Modification of Cellulose Powder Surface by Grafting of Polymers with Controlled Molecular Weight and Narrow Molecular Weight Distribution

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ABSTRACT: To modify cellulose powder surface, the grafting of polymers with controlled molecular weight and narrow molecular weight distribution onto the surface by the termination of living polymer cation with amino groups introduced onto cellulose powder surface was investigated. The introduction of amino groups onto cellulose powder surface was achieved by the treatment of cellulose powder with isatoic anhydride. It was found that cellulose powder having amino groups are readily reacted with living poly(2-methyl-2-oxazoline) (polyMeOZO) cation, which was generated by ring-opening polymerization with methyl p-toluenesulfonate as an initiator, and polyMeOZO with controlled molecular weight and narrow molecular weight distribution was grafted onto the surface. By the termination of living poly(isobutyl vinyl ether) (polyIBVE), which was generated by the polymerization with $HCl/ZnCl_2$ initiating system, with amino groups on cellulose powder, polyIBVE was also grafted onto the surface. The mole number of grafted polymer chain on cellulose powder surfaces decreased with increasing molecular weight of the living polymer cation, because of increasing steric hindrance with increasing molecular weight of living polymer cation. Wettability of cellulose powder surface to water was found to be controlled by grafting of hydrophilic or hydrophobic polymer onto the surface. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 515–522, 2000

Key words: cellulose powder; surface grafting of polymer; amino group; living polymer cation; termination

INTRODUCTION

Cellulose is most abundant among the naturally occurring polysaccharide. And it is a renewable, replaceable, high-molecular-weight polymer, and biodegradable. As it has three hydroxyl groups in the anhydroglucose repeating unit, cellulose is used as raw material for various useful products. Numerous reports have been published concerning the grafting of cellulose. Many different methods of grafting to cellulose have been developed.[1–4] In most methods, radicals are generated along the cellulose backbone in the presence of vinyl monomers that may be polymerized by these radicals. One of the disadvantages in these grafting procedures is that the molecular weight and the molecular weight distribution of the grafts are almost impossible to control or change. The molecular weight is often very high and molecular weight distribution is broad.

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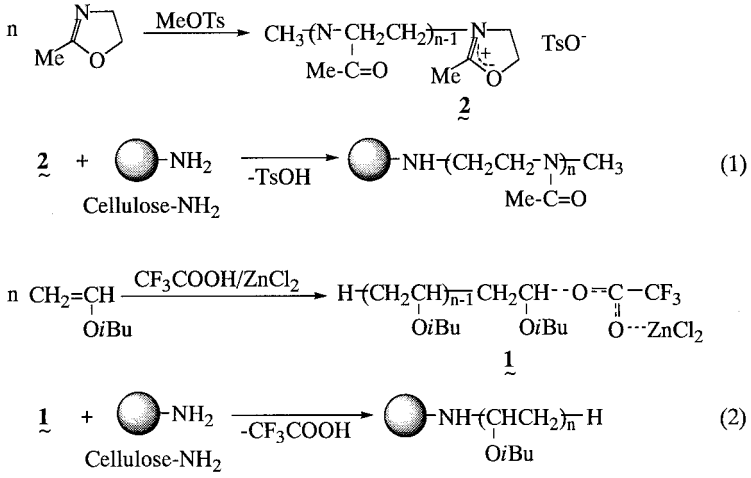


Scheme 1

Recent studies have shown novel method for preparing highly branched cellulose by anionic polymerization using sodium naphthalenide,[5] grafting of monodisperse low-molecular-weight polystyrene onto cellulose acetate,[6] Ce(IV)-induced polymerization of allyl methacrylate with cotton cellulose,[7] and graft copolymerization of a vinyl acetate-methyl acrylate mixture onto cellulose.[8]

On the other hand, in order to modify the surface properties of inorganic powders and pigments, the polymer grafting is known to be one of the most effective methods. Polymer-grafted powders can be dispersed easily in organic solvents, resins, and rubbers. For example, it has been reported that the grafting of various polymers onto inorganic powder, such as ultrafine silica and carbon black surface, is successfully achieved by the polymerization initiated from initiating groups previously introduced onto the surfaces.[9–11]

