Ability of Cellulosic Materials to Initiate Graft Copolymerization by Photo-Irradiation

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Synopsis

The ability of various kinds of cellulose samples to initiate graft copolymerization of methyl methacrylate by photo-irradiation was examined. Untreated samples (absorbent cotton, sulfite pulp, dissolving pulp, and semichemical pulp), extracted samples (1% sodium hydroxide, methanol, and ethanol–benzene mixture as extraction solvent), oxidized samples (periodic acid, sodium hypochlorite, hydrogen peroxide, and nitrogen dioxide), a reduced sample, an oximated sample, and a ferric ion-adsorbing sample were used for the experiments. It was found that impurities in the sample as well as the oxidized states affect the initiation reaction remarkably. It was also noted that the contribution of these factors was remarkable in an irradiation system with a light of wavelength longer than 300 nm, although in the systems using sensitizers or irradiation with a light of shorter wavelength, initiation took place almost indifferent to the cellulose characteristics.

INTRODUCTION

It is well known that wood celluloses contain some carbonyl and carboxyl groups formed in the manufacturing process, hemicellulose and lignin other than the cellulose molecule, and metals and fats in a very small quantity. These supposedly affect the ability to initiate graft copolymerization. The authors, reporting on the ceric ion-induced graft copolymerization, have noted that the reduction of ceric ion and the formation of grafts are markedly influenced by carbonyl and aldehyde groups,[1] hemicellulose,[2] and lignin[3] contained in the cellulose samples. In the hydrogen peroxide (H_2O_2) initiator system,[4] traces of metals contained in cellulose samples were found to be effective in the initiation and the termination of graft copolymerization reaction interacting with H_2O_2. It was also noted that the cellulose sample[5] and the poly(vinyl alcohol) fiber[6] oxidized with H_2O_2 or sodium hypochlorite (NaClO) exhibits conspicuous initiation actions in the system using no special initiator, suggesting a close relationship between the oxidized state and the initiation reaction.

It is a fact that cellulose radicals formed by photo-irradiation can easily initiate graft copolymerization, which is sharply affected by the wavelength of the light,[7] the solvents,[8] and the kind of sensitizers[9,10] employed.

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In the present study, in order to elucidate the fundamental factors contributing to photo-induced graft copolymerization, the relationships between the characteristics of cellulose samples and the initiation behavior were investigated with reference to oxidized states and impurities of cellulose samples.

EXPERIMENTAL

Cellulose Sample

Untreated Sample. Commercial absorbent cotton, bleached sulfite pulp from softwoods (SP_1 and SP_2), bleached semichemical pulp from hardwoods (SCP), and dissolving pulp from softwoods (NDP) were used. Pulp samples were milled and classified to remove fibers less than 40 mesh; these were termed the untreated samples.

Oxidized and Reduced Samples. Untreated samples were treated with an aqueous periodic acid (HIO_4) solution at 45°C for 60 min (ratio of material to liquid, 1:100), resulting in HIO_4-oxidized sample. The NaClO- and H_2O_2-oxidized samples were obtained under the conditions of 120 min and 90 min at 60°C, respectively. Nitrogen dioxide (NO_2) gas was directly applied to the untreated sample, and the NO_2-oxidized samples with various degrees of oxidation were prepared by varying the treating time. Cellulose samples were also treated with $0.1N$ aqueous sodium hydroxide solution containing $0.05N$ sodium borohydride ($NaBH_4$) at room temperature for 72 hr, giving the reduced samples. After treatment, the samples were washed with water, dried under reduced pressure, and used for further experiments.

Extracted Sample. Untreated samples were refluxed with methanol or ethanol–benzene mixture (1:2) for 6 hr, or with 1% aqueous sodium hydroxide solution for 3 hr (ratio of material to liquid, 1:100) for the preparation of extracted sample.

Sample Treated with Semicarbazide or Hydroxylamine. The determination method of total carbonyl groups in the cellulose sample proposed by Watanabe and Kuwana[11] was applied. Namely, untreated sample was allowed to react with a semicarbazide hydrochloride solution (3 g/l.) whose pH was adjusted to 5, at room temperature for 48 hr. In case of treatment with hydroxylamine, the same conditions as used in the determination[12] of total carbonyl groups were applied.

