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EFFECT OF CROSSLINKING TREATMENT ON TEMPERATURE-RESPONSIVE CHARACTER OF GRAFTED CELLULOSES

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EFFECT OF CROSSLINKING TREATMENT ON TEMPERATURE-RESPONSIVE CHARACTER OF GRAFTED CELLULOSES

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Key Words: Photografting, Periodic Acid-Oxidized Cellulose, Temperature-Responsive Polymers, Crosslinking Treatment, Crosslinker

ABSTRACT

N-isopropylacrylamide (NIPAAm)- and methacryloyl-L-alanine methyl ester (MA-ALa-OMe)-grafted cellulose samples were prepared by photografting on dissolving pulp from softwoods, which was oxidized with periodic acid. The grafted samples exhibited a temperature-responsive character, where they swelled and shrank in water at 0°C and 50°C, respectively. The magnitude of the character increased with an increase in the percentage of grafting, and it was nearly equal between the

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NIPAAm- and MA-ALa-OMe-grafted samples. The temperature-responsive character of the grafted samples was improved by treating them with crosslinkers such as *N,N'*-methylenebisacrylamide and di-ethylene glycol dimethacrylate. The extent of the improvement largely depended on the concentration of crosslinker, temperature of crosslinking treatment, and nature of grafted chains.

INTRODUCTION

Poly(*N*-isopropylacrylamide (NIPAAm) is well known to exhibit a lower critical solution temperature around 32°C in aqueous solution. Its hydrogel [1-4] with a crosslinked structure swells in water below and shrinks above that temperature. It was found in a previous paper [5] that photografting of NIPAAm on cellulose is easily proceeded by using the cellulose sample oxidized with periodic acid (HIO_4), where about 80% of NIPAAm monomer used could be introduced into the cellulose sample as grafted chains. Moreover, the resultant NIPAAm-grafted cellulose samples exhibited a temperature-responsive character, where they swelled and shrank in water at temperatures lower and higher than around 30°C, respectively. The phenomenon is ascribed to contribution of the NIPAAm-grafted chains to the swelling and shrinking of the whole grafted sample including the cellulose substrate. It is expected that the character is improved by introduction of a crosslinked structure into grafted chains. It was reported that crosslinking density strongly affects the swelling behavior of NIPAAm/*N*-*n*-propylacrylamide copolymer hydrogels [6]. Therefore, this paper deals with the effect of crosslinking treatment on the temperature-responsive character of grafted celluloses. The crosslinking treatment of grafted cellulose samples with a crosslinker leads to the introduction of crosslinked structure into the samples. In this study, on the other hand, poly(methacryloyl-L-alanine methyl ester (MA-ALa-OMe) other than poly(NIPAAm) was used as grafted chains introduced into the cellulose substrate. The chemical structures of poly(NIPAAm) and poly(MA-ALa-OMe) are shown in Figure 1. The poly(MA-ALa-OMe) [7-9] is known to exhibit a lower critical solution temperature around 23°C in aqueous solution, and its hydrogel has a temperature-responsive character similar to poly(NIPAAm) hydrogel.

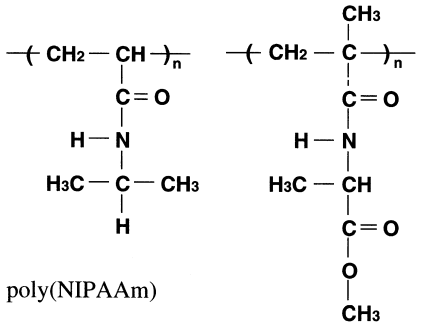

Figure 1. Chemical structures of poly(NIPAAm) and poly(MA-ALa-OMe).

EXPERIMENTAL

Materials

Commercial dissolving pulp from softwoods was used as a cellulose sample. The cellulose sample was treated with 20 mmol/L aqueous HIO_4 solution (ratio of liquor to solid 100:1) at 45°C for 60 minutes to prepare the oxidized sample. The carbonyl content of the oxidized sample, which was determined according to the hydroxylamine method [10], was 45.4 mmol per 100 g of cellulose sample. The oxidation [11] was proven to result in a high activity to initiate photografting of various vinyl monomers. Xanthone, *N*,*N*-methylenebisacrylamide (MBAAm), and diethylene glycol dimethacrylate (EGDMA) were all reagent grade and used without further purification. NIPAAm was purified by recrystallization from benzene and *n*-hexane mixture. MA-ALa-OMe monomer was synthesized according to the procedures described in the literatures [7, 8].

