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Relationship Between Photo-Induced Scission of Cellulose Chains and Graft Copolymerization

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Synopsis

Studies were carried out on the relationship between the scission of cellulose chains and the initiation of photo-induced graft copolymerization of methyl methacrylate. The photo-induced scission of cellulose chains was sharply accelerated by the application of irradiation with light shorter than 300 nm, the use of photosensitizer such as ferric ion, the swelling of cellulose samples, and so on. On the other hand, the scission reaction was markedly suppressed by blocking the carbonyl groups contained in the samples by oximation. A linear increase in the number of grafts was indicated with the number of scissions of cellulose chains in the graft copolymerization. However, a number of scissions not contributing to any formation of grafts was also noticed during the induction period of copolymerization. The factors such as short wavelength light, photosensitizer, and swelling, which contribute to the rises in the rate of graft formation and the scission of cellulose chains, worked also to shorten the induction period. As might be expected, appreciable increases of per cent grafting and shortening of induction period were achieved by preirradiation the cellulose samples with light. From the above, it was concluded that the scission of cellulose chains should be a main factor for the initiation of graft copolymerization in the system.

INTRODUCTION

In previous papers,[1,2] we have examined ESR spectra of cellulose samples irradiated at 77°K with light to clarify the initiation species of photo-induced graft copolymerization onto cellulose,[3–6] and observed the formation of several kinds of cellulose radicals corresponding to singlet, three-line, or five-line spectra, according to irradiation conditions. It has also been confirmed that a singlet component was superimposed in each three-line or five-line spectrum, appearing in all irradiation conditions. The radicals corresponding to the singlet spectrum were inferred to be those from the scission of glucosidic bonds of cellulose molecules. On the other hand, the three-line and five-line spectra are considered to be the results of the dehydrogenation of cellulose chains. It was found that the stability of the other radicals toward warming are considerably low as compared with those showing the singlet spectrum. As the radicals which originated from the dehydrogenation of cellulose chains are sensitive to heat, it is inferred that their life times might be very short at a polymerization temperature[3–6] of 40° to 45°C, and the radicals might be unable to initiate graft copolymerization. Therefore, it is natural to consider that the radicals with the singlet spectrum originated from the scission of cellulose chains could be the initiation species.

In this paper, on the basis of the above view points, the initiation characteristics were compared with the scission behavior of cellulose chains in detail in the photo-induced graft copolymerization.

EXPERIMENTAL

Cellulose Sample

Commercial dissolving pulp from softwoods was milled and classified to remove fibers less than 40 mesh, and this was termed the untreated sample. The untreated sample was allowed to react with a hydroxylamine hydrochloride[7] (50 g/l.) whose pH was adjusted to 5.2 by 1*N* sodium hydroxide, at 55°C for 2 hr to prepare the oximated sample. The ferric ion-sensitized sample[5] was prepared by treating the untreated sample with an aqueous solution of 10 mmoles/l. ferric chloride (Fe^{3+}) at 45°C for 1 hr. The untreated sample was also treated with an aqueous solution of sodium hydroxide with a known concentration at room temperature for 2 hr and washed with water to neutrality. After being immersed in water for 24 hr and filtered, the swollen sample was obtained.

Scission of Cellulose Chains

Scission of cellulose chains was carried out at 40°C for a given duration under nitrogen by irradiating the reaction tubes containing 0.50 g cellulose sample (oven dry) and 40 ml water with light at a distance of approximately 11 cm from the light source, which was a Toshiba high-pressure mercury lamp H400-P (400 W). As reaction vessels, quartz and hard glass tubes approximately 1 mm thick were used. Effects of wavelength region of the irradiating light on the scission of cellulose chains were examined by utilizing the transmission difference[4] of light between the glasses. The irradiated cellulose sample was washed with water and dried, and a sample for the measurement of degree of polymerization (D.P.) was obtained. The D.P. of sample was determined from the viscosity[8] of cupriethylenediamine solution at 25°C. The number of scissions (s) was calculated from the following equation:

$$s = 1/P_t - 1/P_0$$

where P_0 and P_t are D.P. before and after photo-irradiation, respectively.