Analytic Methods of Cellulose Sample

For the determination of total carbonyl groups,[12] the cellulose sample was allowed to react with a hydroxylamine hydrochloride solution (50 g/l.) whose pH was adjusted to 5.2 with $1N$ sodium hydroxide, at 55°C for 2 hr, and the liberated hydrochloric acid was titrated. The pH for standardization was adjusted to 3.2. The carboxyl content[13] was determined by the calcium acetate method. The amount of ash was indicated by the weight

percentage for the sample. The degree of polymerization ($\overline{D.P.}$) of the cellulose sample was obtained from the intrinsic viscosity[14] in a cupriethylenediamine solution at 25°C.

Graft Copolymerization

After filling the hard glass tube containing 0.50 g (oven dry) cellulose and 40 ml water with nitrogen, 2.5 ml methyl methacrylate (MMA) was injected into this system. Graft copolymerization was carried out by keeping the system at 40°C for a given duration under irradiation. The products were washed with water and then extracted with acetone for 24 hr. The per cent grafting, the grafting efficiency, and the average molecular weight of grafted poly(MMA) isolated were determined in the manner given previously.[10] The molar number of grafts per 100 g cellulose was calculated from the per cent grafting and the average molecular weight of grafts and indicated as the number of grafts.

Irradiation with Light

Irradiation was carried out with a Toshiba high-pressure mercury lamp H400-P (400 W) while placing the polymerization system enclosed in a hard glass tube about 1 mm thick at a distance approximately 11 cm from the light source. This lamp can radiate ultraviolet light nearly uniformly with a maximum spectrum intensity at 365 nm, and the light transmitting through the hard glass is limited more than 310 to 320 nm.

RESULTS AND DISCUSSION

Initiating Character of Untreated Sample

The photo-induced graft copolymerization of MMA onto various commercial cellulose samples was examined. As is apparent in Figure 1, each
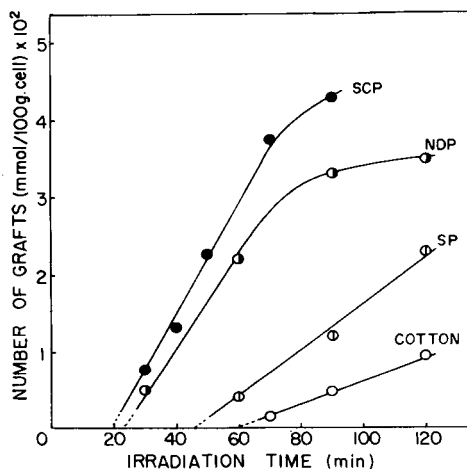

Fig. 1. Photo-induced graft copolymerization onto untreated sample.

polymerization has an induction period which varies with the kind of cellulose sample. A distinct difference among samples is also noted in the number of grafts and in the initiation action for samples, decreasing in the order SCP > NDP > SP₁ > cotton. Figure 2 shows the relationship between the average molecular weight of grafts and the per cent grafting of each copolymer. The molecular weight indicates a value peculiar to each sample and independent to the per cent grafting, decreasing in the order cotton > NDP > SP₁ > SCP. The value can be considered as one of the indications of stability of the grafted polymer radicals inside of the cellulose fibers and/ or the diffusion of monomers into the fibers. Therefore, it is believed that there is an appreciable difference in such states among the samples. Thus, the induction period of polymerization, the rate of graft formation, and the molecular weight of grafts vary with the kind of cellulose sample, and it is evident that the difference in the characteristics of each sample is reflected on the photo-induced graft copolymerization.

