

Water-Absorbing Characteristics of Acrylic Acid-Grafted Carboxymethyl Cellulose Synthesized by Photografting

SHIN KUWABARA and HITOSHI KUBOTA*

Department of Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376, Japan

SYNOPSIS

Cellulosic absorbents for water were synthesized by photografting ($\lambda > 300$ nm) acrylic acid (AA) onto fibrous carboxymethyl cellulose (CMC, degree of substitution [DS] = 0.1–0.4) at 30°C in the presence of *N,N'*-methylenebisacrylamide as a crosslinker. The CMC sample was pretreated with hydrogen peroxide in the presence of sulfuric acid to prepare CMC peroxides with a peracid type as a polymeric photoinitiator. The peroxides were active for the photografting and AA could be grafted onto CMC with percent graftings higher than 150% by photoirradiation of 10 min at 30°C. The amount of water absorbed increased with increasing percent grafting of AA and DS of CMC. The amount was reduced considerably when the absorbents were prepared by the photografting of AA onto crosslinked CMC in the absence of the crosslinker. Graft copolymers which display a decreasing water absorbency as a function of temperature were prepared by two methods: In the first synthesis method, AA and *N*-isopropylacrylamide (NIPAAm) binary monomers were graft-copolymerized onto CMC samples using photoinitiation. In the second method, photografting of AA was followed by a second-step photografting of NIPAAm to produce a terpolymer with two types of side chains of differing repeat unit composition on the CMC substrate. Graft copolymers formed by both methods showed decreasing water absorbency as temperature increased with losses in water absorbency of up to about 60% as the temperature was increased above 30°C. Effects of NIPAAm composition and crosslinker content in the graft copolymers on the decreasing water absorbency as a function of temperature were also examined. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In a previous article,¹ photografting was applied to functionalize cellulose, i.e., epoxy groups were introduced into the cellulose substrate by photografting of glycidyl methacrylate and the resulting grafted celluloses were subjected to reaction with diamines. Moreover, introduction of amidoxime groups² into the substrate was also examined by the photografting of acrylonitrile followed by amidoximation with hydroxylamine. The glycidyl methacrylate- and acrylonitrile-grafted celluloses exhibited a higher reactivity³ toward diamine and hydroxylamine, respectively, than did those prepared by ceric ion-initiated grafting. This article deals with syntheses of

cellulosic absorbents for water and absorbents which display a decreasing water absorbency as a function of temperature by means of photografting.

It is generally known that the methods for synthesizing cellulosic absorbents for water are classified into two types: one is the crosslinking of a water-soluble cellulose derivative and the other is the grafting of hydrophilic vinyl monomers onto cellulosic materials. With the former method, hydrophilic groups, such as carboxymethyl^{4,5} and sulfate⁶ groups, are introduced into cellulose substrate and then the derivatives are crosslinked. In the latter method, on the other hand, water absorbents are prepared by grafting acrylonitrile^{7,8} and acrylic acid (AA)^{9,10} onto cellulosic materials followed by posthydrolysis and postdecrystallization, respectively. Recently, Sakata et al.^{11,12} prepared super water absorbents by grafting acrylamide onto hydroxyethyl cellulose and posthydrolysis. Grafting hydrophilic vinyl monomers onto

* To whom correspondence should be addressed.

cellulose derivatives with an enhanced hydrophilicity seems to be a useful method for preparing cellulosic absorbents for water.

We synthesized cellulosic absorbents for water by photografting using AA and carboxymethyl cellulose (CMC) as a hydrophilic vinyl monomer and a cellulose derivative, respectively. Moreover, the preparation of graft copolymers which display a decreasing water absorbency as a function of temperature was also examined by two photografting methods: In the first method, AA and *N*-isopropylacrylamide (NIPAAm) binary monomers were graft-copolymerized onto CMC. In the second method, AA was first grafted onto CMC and NIPAAm is further grafted onto the AA-grafted CMC. Accordingly, the resulting graft copolymers are composed of two types of grafted chains: polyAA and poly(NIPAAm).

Poly(NIPAAm) is well known to exhibit a lower critical solution temperature of around 32°C in an aqueous solution and its hydrogel swells below and shrinks above the critical temperature. Therefore, the graft copolymers containing the poly(NIPAAm) component might be expected to absorb water below and to dehydrate above the critical temperature. In this study, water absorbency was compared between the two graft copolymers containing the poly(NIPAAm) component to understand the water-absorbing behaviors.

