN, and CMC, with

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different degrees of substitution (DS) were prepared according to the ordinary method[2] from UCEL.

A given amount of water or organic solvent was atomized on the cellulose samples, and then the water or solvent contained was excluded by drying under reduced pressure to prepare sample with a known amount of water or solvent. Water or solvent content was taken as percentage of the sample weight.

Methyl methacrylate (MMA) was purified by distillation under reduced pressure. Acetone, 1,4-dioxane, methanol, and cyclohexane were of all reagent grades and used without further purification.

Photografting

Vapor phase photografting was carried out at 60°C for 60 min using Pyrex glass tube containing 0.1 g sample and 2 mL MMA separately, which was reported in previous papers.[1,3] Irradiation with a high-pressure mercury lamp (400 W) was conducted with a Riko rotary photochemical reactor RH400-10W. Polymerized sample was extracted with acetone or benzene to exclude homopolymers. Percent grafting was taken as the percentage of weight increase of the original sample.

Grafting on Preirradiated Sample

After irradiating the quartz glass tube containing 0.50 g (oven dry) sample with light of $\lambda > 220$ nm at room temperature under nitrogen for 30 min, 10 mL MMA-solvent mixture was injected into the system. Grafting was carried out by keeping the system at 40°C for 60 min without further irradiation.

ESR Measurements

The quartz glass tube of 5 mm diameter containing cellulose samples was flushed with nitrogen gas and irradiated at −196°C for 60 min. The light source was a Toshiba high-pressure mercury lamp H400-P (400 W). ESR spectra were recorded with x-band and 100-kcps field modulation at −196°C with a Japan Electron Optics Laboratory JES-ME-X.

RESULTS AND DISCUSSION

Effect of Water on Photografting on Cellulose Derivatives

An affinity of cellulose sample to water can be modified by introducing various substituent groups into the cellulose substrate. Water retention value[4] is a measure of the affinity to water, and the value has been observed to be in the order, CMC ≫ CN > CA. The vapor phase photograftings of MMA on CMC, CN, and CA with different DS were carried out, and the results are shown in Figure 1.

Ability of each derivative to initiate the grafting decreased in the order CN ≫ CA > CMC. The high activity of CN seems to be based on the high level of photochemical decomposition due to nitrate group[3] in the substrate. The percent graftings of each derivative were observed to increase with increasing the water content. Thus, it was confirmed that water contained in

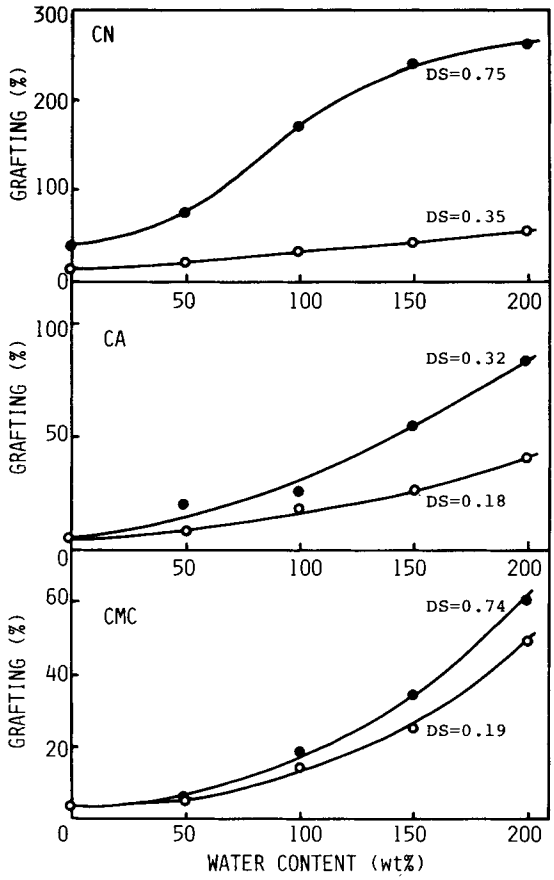

Fig. 1. Effect of water on vapor phase photografting of MMA on cellulose derivatives. Irradiation was carried out at 60°C for 60 min.

the sample has a function of accelerating the vapor phase photografting irrespective of the type of substituent groups introduced. This suggests that the affinity of cellulose substrate to water is not a major factor for initiation.