Graft Copolymerization

By adding 2.5 ml methyl methacrylate (MMA) to the system constituted same as for the examination of scission reaction, graft copolymerization was carried out at 40°C by irradiating with light. The polymerized products were washed with water and extracted with acetone to remove homopolymers. The per cent grafting was taken as the percentage of weight increase of the original cellulose.

Graft copolymer was treated with 72% sulfuric acid[9] to isolate poly-(MMA) as the grafts. The average molecular weight of grafts was determined from the viscosity of benzene solution at 30°C using the following equation[10]:

$$[\eta] = 8.69\times10^{-5}M_n^{0.76}.$$

The molar number of grafts per 100 g cellulose calculated from the per cent grafting and the average molecular weight of grafts was indicated as the number of grafts.

RESULTS AND DISCUSSION

Photo-Induced Scission of Cellulose Chains

Changes of the number of scission with irradiation time in various cellulose samples are shown in Figure 1. It was found that the number of scissions is distinctly different with the kind of cellulose sample and the wavelength of irradiating light, namely, the number was considerably lower in the system of hard glass than quartz glass. In the figure we can see that even both untreated and oximated samples increased largely the number of scissions in the quartz glass system at the initial stage of irradiation, indicating the contribution of high-energy light shorter than 300 nm to the scission of cellulose chains. Furthermore, a nearly equal extent of scission as in the quartz glass system was observed even in the hard glass system when Fe^{3+} was applied to the cellulose sample. Results of the swollen sample are shown in Figure 2. The scission of cellulose chains in-

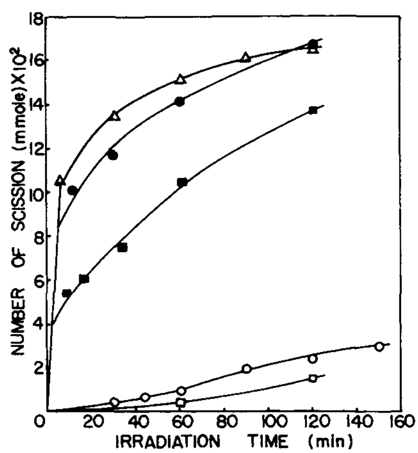

Fig. 1. Changes in number of scissions with time. Hard glass system: (O) untreated sample; (□) oximated sample; (△) Fe^{3+}-sensitized sample. Quartz glass system: (●) untreated sample; (■) oximated sample.

creased with the degree of swelling, suggesting a rise of activity toward light due to swelling. Accordingly, it can be said that both the use of photosensitizer and the swelling of sample are effective factors for the scission of cellulose chains in the hard glass system, in which scission is milder than in the quartz glass system.

Photo-Induced Graft Copolymerization

Results of graft copolymerization of MMA in the irradiation system are shown in Figure 3. There were some differences in the induction period of polymerization among the systems. A significant shortening of the period was observed with the use of short wavelength, photosensitizer, or swelling of sample in the case of untreated sample. On the other hand, the polymerization initiation was somewhat depressed by oximation of the sample,

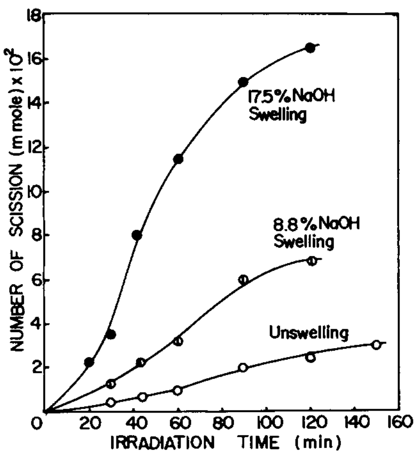

Fig. 2. Changes in number of scissions in swollen samples with time; hard glass system.