EXPERIMENTAL

Materials

Dissolving pulp from softwoods was used as a cellulose sample. Fibrous CMC was prepared by reaction of the cellulose sample with chloroacetic acid according to the ordinary method.¹³ Crosslinking of the fibrous CMC was carried out in a system consisting of 1.0 g CMC and 40 mL aqueous hydrogen peroxide solution (5 mmol/L), in which a given amount of *N,N*-methylenebisacrylamide (MBAAm) was dissolved in a Pyrex glass tube with photoirradiation at 30°C for 30 min. The photoirradiation was performed using the same photochemical reactor as that used for photografting. After washing with water, the irradiated CMC was immersed in water at room temperature for 24 h and then dried under reduced pressure. The treated CMC was denoted as crosslinked CMC (CR-CMC). The MBAAm content was determined by nitrogen analysis and represented as nitrogen %. NIPAAm and MBAAm were all reagent grade and used without further purification. AA was purified by distillation under reduced pressure.

Preparation of CMC and CR-CMC Peroxides

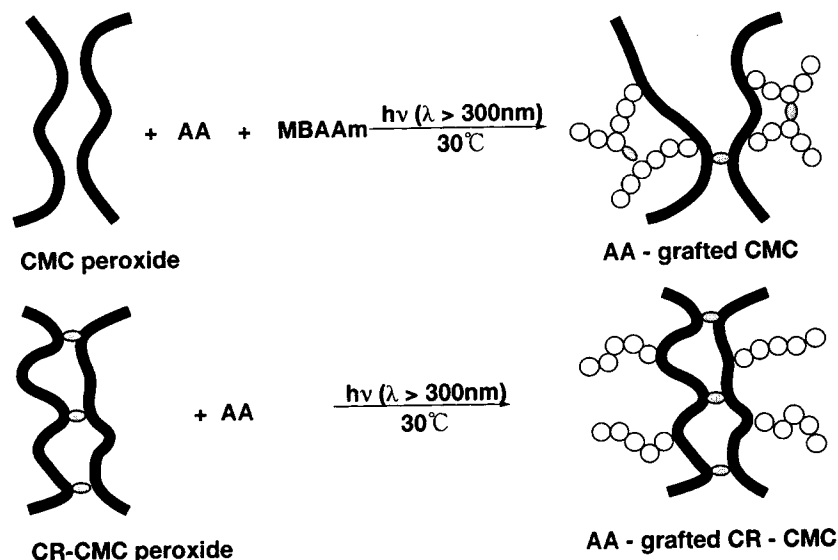
CMC or CR-CMC (0.50 g), 10 mL aqueous hydrogen peroxide (30%), and 2 mL concentrated sulfuric acid were placed in a flask adjusted at 25°C for 3 h. After reaction, the sample was washed with ice water. The peroxide content of the sample was determined iodometrically.¹⁴

Photografting Using CMC and CR-CMC Peroxides

Grafting was carried out in a Pyrex glass tube containing 0.20 g CMC peroxides and 30 mL water, in which 0.015 mol AA and a known concentration of MBAAm were dissolved at 30°C under a nitrogen atmosphere. Grafting using CR-CMC peroxides was performed in the system without MBAAm. The procedures are schematically shown in Scheme I. Irradiation with a high-pressure mercury lamp (400 W) was carried out at 30°C using a Riko rotary photochemical reactor (RH400-10W), around which the Pyrex glass tubes were rotated. The polymerized samples were extracted for 3 days with water to remove homopolymers. The percent grafting and the graft efficiency were taken as the percentage of weight increase of the original sample and the weight percent of grafted polymer relative to total conversion of monomer in a system, respectively.

Preparation of Graft Copolymers Containing the Poly(NIPAAm) Component

In the first synthesis method (one-step method), AA and NIPAAm binary monomers were graft-copolymerized onto CMC, i.e., photografting was carried out in a Pyrex glass tube containing 0.20 g CMC peroxides and 30 mL water, in which given molar ratios of AA and NIPAAm binary monomers (total monomer concentration = 0.015 mol) and known concentrations of MBAAm were dissolved at 30°C under a nitrogen atmosphere. The grafted samples thus obtained were denoted as a one-step sample. The NIPAAm content of the grafted chains was determined by nitrogen analysis. With the second method (two-step method), AA was first grafted onto CMC according to the photografting procedures described in the above section. The resulting AA-grafted CMC (0.20 g) was further subjected to photografting of NIPAAm at 30°C using 30 mL of a 5 mmol/L aqueous hydrogen peroxide solution as a photoinitiator, in which 7.5×10^{-4} mol NIPAAm was dissolved in the absence of MBAAm. The grafted samples were denoted as a two-step sample. Graft copolymers with different percent graftings in



Scheme 1

each system were prepared by varying the irradiation time of up to 30 min. The preparation procedures using CMC are schematically shown in Scheme II. In the case of CR-CMC, the MBAAm crosslinker was not used for the photografting.