Effect of Organic Solvents on Photografting

Figure 2 shows the vapor phase photografting on UCEL using organic solvents in place of water. Organic solvents as well as water behaved in the same manner, and the percent grafting of each system increased with the increase of solvent content in the sample. However, the values were somewhat lower than that of water system, decreasing in the order, water $\gg$ methanol $>$ 1,4-dioxane $>$ acetone $>$ cyclohexane. Figure 3 shows the results of ACEL, which generally has a high activity in photografting.[5] Water gave the highest percent grafting among the solvents, and acetone and cyclohexane showed the lowest level. Thus, the organic solvents as well as water can facilitate the vapor phase photografting, and a polar solvent with high affinity to cellulose seems to be relatively effective.

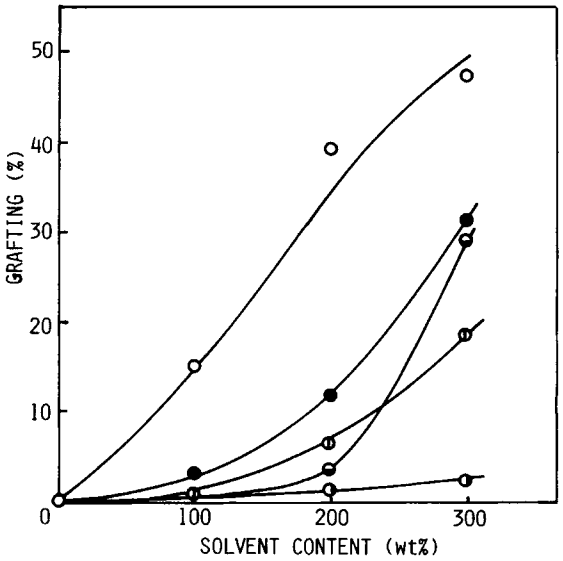

Fig. 2. Effect of organic solvents on vapor phase photografting of MMA on UCEL. Irradiation was carried out at 60°C for 60 min. (○) Water, (●) methanol, (⊙) acetone, (◒) 1,4-dioxane, (◑) cyclohexane.

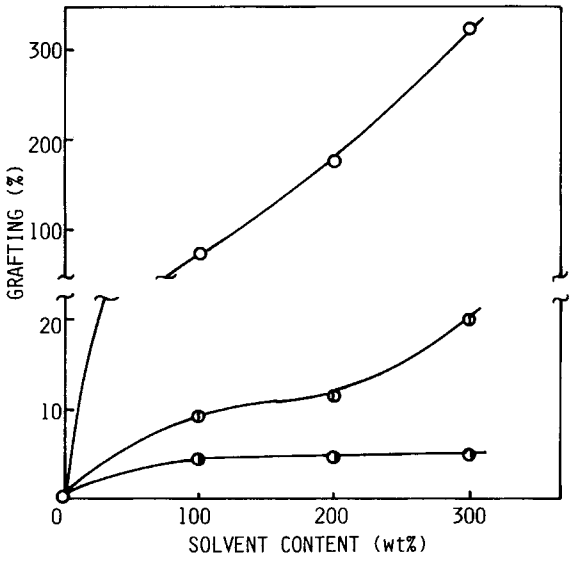

Fig. 3. Effect of organic solvents on vapor phase photografting of MMA on ACEL. Irradiation was carried out at 60°C for 60 min. (○) water, (⊙) acetone, (◐) cyclohexane.