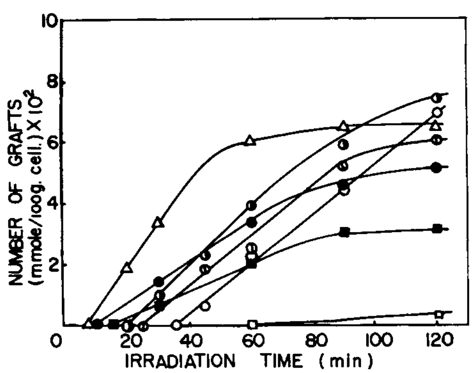

Fig. 3. Photo-induced graft copolymerization in various systems. Hard glass system: (O) untreated sample; (⦶) sample swollen with 8.8% NaOH; (◑) sample swollen with 17.5% NaOH; (Δ) Fe^{3+}-sensitized sample, (□) oximated sample. Quartz glass system: (●) untreated sample; (■) oximated sample.

irrespective of wavelength of irradiating light. Thus, it was clearly demonstrated that graft copolymerization can be increased and induction period shortened when scission of cellulose chains is encouraged. Therefore, it should be true that the scission of cellulose chains is closely connected with the initiation of graft copolymerization.

The molecular weight of grafts of copolymers produced in each irradiation system was in the range of 1 million to 4 million. In general, the molecular weight of grafts in the quartz glass system was lower than that in the hard glass system, however, no distinct difference was observed among the cellulose samples.

Relationships between the number of scissions and the number of grafts of the copolymer are shown in Figure 4. The number of grafts has a tendency to increase linearly as the number of scissions. However, the slope of each straight line differs with the kind of cellulose sample and the wavelength of irradiating light; that is, a gentle slope is present for the systems applying either short wavelength light or Fe^{3+} sensitizer. This implies that in these systems the proportion of the number of chain scission available for the formation of grafts is fairly low, and the chain scission reaction works generally to depress the efficiency of graft formation. The readings of the intersection of the abscissa in Figure 4 correspond to the numbers of scission occurring during the induction period. Large values were observed for either short wavelength light or Fe^{3+} sensitizer. It is interesting that the value was larger for polymerization with shorter induction period.

The swollen sample was similarly examined, and the results are shown in Figure 5. A straight-line relation was shown between the number of grafts and the number of scissions. A gentle slope resulted for samples with a higher degree of swelling, suggesting the existence of much chain scission in the sample during the induction period.

Relationships among the induction period of polymerization, the rate of graft formation, and the number of scissions during the induction period are shown in Figure 6. It was generally apparent that the induction pe-

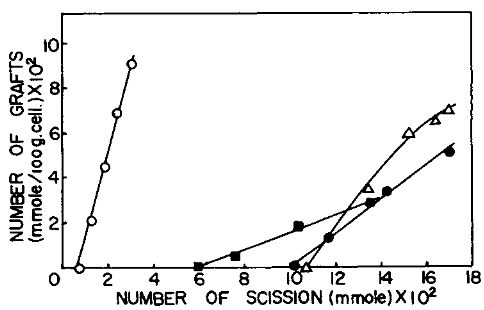

Fig. 4. Relationship between number of grafts and number of scissions. Hard glass system: (○) untreated sample; (△) Fe^{3+}-sensitized sample. Quartz glass system: (●) untreated sample; (■) oximated sample.

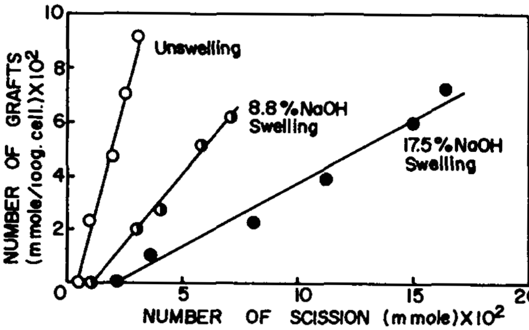

Fig. 5. Relationship between number of grafts and number of scissions in swollen samples.

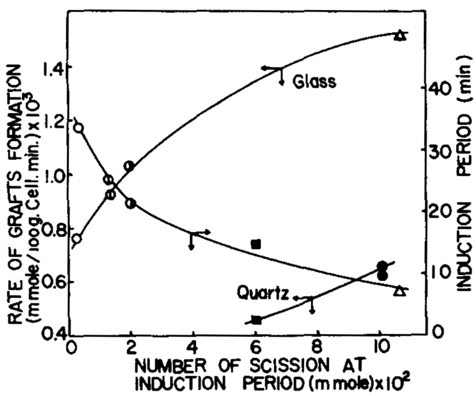

Fig. 6. Relationships among induction period of polymerization, rate of graft formation, and number of scissions during induction period: (O, ●) untreated sample; (◐) sample swollen with 8.8% NaOH; (◑) sample swollen with 17.5% NaOH; (Δ) Fe^{3+}-sensitized sample; (■) oximated sample.