Measurement of Water Absorbency

AA-grafted CMC and CR-CMC (H-type sample) were treated with aqueous solution of 0.5 mol sodium hydroxide at 25°C for 2 h to yield their sodium salt (Na-type sample). The grafted sample (W_0 g), which

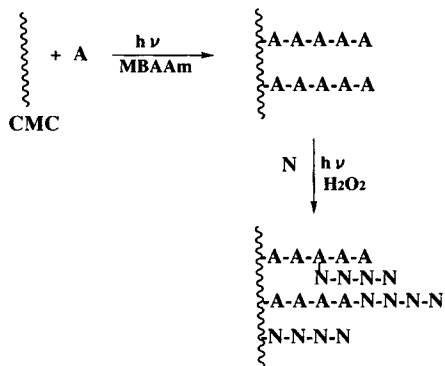
was put into a tea bag of nonwoven fabric, was immersed in deionized water at various temperatures for 24 h. The treated tea bag was allowed to hang on a holder for 20 min to separate the swollen sample (W_s g) from the unabsorbed water. Water absorbency was defined as follows:

$$\text{Water absorbency (g/g)} = \frac{W_s - W_0}{W_0}$$

(1) Photografting of AA(A) and NIPAAm(N) binary monomers



(2) Two-step photografting

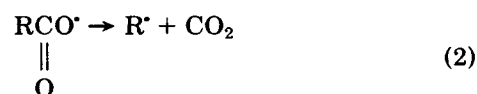
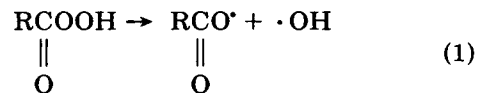


Scheme 2

RESULTS AND DISCUSSION

Photografting Induced by CMC Peroxides

Photografting of AA on CMC and CR-CMC peroxides in the presence and absence of MBAAm, respectively, was compared to a known ability of the peroxides to initiate the grafting, and the results are shown in Figures 1 and 2. It is supposed that CMC peroxides are photo-decomposed according to eqs. (1) and (2), and CMC radicals RCOO^\bullet and



R^\bullet [eqs. (1) and (2)] initiate the grafting. On the other hand, the decomposition of CMC peroxides

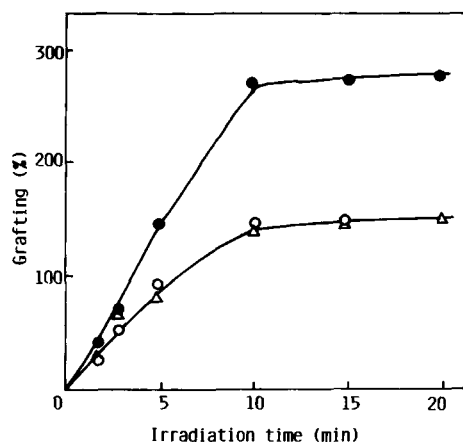


Figure 1 Photografting of AA on CMC and CR-CMC at 30°C: (○) CMC, [MBAAm] = 0.1 wt %; (●) CMC, [MBAAm] = 0.3 wt %; (△) CR-CMC with N% = 0.85, [MBAAm] = 0. Amount of peroxide = 15–17 meq/100 g CMC; DS of CMC = 0.15.

[eq. (1)] results in the formation of hydroxyl radicals. It is conceivable that the hydroxyl radicals contribute to the initiation of polymerization leading to the formation of homopolymers.

AA could be easily grafted onto CMC and CR-CMC with a short irradiation time at 30°C (Fig. 1). With photografting on CMC in the presence of MBAAm, the system with 0.3 wt % MBAAm gave a higher percent grafting than that with 0.1 wt % MBAAm. This suggests that double bonds in MBAAm residues incorporated into the CMC substrate and/or AA-grafted chains contribute to further grafting initiation. It was reported that the use of a polyfunctional monomer such as divinylbenzene¹⁵ largely accelerates the photografting of styrene onto cotton cellulose. On the other hand, the MBAAm in the system also participated in the formation of homopolymers, leading to a lower graft efficiency compared to the system of CR-CMC in the absence of MBAAm (Fig. 2). It was found, thus, that peroxides with a peracid type on CMC and CR-CMC are very active for photografting of AA and the AA-grafted CMC and CR-CMC can be easily prepared by the grafting using CMC peroxides.