Effect of Water on Formation of Cellulose Radicals

ESR spectrum of UCEL irradiated at −196°C for 60 min with light of $\lambda > 220$ nm was measured, and relationship between the spectrum intensity and water content of UCEL is shown in Figure 4. Intensity was decreased by about 20%, and was observed for the wet sample containing 300 wt% water, indicating a negative effect of water on the formation of cellulose radicals.

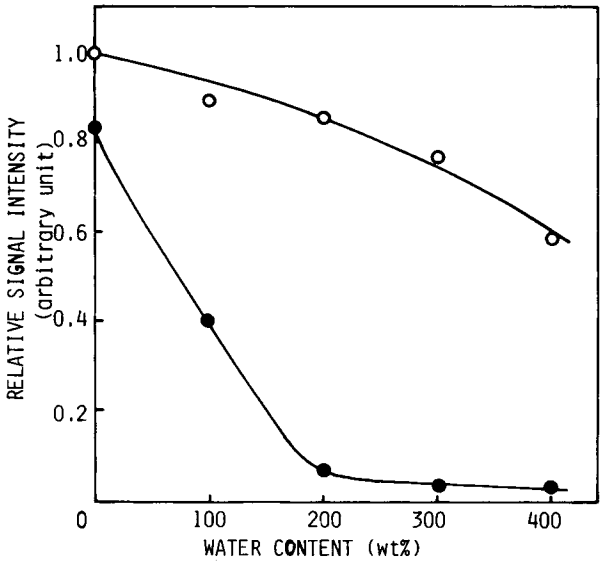

Fig. 4. Relationship between relative spectrum intensity of UCEL irradiated at −196°C for 60 min with light of $\lambda > 220$ nm and water content. (○) Observed at −196°C immediately after photoirradiation. (●) Observed at −196°C after warming the irradiated sample at room temperature for 1 min.

After irradiation at −196°C, the sample was kept at room temperature for 1 min, and which was brought again to −196°C for the measurements of ESR spectra. The intensities are also included in Figure 4. The decrease in intensity by the warming was more remarkable for the wet sample than the dry sample. Accordingly, water in the sample seems to reduce the number of cellulose radicals formed. Thus, acceleration of grafting by water cannot be explained by the effect of photoirradiation on the formation of cellulose radicals.

Effect of Solvents on Decay of Cellulose Radicals

Radical decay due to solvents was examined by adding solvents to UCEL irradiated under nitrogen atmosphere. After a given time, the spectrum intensities were measured, and the results are shown in Figure 5. Radical decay was facilitated by solvents, and the magnitude of the effect was in the order of water ≈ methanol ≫ acetone > cyclohexane. A similar phenomenon on radical decay was recorded for ACEL. The rate of radical decay was compared with that of vapor phase photografting, which is shown in Figure 2. Thus, it is clear that the solvent with highest effect on radical decay is also effective for grafting.

Radical decay due to solvent is supposed to be induced by chain transfer of radicals to solvent and/or increase of mobility of cellulose molecule due to solvent. That is, the rate of radical decay seems to depend upon the affinity of each solvent for cellulose fibers and its ability to penetrate into fibers. Nakamura et al.[6,7] reported that the concentration of cellulose radicals induced by gamma ray irradiation is markedly reduced when the samples are dipped in water or methanol, but remains high when acetone is used. Mares