Recently, we have reported the grafting of polymers with controlled molecular weight and narrow molecular-weight distribution onto ultrafine silica[12] and carbon black[13] by the termination of living polymer cation with amino groups introduced onto these surfaces. In the preceding paper, we have pointed out that surface amino groups of chitosan powder readily react with living polymer cations to give the corresponding polymer-grafted chitosan powder.[14]

In the present paper, in order to modify cellulose powder surface in heterogeneous system, the grafting of polymers with controlled molecular weight and narrow molecular-weight distribution onto cellulose powder surface by the termination of living polymer cation with amino groups introduced onto the surface was investigated (Scheme 1). The effect of molecular weight of living polymers on the grafting onto the surface and wettability control of cellulose powder surface by grafting of polymers are also discussed.

EXPERIMENTAL

Materials and Reagents

Cellulose powder (Kanto Chemical Co., Inc.) was used without further purification. It was dried in vacuo at 50°C for 48 h before use. The particle size of the cellulose powder was determined to be 20–100 μm by SEM.

2-Methyl-2-oxazoline (MeOZO) (Aldrich Chemical Co., Inc.) was dried over calcium hydride and distilled just before use. Isobutyl vinyl ether (IBVE) (Tokyo Kasei Kogyo Co., Ltd.) was washed with 5% alkaline aqueous solution and water, dried over potassium hydroxide, refluxed over sodium, and distilled just before use.

N,N-Dimethylacetamide (DMAc) and acetonitrile (Kanto Chemical Co., Inc.) were dried over calcium hydride, distilled over diphosphorous pentaoxide, and distilled over calcium hydride just before use. Tetrahydrofuran (THF) (Kanto Chemical Co., Inc.) was refluxed over sodium and distilled just before use. Toluene (Kanto Chemical Co., Inc.) was washed with concentrated sulfuric acid, alkaline aqueous solution, and pure water, dried over calcium chloride, refluxed over sodium, and distilled before use.

Isatoic anhydride (MERCK-Schuchardt), lithium chloride (Kanto Chemical Co., Inc.), 1,8-diazabicyclo [5.4.0]-7-undecene (DBU) (Tokyo Kasei Kogyo Co., Ltd.) , and methyl *p*-toluenesulfonate (MeOTs) (Tokyo Kasei Kogyo Co., Ltd.) were used without further purification.

Hydrogen chloride (HCl) (anhydrous, 1.0 M solution in diethyl ether) and zinc chloride ($ZnCl_2$) (1.0 M solution in diethyl ether) was obtained from Aldrich Chemical Co., Inc., which were diluted with toluene (0.01 mol/L and 0.20 mol/L, respectively) and stored in ampules.

Introduction of Amino Groups Onto Cellulose Powder Surface

The introduction of amino groups onto cellulose powder surface was achieved by the method of literature.[15,16] A typical example is as follows. Into a 300-mL flask, 2.5 g of cellulose powder and 40 mL of DMAc were charged, and the mixture was stirred with a magnetic stirrer for 1 h at room temperature. Then 4.82 g of isatoic anhydride and 3.3 mL of DBU were added, and the mixture was stirred at 80°C for 24 h. After the reaction, the mixture was centrifuged at 5.0×10^3 rpm and the precipitate was extracted with methanol for 48 h using a Soxhlet apparatus. The resulting cellulose powder was dried in vacuo at room temperature.

Determination of Amino Group Content of Cellulose Powder

The content of amino groups introduced onto the surface of cellulose powder was determined by titration.[17] A typical example is as follows. Into a 100-mL flask, 0.20 g cellulose powder and 20 mL of 0.01 N HCl aqueous solution were charged, and the mixture was stirred over 3 h with a magnetic stirrer at room temperature. After the reaction, the mixture was filtered and 2.0 mL of the filtrate was titrated with aqueous solution of sodium hydroxide using phenolphtalein as an indicator.

Preparation of Living PolyMeOZO Cation

Living polyMeOZO cation was prepared by the cationic ring-opening polymerization of MeOZO using of MeOTs as a catalyst according to the method of Saegusa et al.[18,19] Into a 100-mL flask equipped with a three-way stopcock, containing 12 mmol of MeOZO and 10.0 mL of acetonitrile, 0.7 mmol of MeOTs was added via a syringe. The polymerization was conducted at 80°C for 20 h under dry nitrogen. The conversion determined from residual MeOZO concentration determined by gas chromatography reached to 100% at that time.