Water Absorbencies of AA-Grafted CMC and CR-CMC

Water absorbencies of AA-grafted CMC and CR-CMC were compared to examine the effect of the location of crosslink points in the grafted samples, and the results are shown in Figures 3 and 4. It is conceivable that the crosslink points may locate at

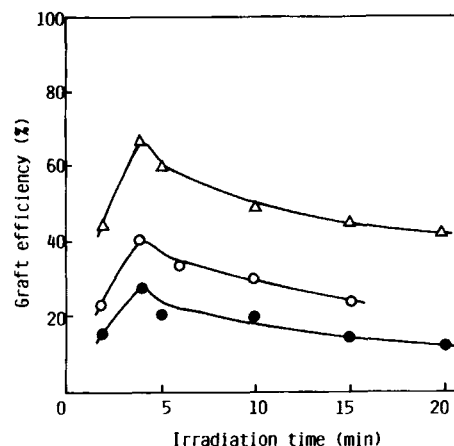


Figure 2 Photografting of AA on CMC and CR-CMC at 30°C: (○, ●) CMC; (△) CR-CMC. Grafting conditions were the same as those for Figure 1.

both CMC substrate and AA-grafted chains in the AA-grafted CMC, which is prepared by photografting in the presence of MBAAm. As shown in Scheme I, on the other hand, the crosslink points locate only at the CMC substrate in the AA-grafted CR-CMC. The water absorbency increased with increasing the percent grafting, which was commonly observed for the two grafted samples. Moreover, a higher value was observed for the grafted sample with a higher DS of CMC. The water absorbency was higher for the AA-grafted CMC than for the AA-grafted CR-CMC (Fig. 3). Figure 4 shows the water absorbency of Na-type sample. The water absorbency increased markedly with converting carboxyl groups in the grafted sample to sodium salt. With the Na-type

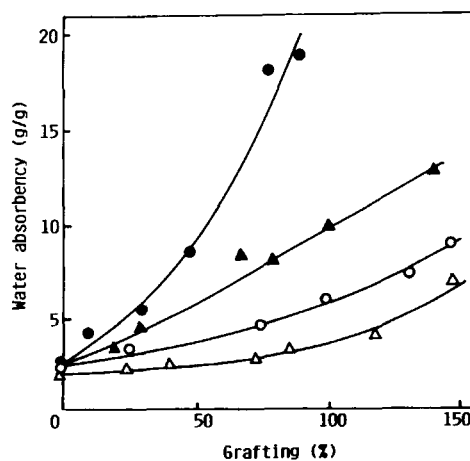


Figure 3 Water absorbency of AA-grafted CMC and CR-CMC (H-type sample) at 25°C. AA-grafted CMC: (○) DS = 0.15; (●) DS = 0.42; N% = 0.8–0.9. AA-grafted CR-CMC: (△) DS = 0.15; (▲) DS = 0.42; N% = 0.8–0.9.

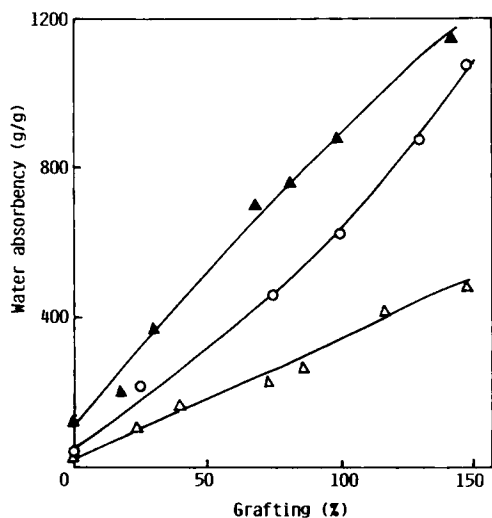


Figure 4 Water absorbency of AA-grafted CMC and CR-CMC (Na-type sample) at 25°C. AA-grafted CMC: (○) DS = 0.15; N% = 0.8–0.9. AA-grafted CR-CMC: (△) DS = 0.15; (▲) DS = 0.42; N% = 0.8–0.9.

sample, AA-grafted CMC also exhibited a higher water absorbency than that of AA-grafted CR-CMC though the AA-grafted CMC, which was prepared from CMC with degree of substitution (DS) = 0.42, was completely dissolved in water by the conversion. It was found accordingly that crosslink points are necessary to locate properly at both the CMC substrate and AA-grafted chains in order to synthesize AA-grafted CMC with high water absorbency.