The description of the samples, namely, chemical character, and the results of graft copolymerization are compared in Table I. Differences in $\overline{D.P.}$, total carbonyl content, and amount of ash are observed among the
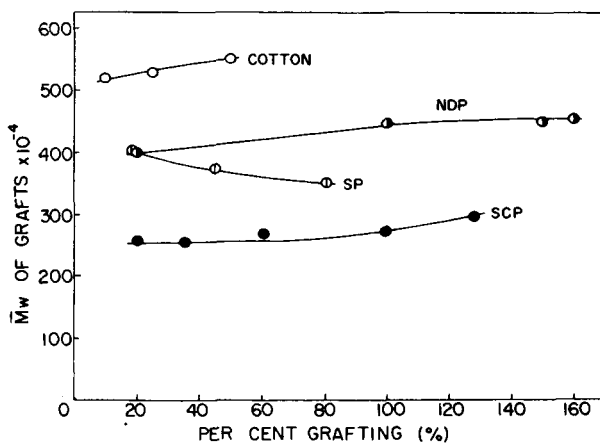

Fig. 2. Relationship between average molecular weight of grafts and per cent grafting.

TABLE I
Description of Cellulose Sample and Photo-Induced Graft Copolymerization

Sample	$\overline{D.P.}$	Ash, %	COOH, mmole per 100 g cell.	Total C=O, mmole per 100 g cell.	Rate of grafting, %/min	Rate of graft formation × 10⁴, mmole per 100 g cell/min	Induction period, min
Cotton	1400	0.04	1.52	2.5	0.9	1.5	60
SP₁	876	0.05	1.76	7.6	1.1	3.0	45
NDP	780	0.12	2.20	9.3	2.0	5.8	23
SCP	470	0.48	5.85	21.5	2.6	8.0	19

samples. In general, it is indicated that the larger the amounts of ash and total carbonyl groups, the faster the rate of graft formation and the shorter the induction period.

Initiating Character of Extracted Sample

The initiating character of the sample extracted with various solvents was investigated, and the results are shown in Table II. The ash content indicates reduction by extraction, and it is conceivable that the other impurities might also be eliminated from the sample in the same way. For the extracted samples, the induction periods were commonly prolonged, and the polymerizations were initiated after 50 to 60 min of irradiation. The per cent grafting at 120 min of irradiation was approximately equal to the result of untreated sample; however, the average molecular weight of grafts was somewhat higher, indicating a lower number of grafts. Thus, it is confirmed that the initiating character of samples is clearly deactivated by extraction treatment.

TABLE II
Photo-Induced Graft Copolymerization on Extracted Sample

Sample	Ash, %	Induction period, min	Number of grafts $\times 10^2$,[a] mmole per 100 g cell.	$\bar{M}_w$ of grafts $\times 10^{-4a}$
Untreated NDP	0.12	23	3.53	455
NDP extracted with methanol	0.05	50	1.83	710
NDP extracted with 1% sodium hydroxide	0.02	60	3.11	580
NDP extracted with ethanol–benzene mixture	0.06	60	2.42	624

[a] Irradiation time, 120 min.

Initiating Character of Oxidized and Reduced Samples

Darunwalla, D'Silva, and Mehta[15] have suggested that the photodegradation of cellulose begins with the oxidation on hydroxyl groups of cellulose, namely, on the primary alcohol, forming oxidized groups such as carbonyl and carboxyl, which contribute effectively to the scission reaction of glucosidic bonds. Cremonesi, Focher, and D'Angiuro[16] have observed that the HIO_4-oxidized cotton works advantageously on the initiation in the photo-induced graft copolymerization of methacrylic acid owing to the oxidized groups introduced. Thus, the oxidized states of cellulose supposedly are closely connected with the activity toward light. As shown in Table I, each sample used in this study contains a certain amount of carbonyl group, indicating higher initiating character for a sample with larger total carbonyl content. Accordingly, in order to examine the contribution of oxidized groups further, the samples oxidized with various oxidizing agents were employed for polymerizations.

The comparisons between the initiating characters of two samples, the HIO_4-oxidized sample and the $NaBH_4$-reduced sample which has been oxidized with HIO_4 beforehand, are shown in Figure 3. Obvious changes in the total carbonyl contant are observed by the treatment of oxidation and reduction. As the formation of grafts of the samples are much influenced by the carbonyl content, it is believed that the oxidized groups introduced by the oxidation contribute truly to the activity of the sample toward light.