Photografting

Photografting was carried out in a Pyrex glass tube containing the oxidized sample 0.20 g and 20 mL water, in which a given amount of monomer (0.44 mol/L) was dissolved, under nitrogen atmosphere. Irradiation with a high-pressure mercury lamp (400W) was performed at 50°C using a Riko rotary photochemical reactor RH400-10W.

With photografting using xanthone as a photoinitiator, the oxidized sample was immersed in 10 mL acetone solution containing 0.1 wt% xanthone at

25°C for 10 minutes, filtered, and then dried under reduced pressure to obtain xanthone-sensitized sample. Photografting using the xanthone-sensitized sample was performed in the same system as that described above.

Polymerized samples were extracted for 48 hours with water to remove the homopolymer. The percentage of grafting was taken as the percentage of weight increase of the original cellulose sample.

Crosslinking Treatment

Crosslinking treatment was carried out in a Pyrex glass tube containing the grafted sample 0.30 g and 30 mL aqueous hydrogen peroxide solution (5 and 10 mmol/L), in which known quantities of crosslinker (MBAAm and EGDMA) were dissolved, under nitrogen atmosphere. Irradiation was performed at 30°C for 30 minutes using the same reactor as that described above section.

Measurement of Swelling

The grafted sample (W_o g), which was put into a tea-bag of nonwoven fabric, was immersed in water at 0°C and 50°C for 24 hours, alternately. The treated bag was allowed to hang on a holder for 30 minutes to separate the swollen sample (W_s g) from the unabsorbed water. The degree of swelling was defined as follows:

$$\text{Swelling (\%)} = 100 \times (W_s - W_o)/W_o$$

RESULTS AND DISCUSSION

Figure 2 shows photografting of NIPAAm and MA-ALa-OMe on HIO_4-oxidized cellulose sample. The photografting of NIPAAm easily proceeded to give about 400% grafting at the irradiation time of 30 minutes. The value implies that about 80% of NIPAAm monomer used participate in the grafting reaction to be introduced into cellulose substrate as grafted chains. With MA-ALa-OMe monomer, about 150% grafting was afforded at the irradiation time of 180 minutes. It was confirmed that the use of HIO_4-oxidized cellulose sample enables MA-Ala-OMe monomer other than NIPAAm to photograft easily. The activity of the oxidized sample is conceivable to be originated in the oxidized states [11] such as aldehyde groups attached to cellulose substrate by HIO_4-oxidation. Photografting of MA-Ala-OMe on xanthone-sensitized sample was further

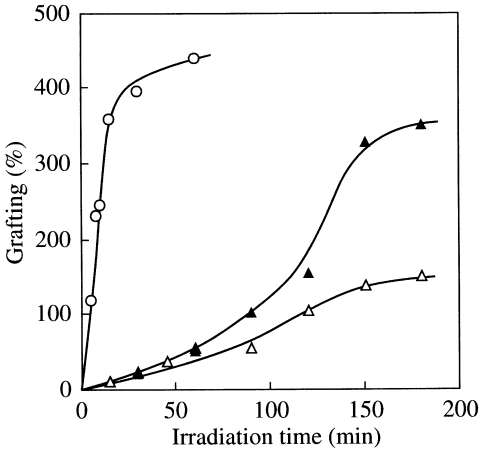

Figure 2. Photografting of NIPAAm and MA-ALa-OMe on HIO_4-oxidized cellulose sample. (O) NIPAAm, (Δ) MA-ALa-OMe, (▲) MA-ALa-OMe/xanthone-sensitized sample. Carbonyl content = 45.4 mmol/100 g sample, [monomer] = 0.44 mol/L, temperature = 50°C.

examined to improve the percentage of grafting, and the result is also presented in the figure. About 350% grafting could be obtained at the irradiation time of 180 minutes by using xanthone photoinitiator. The phenomenon is supposed to be ascribed to easier formation of cellulose radicals capable of initiating the grafting reaction due to hydrogen-abstracting effect of photoexcited xanthone on the sample.