Water Absorbency of Graft Copolymers Containing the Poly(NIPAAm) Component

The preparation of graft copolymers containing the poly(NIPAAm) component as grafted chains was examined by two methods, such as the one-step and two-step methods. With the former method, photografting of AA and NIPAAm binary monomers onto CMC is carried out in the presence of MBAAm. Therefore, the two monomer components are copolymerized to introduce them into the CMC substrate. In case of the latter method, AA is first grafted onto the CMC substrate using photoinitiation in the presence of MBAAm and NIPAAm is further photografted onto the AA-grafted CMC. It is supposed that the NIPAAm component may be grafted onto the CMC substrate and/or the AA-grafted chains as shown in Scheme II.

Figure 5 presents the water absorbency of the one-step sample when immersed in water at various temperatures for 24 h. The water absorbency of each grafted sample decreased at about 25 to 30°C with

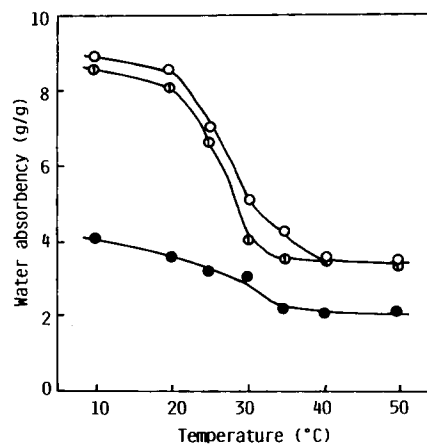


Figure 5 Relationship between water absorbency and temperature in one-step sample (H-type sample) prepared from CMC (DS = 0.24). Composition of grafted chains, AA/NIPAAm: (○) 59/41; (○) 48/52; (●) 0/100. Grafting % = 400–410; N% = 1.9–2.1.

increasing temperature. About 50–60% of the water absorbency at 10°C was lost when the temperature was increased above 30°C. Thus, the grafted samples swelled and shrank in water below and above the temperature, respectively. Figure 6 shows the comparative result on the water absorbency between the one-step and two-step samples. The amount of the latter sample was considerably higher than that of the former sample and steeply decreased at about 30°C with an increase in temperature. The same results were observed for Na-type samples. It is in-

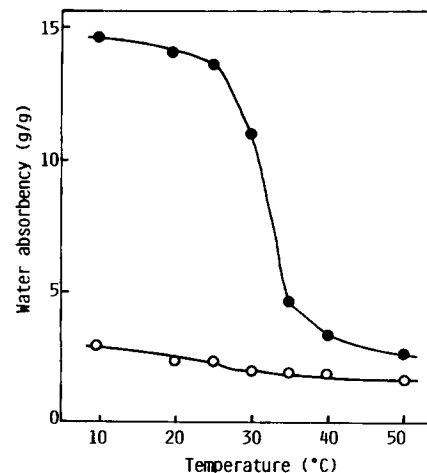


Figure 6 Relationship between water absorbency and temperature in (○) one-step and (●) two-step samples (H-type sample) prepared from CMC (DS = 0.24). One-step sample: AA/NIPAAm = 48/52; grafting % = 198; N% = 2.0. Two-step sample: AA/NIPAAm = 51/49; grafting % = 205; N% = 2.1.

ferred that NIPAAm-grafted chains of the two-step sample are likely to penetrate into the CMC substrate inside compared to those of the one-step sample since the NIPAAm component is further grafted onto the AA-grafted CMC. Moreover, no crosslink points exist on the NIPAAm-grafted chains. These may result in a sharply decreasing water absorbency as a function of temperature in the two-step sample.

It was observed that one-step and two-step samples (AA/NIPAAm = 50/50) prepared from CR-CMC do not exhibit the property that water absorbency decreases with increasing temperature when immersed in water at various temperatures. Accordingly, effects of NIPAAm composition and MBAAm content in the two-step sample prepared from CR-CMC on the property were examined, and the results are shown in Figures 7 and 8. The grafted samples with higher NIPAAm composition (Fig. 7) and with lower MBAAm content (Fig. 8) exhibited the property. It was found that control of the NIPAAm composition and the MBAAm content is required for generation of the property in two-step sample prepared from CR-CMC.