Preparation of Living PolyIBVE Cation

The preparation of living polyIBVE cation was carried out by the living cationic polymerization of IBVE using $HCl/ZnCl_2$ initiating system according to the method of Higashimura and Sawamoto.[20,21] The polymerization was carried out in a 100-mL flask equipped with a three-way stopcock under dry nitrogen. The polymerization was initiated by adding 1.0 mL of $ZnCl_2$ solution (0.20 mol/L in toluene) into 8.0 mL of IBVE solution (0.50 mol/L in toluene) containing 1.0 mL of HCl solution (0.01 mol/L in toluene). The polymerization was conducted at 0°C for 1 h and the conversion determined from residual IBVE concentration determined by gas chromatography reached to 100% at that time.

Quenching of Living Polymer Cation

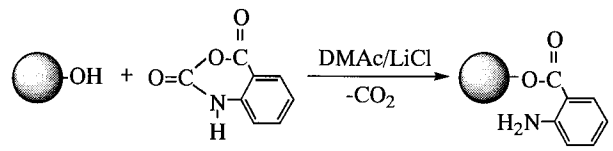
The quenching of living polyMeOZO and polyIBVE cation was achieved by the addition of 5.0 mL of 10% ammonical methanol to the polymerization mixture after 1 h and 20 h, respectively, at which the conversion of IBVE and MeOZO reached 100%.

Reaction of Cellulose Powder with Living Polymer Cation

Into a 100-mL flask that contained 0.10 g of cellulose powder having amino groups, 16.0 mL of solution (0.25×10^{-2} mol/L in acetonitrile) of living polyMeOZO was added in a glove box, whose atmosphere was replaced with dry nitrogen. The flask was sealed and the mixture was stirred with a magnetic stirrer at 80°C. After a definite time, the grafting reaction was terminated by the addition of methanol. For the grafting reaction of polyIBVE, 10.0 mL of polymer solution (8.0×10^{-5} mol/L in toluene) was reacted with 0.10 g of cellulose powder.

Determination of Percentage of Grafting

The cellulose powder obtained from the above grafting reaction with living polymer cation was dispersed in a good solvent for polymer (methanol for polyMeOZO and THF for polyIBVE), and the dispersion was centrifuged at 5.0×10^3 rpm. The



Scheme 2

precipitated cellulose powder was dispersed in methanol or THF and centrifuged again. These procedures were repeated several times. Then ungrafted polymer was completely extracted with a good solvent of polymer using a Soxhlet apparatus until no more polymer could be extracted in the solvent. After the above procedures, the polymer-grafted cellulose powder was dried in vacuo at 50°C. The percentages of grafting was determined by the following equation:

$$\text{Grafting (\%)} = (A/B) \times 100$$

where A (g) is weight of living polymer grafted and B (g) is weight of cellulose powder charged. The amount of living polymer grafted onto cellulose powder surface was determined from the difference in weight of cellulose powder before and after the grafting reaction.

Infrared Spectra

The infrared spectra of modified cellulose powder was recorded on a Hitachi Infrared Spectrophotometer Model 270-30 using KBr pellet.

Determination of Molecular Weight

The molecular weight and molecular weight distribution of polyMeOZO and polyIBVE were estimated by gel permeation chromatography (GPC) using polystyrene standards. For GPC measurements, a CCPD instrument (TOSOH) equipped with a polystyrene gel column (TSK-GEL G3000HHR) was used.

Wettability of Cellulose Powder

The wettability of cellulose powder and polymer-grafted cellulose powder was estimated by the penetrating rate of ion-exchanged water through a column packed with cellulose powder or polymer-grafted cellulose powder. A typical example is as follows. Into a glass column (inside diameter: 2 mm), 0.10 g polymer-grafted cellulose powder was packed and water was added from the top of the column. Then the penetrating rate of water through the column was determined.