A temperature-responsive character of the resulting grafted cellulose samples was examined when immersed in water at 0°C and 50°C for 24 hours, alternately, and then the degree of swelling was measured. The degree of swelling of NIPAAm-grafted sample is shown in Figure 3. The NIPAAm-grafted sample (untreated sample) exhibited the temperature-responsive character, where it swelled and shrank in water at 0°C and 50°C, respectively. Moreover, the character was reversible between 0°C and 50°C. MA-ALa-OMe-grafted sample also showed the temperature-responsive character similar to the NIPAAm-grafted sample. The extent of the character was compared among NIPPAm- and MA-ALa-OMe-grafted samples, and the results are shown in Figure 4. The vertical axis of the figure is “thermo-sensitivity” [12], which is a measure for evaluating the character, and is defined as the ratio of swelling of the grafted samples at 0°C and 50°C. The value increased with an increase in

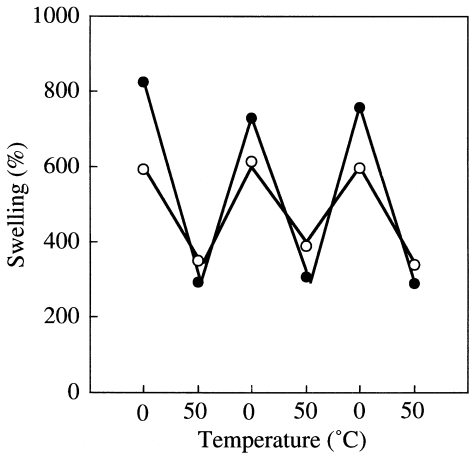

Figure 3. Degree of swelling of NIPAAm-grafted cellulose samples. (O) untreated sample (grafting = 328%), (●) grafted sample (grafting = 318%) treated with 0.05 wt% MBAAm.

the percentage of grafting, and the extent of the character was nearly equal among the two grafted samples.

Figure 3 also presents the temperature-responsive character of NIPAAm-grafted sample (treated sample), which was treated with MBAAm crosslinker. The degree of swelling of the treated sample increased and decreased at 0°C and 50°C,

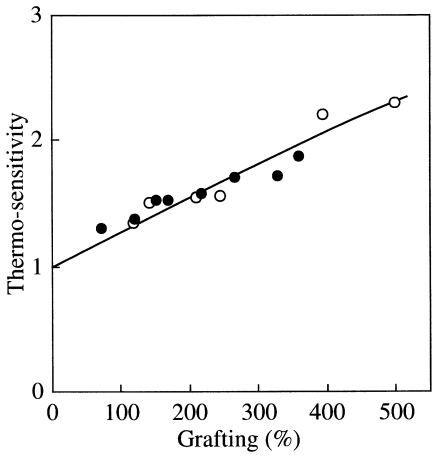

Figure 4. Relationship between thermo-sensitivity and percentage of grafting in (O) NIPAAm- and (●) MA-ALa-OMe-grafted samples.

respectively, compared to those of the untreated sample. The reaction of NIPAAm-grafted sample with MBAAm crosslinker may lead to formation of a crosslinked structure in the grafted sample and the resultant network texture effectively contributes to absorption of water, resulting in the increased degree of swelling at 0°C. On the other hand, the formation of crosslinked structure results in the limited mobility of NIPAAm-grafted chains and also promotes a hydrophobic interactions between the grafted chains to increase the shrinking nature of grafted sample, leading to the decreased degree of swelling at 50°C. In the present study, the crosslinking treatment of NIPAAm-grafted sample with MBAAm crosslinker was carried out using hydrogen peroxide as a photoinitiator. So, the hydrogen peroxide is decomposed by photoirradiation [13-15] to yield hydroxyl radicals capable of abstracting hydrogen atom from the grafted sample. Accordingly, MBAAm in the system may add to the resultant polymer radicals on the grafted sample, such as NIPAAm-grafted chain and cellulose substrate components, to form the crosslinked structure between (1) cellulose substrates, (2) NIPAAm-grafted chains, and (3) cellulose substrate and NIPAAm-grafted chain. At the present time, the crosslink points are not specified yet. It is conceivable, however, that the crosslinked structure is mainly formed between NIPAAm-grafted chain components, which account for about 75% of the weight of the grafted sample with 320% grafting in Figure 3.