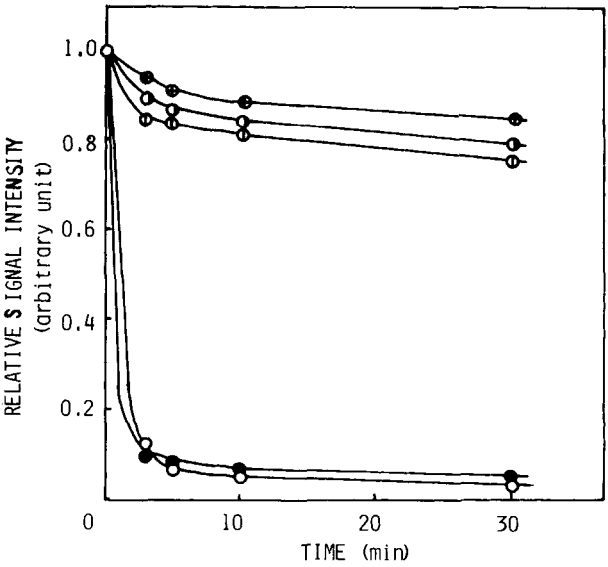

Fig. 5. Effect of various solvents on decay of cellulose radicals produced by photoirradiation. A quartz glass tube containing UCEL was exposed at room temperature for 30 min under nitrogen atmosphere to light of $\lambda > 220$ nm, and then a known quantity of solvent was injected into the sample tube. After a given time at room temperature, the spectrum intensities were measured at -196°C. (⊕) Control, (◑) cyclohexane, (⊙) acetone, (●) methanol, (○) water.

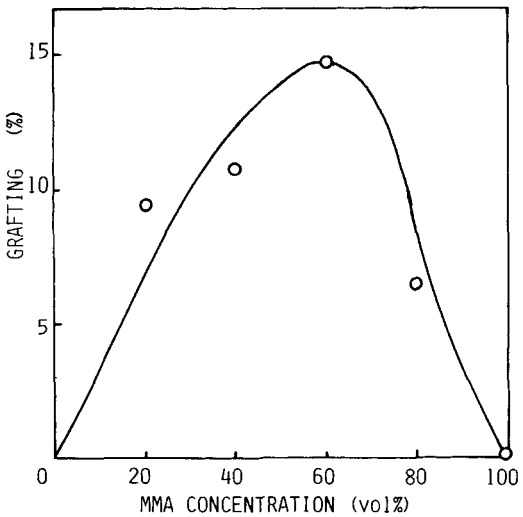

Fig. 6. Grafting of MMA on preirradiated UCEL. UCEL was preirradiated at room temperature for 30 min with light of $\lambda > 220$ nm. Grafting was carried out at 40°C for 60 min in water solvent.

TABLE I
Effect of Various Solvents on Grafting[a] of MMA on Preirradiated UCEL[b]

Solvent	Grafting (%)	
	Preirradiation time (min)	
	0	30
Water	0	14.7
Methanol	0	4.1
Acetone	0	0
Cyclohexane	0	0

[a]Grafting was carried out at 40°C for 60 min in the system of 60% MMA.
[b]UCEL was irradiated at room temperature for 30 min with light of $\lambda > 220$ nm.

et al.[8] and Reine et al.[9] in a similar study observed that radical decay is enhanced by solvents such as methanol, dimethyl sulfoxide, *N,N*-diemthylformamide, and acetone, and the effect depends upon the nature of the solvents to diffuse into the fiber structures.

Grafting on Preirradiated Cellulose

The grafting of MMA on UCEL, which was preirradiated at room temperature for 30 min, was performed, and the results are shown in Figure 6. No initiation of the grafting was observed for the system of 100% MMA. However, initiation took place using water, showing a maximum percent grafting at a MMA concentration of about 60%. The graftings were also performed by using organic solvents in the system of 60% MMA (Table I). Grafting initiated in water and methanol solvents, however, no initiation was recorded for acetone and cyclohexane solvents. Therefore, it was confirmed that the solvents, which can enhance radical decay, are also effective for initiation of grafting. This seems to be ascribed to easier diffusion of water or methanol into cellulose fibers than is achieved by acetone or cyclohexane.

The function of solvent described above might be applicable to vapor phase photografting system. That is, it is supposed that water contained in the sample promotes the diffusion of monomer into cellulose fibers, which may contribute favorably to initiation of grafting.

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