RESULTS AND DISCUSSION

Introduction of Amino Groups onto the Surface of Cellulose Powder

It has been reported that amino groups can be introduced onto cellulose powder surface by the reaction of hydroxyl groups of cellulose with isatoic anhydride (Scheme 2).[15,16] Figure 1 shows the IR spectra of cellulose powder treated with isatoic anhydride and untreated cellulose powder. In the IR spectrum of isatoic anhydride-treated cellulose powder, a new absorption at 1640 cm^{-1}, which is characteristic of amino group, was observed. This result clearly shows that amino groups were successfully introduced onto the cellulose powder surface.

Cellulose powder having amino groups was abbreviated as Cellulose-NH_2. The amount of amino groups introduced onto the surface was determined by titration with hydrogen chloride.[17] In this study, cellulose powder having 0.086, 0.095, and 0.218 mmol of amino groups were prepared by changing ratio of isatoic anhydride and cellulose powder.

Grafting Reaction of Living PolyMeOZO Cation with Cellulose-NH_2

Living polyMeOZO cation is very sensitive to nucleophiles such as amines.[22] Therefore, the graft-

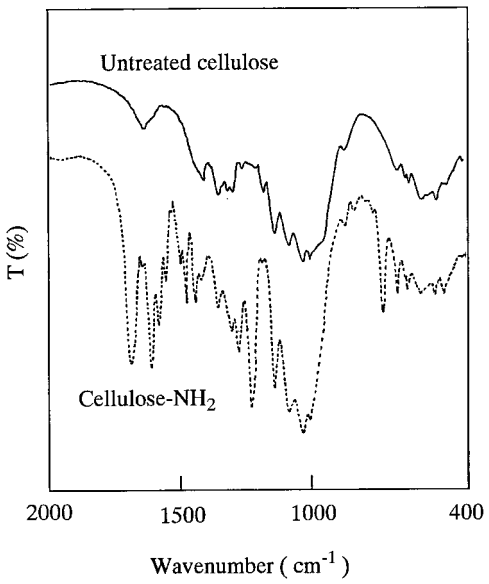


Figure 1 IR spectra of untreated cellulose and Cellulose-NH_2.

Table I Grafting Reaction of Living PolyMeOZO Cation with Cellulose-NH_2

Cellulose	Amino Group (mmol/g)	PolyMeOZO	Grafting (%)	R^a (%)
Untreated	—	Living	trace	—
Cellulose-NH_2	0.086	Quenched	0.6	—
Cellulose-NH_2	0.086	Living	9.8	51.8

[a] Percentage of amino groups used for the grafting of polyMeOZO.

Cellulose, 0.10 g; polyMeOZO ($Mn = 2.2 \times 10^3$; $Mw/Mn = 1.22$), 16.0 mL (2.5 mmol/L in acetonitrile).

ing of polyMeOZO onto cellulose powder surface by the termination of living polyMeOZO with surface amino groups on modified cellulose powder was examined in heterogeneous system (Scheme 1, part (1)).

Table 1 shows the results of the grafting reaction of Cellulose-NH_2 with living polyMeOZO (Mn $= 2.2 \times 10^3$; Mw/Mn = 1.22). By the reaction of untreated cellulose powder with living polyMeOZO, no grafting onto the cellulose powder surface was observed. In addition, after the quenching of living polyMeOZO with ammonical methanol, the polymer hardly reacted with Cellulose-NH_2. On the contrary, polyMeOZO was found to be grafted onto the cellulose powder surface by the reaction of the living polyMeOZO with Cellulose-NH_2.

This indicated that living polyMeOZO cation was successfully terminated with amino groups and polyMeOZO with narrow molecular-weight distribution and well-defined molecular weight is grafted onto the surface with amino bonds as shown in Scheme 1, part (1). The percentage of amino groups used for the grafting reaction with living polyMeOZO (R) was 51.8%. This value was much larger than that for the grafting of polyMeOZO onto silica having amino groups. This may be due to the fact that the blocking effect by neighboring grafted polymer chains were reduced in the grafting with Cellulose-NH_2, because of lower density of surface amino groups.