The results of polymerization of samples oxidized with various oxidizing agents are shown in Table III. Regarding the HIO_4-oxidized sample, as the degree of oxidation was raised, the total carbonyl content and the per cent grafting were both increased, suggesting a rise in the activities of the oxidized samples toward light. On the other hand, the NaClO- and H_2O_2-oxidized samples reduced the initiating characters remarkably, allowing
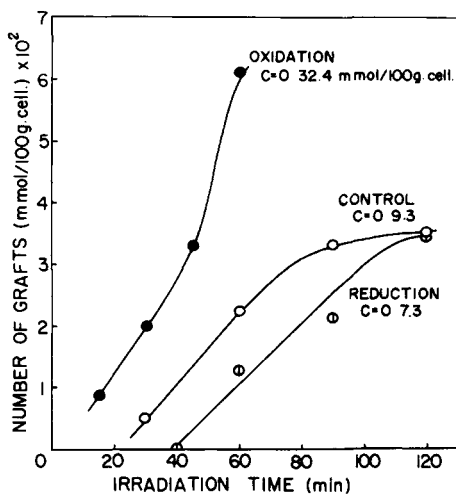

Fig. 3. Effect of oxidation and reduction of sample on photo-induced graft copolymerization.

no initiation even after 60 min of irradiation, though increases were observed in the total carbonyl contents for the samples. As for the NO_2-oxidized sample, it was similarly found that the sample with the higher degree of oxidation revealed a lower per cent grafting. So, it is confirmed that each oxidized state introduced by oxidation differs in accordance with the kind of reagent employed, namely, HIO_4, NaClO, H_2O_2, and NO_2 afford samples with different initiating characters. The polymerizations in the quartz tube system are shown in parentheses in Table III. The quartz tube can transmit light of wavelength shorter than 300 nm, and the graft copolymerization on the NaClO- and H_2O_2-oxidized samples was observed to be activated by replacing the hard glass tube by the quartz tube, indicating a per cent grafting that was the same as that of the untreated sample. Namely, it is clear that the performance of graft copolymerization

TABLE III
Photo-Induced Graft Copolymerization on Various Oxidized Samples[a]

Sample	Concn. of oxidizing agent, mmole/l.	Total C=O, mmole per 100 g cell.	Per cent grafting, %	Grafting efficiency, %[b]
Untreated NDP	0	10.9	98.7	77.1
			(59.0)	
NDP oxidized with HIO₄	1	15.0	128.3	80.9
	3	19.7	165.0	80.2
	7	30.7	220.0	—
	10	32.4	249.9	71.0
			(77.0)	
	20	58.8	213.9	73.1
NDP oxidized with NaClO	5	17.7	0	—
	10	17.0	0	—
			(57.8)	
	20	16.8	0	—
	50	31.8	0	—
NDP oxidized with H₂O₂	1	—	2.3	—
	5	17.5	0	—
	10	17.2	0	—
			(77.3)	
	20	16.5	0	—
Untreated SP₂	0	7.2	61.9	70.8
SP₂ oxidized with NO₂				
1	—	8.5	25.0	78.6
2	—	14.6	19.6	69.4
3	—	42.7	6.2	53.4

[a] Irradiation time, 60 min; values in parentheses are per cent grafting in the quartz tube system.

[b] Grafting efficiency is taken as the weight per cent of grafted polymer relative to total conversion of monomer in a system.

is almost indifferent to the oxidized states of samples under irradiation with high-energy light.

Table IV shows the initiating character of the sample once oxidized and then reduced with NaBH₄. As shown in Figure 3, the high initiating character of the HIO₄-oxidized sample was remarkably deactivated by the reduction treatment, while, on the contrary, that of the NaClO- and H₂O₂-oxidized samples was improved sharply after reduction. Therefore, it is true that the initiating character of graft copolymerization induced by light is affected by the kind of functional groups originated in the oxidation or reduction treatment; however, they must not be decided simply by the content of carbonyl groups in the sample.