Based on the above investigations, it is concluded that cellulosic absorbents for water can be prepared by photografting of AA on CMC, into which peroxide groups with peracid type are introduced, in the presence of the MBAAm crosslinker. Moreover, water absorbents, which display a decreasing water absorbency as a function of temperature, could also be synthesized by two photografting methods, i.e., one is the photografting of AA and NIPAAm binary

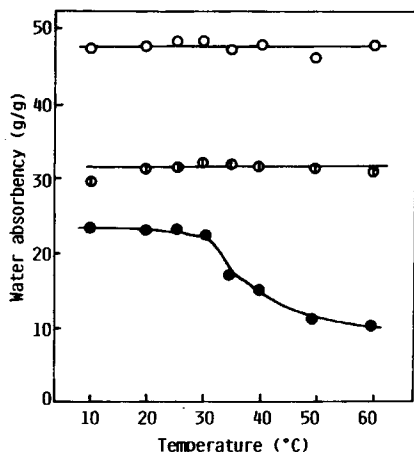


Figure 7 Relationship between water absorbency and temperature in two-step sample (Na-type sample) prepared from CR-CMC (DS = 0.12, N% = 0.85). AA/NIPAAm: (O) 47/53; (⊙) 27/73; (●) 11/89; grafting % = 240–250.

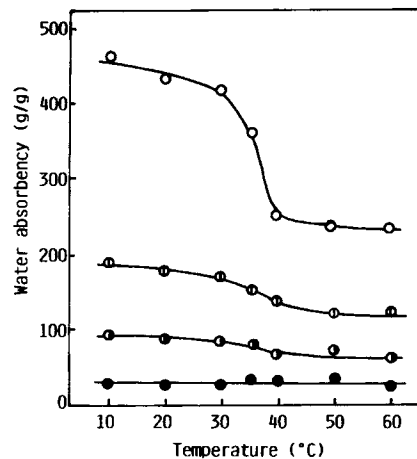


Figure 8 Relationship between water absorbency and temperature in two-step sample (Na-type sample) prepared from CR-CMC (DS = 0.12, N%: (O) 0; (⊙) 0.23; (●) 0.56; (●) 0.85; AA/NIPAAm = 32/68; grafting % = 290–300.

monomers onto CMC and the other is the photografting of NIPAAm onto AA-grafted CMC.

REFERENCES

- H. Kubota and S. Ujita, *J. Appl. Polym. Sci.*, **56**, 25 (1995).
- H. Kubota and Y. Shigehisa, *J. Appl. Polym. Sci.*, **56**, 147 (1995).
- H. Kubota and S. Suzuki, *Eur. Polym. J.*, **31**, 701 (1995).
- T. Motohashi, *Kobunshikako*, **33**, 452 (1984).
- T. Fushimi, *Development and Application of Highly Water-absorbing Polymers*, Kogyo Chosakai, Tokyo, 1990, p. 20.
- K. Arai and H. Goda, *Sen-i Gakkaishi*, **49**, 482 (1993).
- P. Lepoutre, S. H. Hui, and A. A. Robertson, *J. Appl. Polym. Sci.*, **17**, 3143 (1973).
- P. Lepoutre, S. H. Hui, and A. A. Robertson, *J. Macromol. Sci. Chem. A*, **10**, 681 (1976).
- J. L. Williams and V. T. Stannett, *J. Appl. Polym. Sci.*, **23**, 1265 (1979).
- S. B. Vitta, E. P. Stanel, and V. T. Stannett, *J. Appl. Polym. Sci.*, **32**, 5799 (1986).
- N. Miyata and I. Sakata, *Sen-i Gakkaishi*, **47**, 95 (1991).
- M. Yoshinobu, M. Morita, and I. Sakata, *J. Appl. Polym. Sci.*, **45**, 805 (1992).
- R. L. Whistler, *Methods in Carbohydrate Chemistry III, Cellulose*, Academic Press, New York, 1963, p. 322.
- H. Kubota, *React. Polym.*, **17**, 263 (1992).
- S. R. Shukla and A. R. Athalye, *Polymer*, **33**, 3729 (1992).

Received September 1, 1995

Accepted November 28, 1995