Effect of Molecular Weight of Living PolyMeOZO on the Grafting

The effect of molecular weight of living polyMeOZO cation on the grafting reaction with Cellulose-NH_2 was examined. The results are shown in Figure 2. It is interesting to note that the percentage of grafting and the number of grafted chain (Gn) decreased with increasing molecular weight of living polyMeOZO as well as that of grafting onto chitosan powder.[14] This may be due to surface amino groups of cellulose powder being shielded by neighboring grafted polymer chains. This effect on the grafting was enhanced with an increase of molecular weight of the living polymer cation.

Effect of Amino Group Content of Cellulose-NH_2 on the Grafting of PolyMeOZO

The effect of amino group content of Cellulose-NH_2 on the grafting of living polyMeOZO cation (Mn $= 2.2 \times 10^3$; Mw/Mn = 1.22) was investigated. The results are shown in Figure 3. The percentage of grafting of polyMeOZO increased with increasing amino group content of Cellulose-NH_2 as expected.

However, the percentage of amino groups used for the grafting site (R) was found to gradually decrease with increasing amino group content. This may be due to the fact that the percentage of surface amino groups shielded by neighboring grafted chains gradually increases with increasing density of amino groups on Cellulose-NH_2.

Grafting Reaction of Living PolyIBVE Cation with Cellulose-NH_2

The grafting reaction of polyIBVE cation onto cellulose powder by the termination of living polyIBVE cation with surface amino groups on cellulose pow-

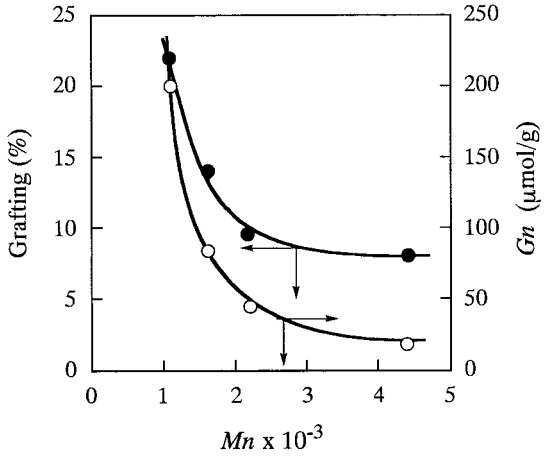


Figure 2 Effect of molecular weight of living polyMeOZO on grafting onto Cellulose-NH_2. Cellulose-NH_2, 0.10 g; polyMeOZO, 5.0 mmol in acetonitrile; 25.0°C.

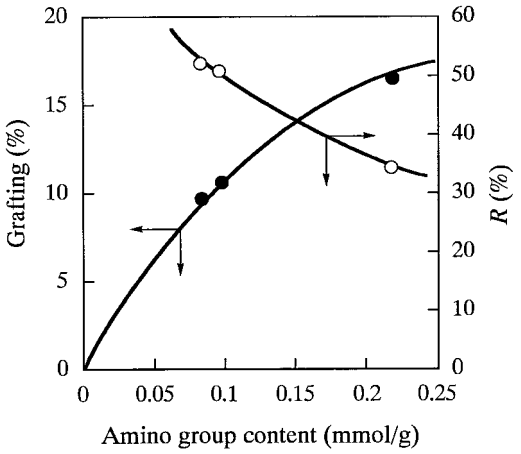


Figure 3 Effect of amino group content of Cellulose-NH_2 on the grafting of living polyMeOZO onto the surface. Cellulose-NH_2, 0.10 g; polyMeOZO (Mn = 2.2 × 10^3, Mw/Mn = 1.22), 5.0 mmol in acetonitrile; 25.0°C.

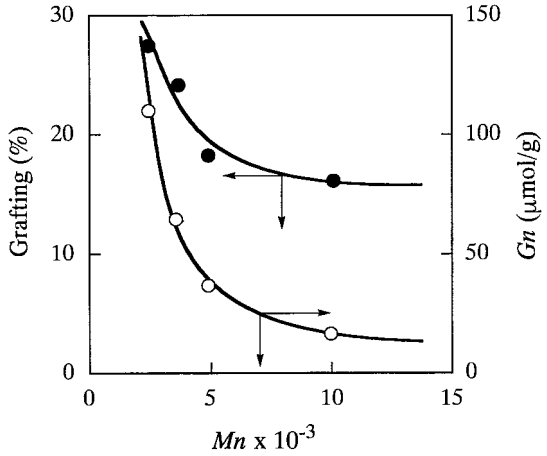


Figure 4 Effect of molecular weight of living polyIBVE on grafting onto Cellulose-NH_2. Cellulose-NH_2, 0.10 g; polyIBVE, 1.2 mmol in toluene; 25.0°C.

der was also investigated in heterogeneous system (Scheme 1, part (2)). The grafting reaction of living polyIBVE (Mn = 5.0 × 10^3; Mw/Mn = 1.10) cation with Cellulose-NH_2 was carried out at room temperature under several conditions. The results are summarized in Table 2.