Figure 5 shows the effect of concentration of crosslinker on temperature-responsive character of NIPAAm-grafted sample. The concentration of cross-

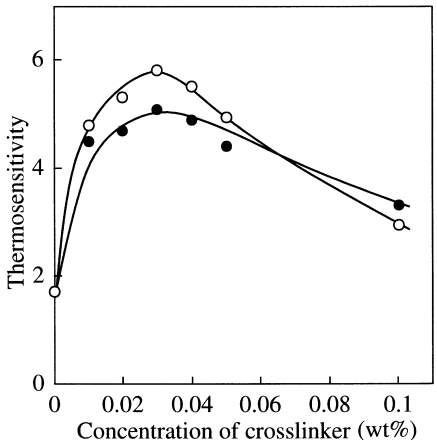

Figure 5. Effect of concentration of crosslinker on temperature-responsive character of NIPAAm-grafted cellulose sample. (O) MBAAm, (●) EGDMA, grafting = 400-410%.

linker, 0.05 wt%, in the horizontal axis corresponds to about one mol% of NIPAAm-grafted chains in the grafted sample with 400% grafting. The thermo-sensitivity increased with an increase in the concentration of crosslinker, and then decreased beyond a certain concentration of crosslinker, which was commonly observed for MBAAm and EGDMA. The swelling and shrinking nature of grafted sample is once facilitated with the introduction of crosslinked structure into the sample as shown in Figure 3, and this causes the increased thermo-sensitivity, while crosslinking density increases with increasing the concentration of crosslinker to reduce the degree of swelling, leading to the decreased thermo-sensitivity. The results of MA-ALa-OMe-grafted sample are shown in Figure 6. Again, a maximum thermo-sensitivity was observed at a certain concentration of crosslinker though the value is considerably lower than that of the NIPAAm-grafted sample. This suggests that formation of crosslinked structure in the MA-ALa-OMe-grafted sample is not easy to proceed in comparison with the NIPAAm-grafted one since tertiary hydrogen atoms on the MA-ALa-OMe-grafted chains are less than NIPAAm-grafted chains, resulting in the difficult performance of abstraction of hydrogen atom by hydroxyl radicals.

Table 1 shows the effect of temperature of crosslinking treatment on temperature-responsive character of NIPAAm-grafted sample. The highest thermo-

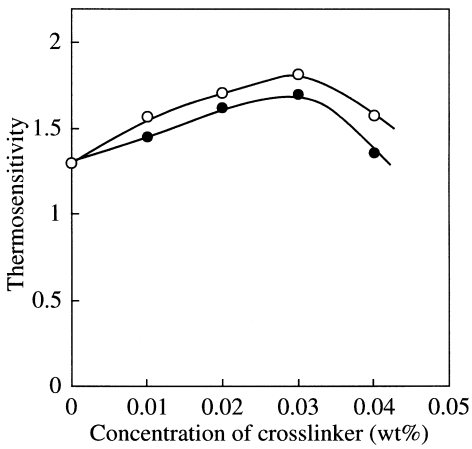

Figure 6. Effect of concentration of crosslinker on temperature-responsive character of MA-ALa-OMe-grafted cellulose sample. (O) MBAAm, (●) EGDMA, grafting = 330-340%.

TABLE 1. Effect of Temperature of Crosslinking Treatment[a] on Thermosensitivity[b] of NIPAAm-Grafted Cellulose Sample[c]

Temperature, °C	Thermo-sensitivity	
	$[H_2O_2]$=5 mmol/L	$[H_2O_2]$=10 mmol/L
5	2.6	2.4
30	5.3	3.8
50	3.0	2.5

[a] Photoirradiation was carried out for 30 min.
[b] Thermo-sensitivity was defined as the ratio of swelling of the grafted samples at 0°C and 50°C.
[c] Grafting=400%

sensitivity was observed at 30°C, which was commonly recorded for the systems with hydrogen peroxide concentrations of 5 and 10 mmol/L. It is supposed that NIPAAm-grafted chains are difficult to participate in the formation of crosslinked structure due to its shrinkage in water at 50°C measured, leading to the reduced thermo-sensitivity.

CONCLUSION

It was proven that NIPAAm and MA-ALa-OMe monomers could be grafted onto cellulose substrate by photografting using HIO_4-oxidized cellulose sample. The resultant grafted celluloses exhibited a temperature-responsive character, where it swelled and shrank in water at 0°C and 50°C, respectively. Crosslinking treatment of the grafted samples with crosslinkers such as MBAAm and EGDMA resulted in an increased thermo-sensitivity, but a maximum value was afforded at a certain concentration of crosslinker. It is concluded accordingly that proper crosslinking treatment of the grafted celluloses with MBAAm and EGDMA crosslinkers is useful for improving the temperature-responsive character of the grafted samples, which is largely influenced by the conditions of crosslinking treatment such as concentration of crosslinker and temperature of the treatment.

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