Initiating Character of the Sample Treated with Hydroxylamine

Table V shows the initiating character of the samples in which carbonyl groups are converted to oximes and carbazones applying hydroxylamine and semicarbazide, respectively. As for the untreated and HIO₄-oxidized

TABLE IV
Photo-Induced Graft Copolymerization on Reduced Sample[a]

	Total C=O, mmole per 100 g cell.		Per cent grafting, %	
Sample	Control	Reduction	Control	Reduction
Untreated NDP	10.9	9.5	98.7	82.2
NDP oxidized with HIO₄	32.4	7.3	249.9	48.9
NDP oxidized with NaClO	17.0	11.1	0	114.8
NDP oxidizied with H₂O₂	17.2	8.9	0	103.4

[a] Irradiation time, 60 min. Each oxidized sample was prepared by treating the untreated sample with 10 mmole/l. oxidizing agent and then reducing with NaBH₄.

samples, the initiating character was almost lost after the treatments. However, the activity of initiation was recovered considerably by the treatment with hydrochloric acid, indicating a per cent grafting the same as that of the untreated sample. Accordingly, it is believed that these reagents cause the cellulose samples to depress activity toward light, resulting in a complete disappearance of initiating action with light. However, under the irradiation of light with short wavelength, the graft copolymerization onto the oximated sample was started with values as shown in parentheses in Table V. Because of the easy initiations of graft copolymerization even on the NaClO- and H₂O₂-oxidized samples as well as the oximated sample under irradiation of short wavelength light, it can be said that the characteristics of cellulose samples contributing to the initiation have a great significance only in the system under irradiation with light intercepting a short wavelength region.

TABLE V
Photo-Induced Graft Copolymerization on Sample Treated with
Hydroxylamine or Semicarbazide[a]

Sample	Reagent	Treatment condition	Per cent grafting, %
Untreated NDP	none	—	98.7 (59.0)
Untreated NDP	hydroxylamine	55°C, 2 hr	0 (41.3)
Untreated NDP	semicarbazide	room temp., 48 hr	0
NDP oxidized with HIO₄	none	—	249.9
NDP oxidized with HIO₄	hydroxylamine	55°C, 2 hr	0
NDP oxidized with HIO₄	semicarbazide	room temp., 48 hr	0
NDP oximated with hydroxyl-amine	hydrochloric acid	0.5N, 80°C, 1 hr	91.6

[a] Irradiation time, 60 min; values in parentheses are per cent grafting in the quartz tube system. HIO₄-oxidized sample was prepared by treating the untreated NDP with 10 mmole/l. aqueous HIO₄ solution at 45°C for 60 min.

Initiating Character of Ferric Ion (Fe^{3+})-Adsorbing Sample

The effect of samples on photo-induced graft copolymerization employing sensitizers was investigated, and the results are shown in Table VI. Cellulose samples were allowed to react with 5 mmole/l. aqueous ferric chloride solution at 45°C for 60 min (ratio of material to liquid, 1:80) to prepare the Fe^{3+}-adsorbing samples[9] in Table VI. As for the NaClO- and H_2O_2-oxidized samples or the oximated sample, a distinct improvement in the initiating activity was indicated by the use of Fe^{3+} as sensitizer, while a notable decrease in the per cent grafting was observed for the HIO_4-oxidized sample by using Fe^{3+}. Since almost the same level of initiating character is observed for each sample after sensitized with Fe^{3+}, it is believed that the sensitizer contributes to the cellulose samples with an action of initiation indifferent to the oxidized state of the sample.

TABLE VI
Photo-Induced Graft Copolymerization on Fe^{3+}-Adsorbing Sample[a]

Sample	Amount of adsorbed Fe^{3+}, mmole per 100 g cell.	Per cent grafting, %	Number of grafts $\times$ 10^2, mmole per 100 g cell.
Untreated NDP	0	98.7	2.19
	17.2	124.5	3.21
Oximated NDP	0	0	—
	16.4	52.1	1.77
NDP oxidized with HIO_4	0	249.9	6.14
	16.9	156.6	3.46
NDP oxidized with NaClO	0	0	—
	20.9	161.4	3.63
NDP oxidized with H_2O_2	0	0	—
	20.9	156.9	3.46

[a] Irradiation time, 60 min. Each oxidized sample was prepared by treating the untreated NDP with 10 mmole/l. oxidizing agent.

On the basis of the results of the photo-induced graft copolymerization onto various cellulose samples as mentioned above, it can be said that both impurities and oxidized states of the cellulose sample are considered to be important factors for the initiation; however, the contributions of the factors are true in the irradiating system with light intercepting a short wavelength region and not true in the system using light without intercepting a short wavelength region or using a sensitizer.

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