riod is shortened and the rate of graft formation is increased as the number of scissions rises at the induction period. However, as for the rate of graft formation, a distinct difference was observed between the hard glass and the quartz glass systems. Thus, it is believed that the radicals due to the scission of cellulose chains can be the main cause for initiating graft copolymerization, because the scission of cellulose chains is very clearly reflected in the induction period and the graft formation.

It is well known that an induction period of polymerization is generally observed in a system where some oxygen is present. A trace amount of oxygen adhering to the cellulose fibers can exist in our system, too, despite evacuation of the system. Such oxygen might act to scavenge cellulose radicals produced in the system, leading to depression of the activity of radicals to initiate polymerization. Accordingly, it is thought that the time required for the consumption of oxygen in the system by radicals corresponds to the induction period. Thus, it is believed that oxygen is quickly consumed in the system where a lot of cellulose radicals are produced, resulting in the shortening of the induction period. This can clearly be seen from Figure 6.

Effect of Preirradiation on Graft Copolymerization

On the basis of the above examinations, it was clear that many chain scissions indifferent to the graft formation take place during the induction period of graft copolymerization. Therefore, if the chain scissions of the initial stage are completed by the irradiation beforehand on the sample, effects contributing to the shortening of induction period and the activation of graft copolymerization could be expected. For that purpose, following preirradiation of the cellulose sample for a given duration, graft copolymerization was carried out under irradiation with light by adding 2.5 ml MMA to the system. Figure 7 shows the results of the untreated sample. As expected, a shorter induction period and easier initiation of graft copolymerization were observed with longer preirradiation of the sample. Results of preirradiation on the other cellulose samples are shown in Table I. The preirradiated samples indicated the increases in per cent grafting

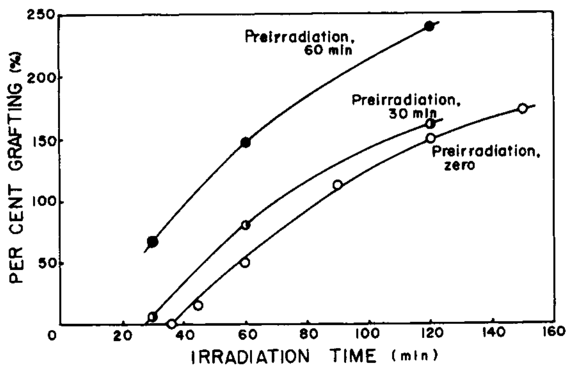

Fig. 7. Effect of preirradiation on photo-induced graft copolymerization onto untreated sample in hard glass system.

TABLE I

Effect of Preirradiation on Photo-Induced Graft Copolymerization[a]

Cellulose sample	Per cent grafting, % 0 min[b]	30 min	60 min
Untreated sample (G)	0	3.5	69.1
Untreated sample (Q)	35.6	94.2	72.6
Fe^{3+}-sensitized sample (G)	52.3	83.4	67.4
Oximated sample (Q)	16.9	58.2	46.4
Sample swollen with 8.8% NaOH (G)	10.0	62.9	37.6
Sample swollen with 17.5% NaOH (G)	48.0	78.1	56.3

[a] G = Hard glass system; Q = quartz glass system. Polymerization time, 30 min.
[b] Preirradiation time.

and the shortening in induction period in each system. However, the per cent grafting rather decreased at 60-min preirradiation, with the exception of untreated sample in the hard glass system. It is considered that too long a preirradiation might even break the portions effective in initiating the graft copolymerization in the sample, resulting in restriction of graft formation. As for the untreated sample in the hard glass system, it seems that the chain scissions useless for the forming of grafts are not yet attained with preirradiation of 60 min, and the preirradiation works effectively on the improvement of the per cent grafting. Thus, it is recognized that the chain scissions indifferent to graft formation can be broken off by preirradiation of the cellulose sample, resulting in a fairly effective shortening of the induction period of graft copolymerization.

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