By the reaction of untreated cellulose powder with living polyIBVE, no grafting onto the cellulose powder surface was observed. In addition, after the quenching of living polyIBVE cation with ammonical methanol, the polymer hardly reacted with Cellulose-NH_2. On the contrary, polyIBVE was found to be grafted onto the cellulose powder surface by the reaction of the living polyIBVE with Cellulose-NH_2. This indicated that living polyIBVE cation was successfully terminated with amino groups and polyIBVE with narrow molecular-weight distribution and well-defined molecular weight is grafted onto the surface with amino ester bonds as shown in Scheme 1, part (2).

Table II Grafting Reaction of Living PolyIBVE Cation with Cellulose-NH_2

Cellulose	Amino Group (mmol/g)	PolyIBVE	Grafting (%)	R^a (%)
Untreated	—	Living	trace	—
Cellulose-NH_2	0.086	Quenched	1.5	—
Cellulose-NH_2	0.086	Living	18.3	42.6

[a] Percentage of amino groups used for the grafting of polyMeOZO.

Cellulose, 0.10 g; polyMeOZO (Mn = 5.0 × 10^3; Mw/Mn = 1.10), 10.0 mL (8.0 × 10^{-2} mmol/L in toluene).

The percentage of amino groups used for the grafting reaction with living polyIBVE (R) was 42.6%. Although polyIBVE grafting is larger than polyMeOZO grafting, R for polyIBVE is smaller than that for polyMeOZO. This may be due to the fact that molecular weight of polyIBVE is larger than that of polyMeOZO, because effect of steric hindrance increases with increasing molecular weight.

Effect of Molecular Weight of Living PolyIBVE on the Grafting

The effect of molecular weight of living polyIBVE on the grafting reaction with Cellulose-NH_2 was examined. The results are shown in Figure 4. It is interesting to note that the percentage of grafting and the number of grafted chain (Gn) decreased with increasing molecular weight (Mn) of living polyIBVE. This may be due to surface amino groups of cellulose powder being shielded by neighboring grafted polymer chains. This effect on the grafting was enhanced with increasing molecular weight of the living polymer.

Effect of Amino Group Content of Cellulose-NH_2 on the Grafting of PolyIBVE

The effect of amino group content of Cellulose-NH_2 on the grafting of living polyIBVE was in-

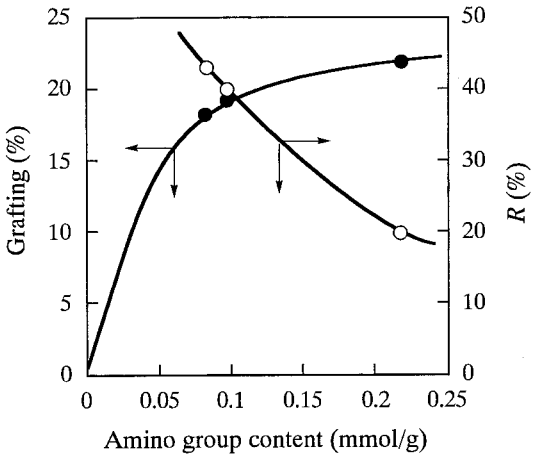


Figure 5 Effect of amino group content of Cellulose-NH_2 on the grafting of living polyIBVE onto the surface. Cellulose-NH_2, 0.10 g; polyIBVE ($Mn = 5.0 \times 10^3$, $Mw/Mn = 1.10$), 1.2 mmol in toluene; 25.0°C.

vestigated. The results are shown in Figure 5. The percentage of grafting of polyIBVE increased with increasing amino group content of Cellulose-NH_2 as well as grafting of polyMeOZO. The percentage of amino group used for the grafting site (R) was found to gradually decrease with increasing amino group content. This may be due to the fact that the percentage of amino groups shielded by neighboring grafted chains gradually increases with increasing the density of amino groups on Cellulose-NH_2 as mentioned above.

Figure 6 shows the relationship between logMn and logGn in the above grafting reaction. It was found that logGn is directly proportional to logMn. The same tendency was reported in the grafting reaction of reactive groups on carbon black surface with polymers having terminal functional groups.[23] From the results of Figure 6, K and α for the grafting reaction of polyIBVE were determined from the intercept and slope of the line, respectively.

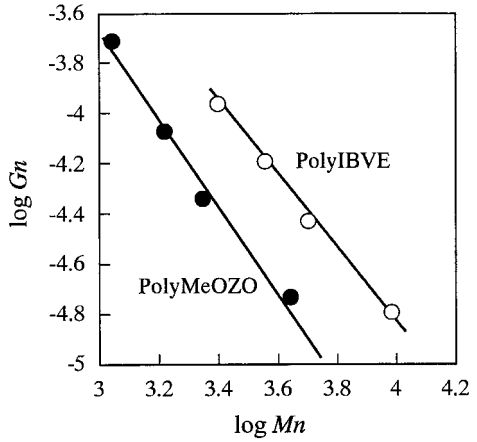


Figure 6 Relationship between logMn and logGn in the grafting reaction of living polymer cation with Cellulose-NH_2.

Table III Constants K and α of $Gn = K \times Mn^{\alpha}$ for the Grafting Reaction of Living Polymer with Cellulose-NH_2

Living Polymer	K	α
PolyMeOZO	26.9	−1.70
PolyIBVE	6.02	−1.40

Table 3 shows the values of K and α for the grafting reaction of living polyMeOZO and polyIBVE onto Cellulose-NH_2. It was found that the values of K and α for cellulose powder were larger than that for chitosan powder.[14] This may be due to the steric hindrance of living polymer cation with amino group on Cellulose-NH_2, which is larger than that on chitosan powder, because of the structural difference of amino groups.

Wettability of Polymer-Grafted Cellulose Powder

Figure 7 shows the penetrating rate of water through the column packed with untreated, polyMeOZO-grafted, polyIBVE-grafted cellulose powder. It was found that untreated cellulose powder surface showed considerable hydrophilic nature and the wettability scarcely changed by introduction of surface amino groups. The hydrophilic na-

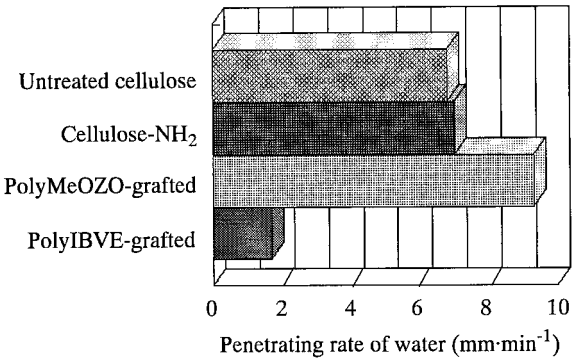


Figure 7 Penetrating rate of water through the column packed with polymer-grafted cellulose. PolyMeOZO and polyIBVE grafting are 9.8% and 18.3%, respectively.

ture of the cellulose surface increased by the surface grafting of hydrophilic polyMeOZO. On the contrary, by the grafting of hydrophobic polyIBVE, the wettability of cellulose powder surface turned from hydrophilic to hydrophobic. The results indicate that the wettability of cellulose powder surface is readily controlled by surface grafting of polymers.

CONCLUSIONS

1. PolyMeOZO and polyIBVE with controlled molecular weight and narrow molecular-weight distributions were readily grafted onto cellulose powder having amino groups. These were obtained by the termination of the corresponding living polymer cation with amino groups on the surface.
2. Mole number of polymer chains grafted onto cellulose powder decreased with increasing molecular weight of living polymer cation, because of steric hindrance of neighboring grafted polymer.
3. Wettability of cellulose powder surface was found to be controlled by the grafting of hydrophilic or hydrophobic polymer onto the surface.

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