

Grafting Reaction of Living Polymer Cations with Amino Groups on Chitosan Powder

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ABSTRACT: The grafting of polymers having controlled molecular weight and narrow molecular weight distribution onto chitosan powder by the termination of living polymer cation with amino groups on chitosan powder was investigated in heterogeneous system. The amino groups of chitosan powder successfully reacted with living poly(isobutyl vinyl ether) [poly(IBVE)] and poly(2-methyl-2-oxazoline) [poly(MeOZO)] cation with controlled molecular weight and narrow molecular weight distribution to give the corresponding polymer-grafted chitosan powders. The percentage of poly(MeOZO) grafting gradually increased and reached 24.5% after 4 days. The solubility of poly(MeOZO)-grafted chitosan in water increased with an increase in the amount of grafted polymer. It was suggested that grafting reaction of living polymer cation with chitosan powder proceeds from surface amino groups to inner amino groups of the powder with progress of the reaction. The mole number of grafted polymer chain on chitosan powder decreased with an increase in the molecular weight of the living polymer cation because the steric hindrance of functional groups of chitosan powder increased with the increasing molecular weight of living polymer. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1883–1889, 1998

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

INTRODUCTION

Chitin and chitosan are natural polymers that exist widely in nature and have been known as an ingredient of the shells of crustaceans since long ago. But only a few studies to use them effectively have been reported until recently. While chitin is insoluble in water and many commercial solvents, chitosan is readily soluble in various acidic solvents, such as formic acid and acetic acid. Recent studies have shown that chitosan can act as a thickener, stabilizer, and suspending agent in fab-

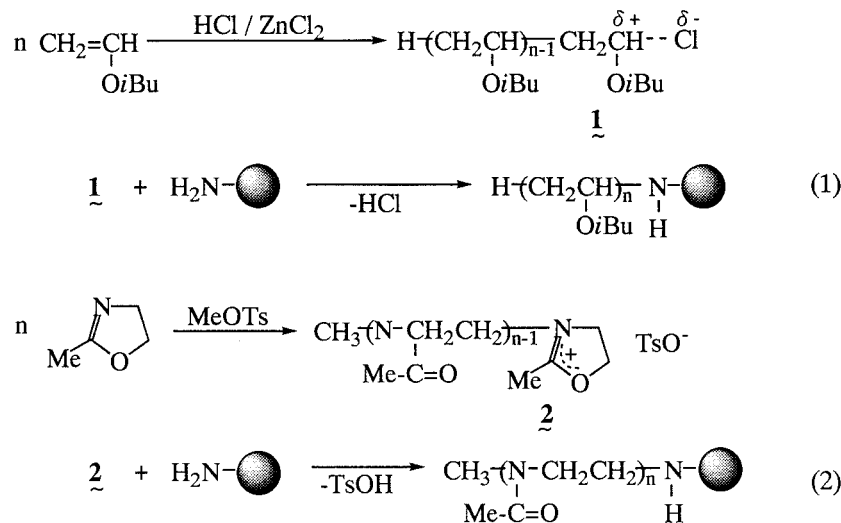
ricated foods and packaging materials and can form gels and films.¹ Hence, it also has applications in separation and purification processes.

Chemical modifications will open ways to various utilizations of this abundant natural polymer. Of possible modifications, graft copolymerization is anticipated to be quite promising for developing sophisticated functions; it would enable a wide variety of molecular designs to afford novel types of tailored hybrid materials composed of natural polysaccharides and synthetic polymers. The properties of the resulting graft copolymers may be widely controlled by the characteristics of the side chains, including molecular structure, length, and number.

Recent studies have shown graft copolymerization of 2-methyl-2-oxazoline (MeOZO) onto chitin

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Scheme 1 & 2

in solution,² graft copolymerization of methyl methacrylate onto mercapto-chitin,³ and the development of polyurethane-chitin powder composites.⁴

On the other hand, in order to modify the surface properties of inorganic powders and pigments, polymer grafting is known to be one of the effective methods. Polymer-grafted powders can be dispersed easily in organic solvents, resins, and rubbers. For example, we reported the grafting of various polymers onto inorganic powder surfaces, such as ultrafine silica and carbon black, by the polymerization initiated by initiating groups previously introduced onto the surfaces.⁵⁻⁷

Recently, we reported the grafting of polymers with controlled molecular weight and narrow molecular weight distribution onto ultrafine silica⁸ and carbon black⁹ by the reaction of living polymer cation with amino groups introduced onto the surfaces.

In the present article, to modify the chitosan powder in heterogeneous system, the grafting of polymers onto the chitosan powder by the termination of living polymer cations with amino groups of chitosan (Schemes 1 and 2) was investigated. The effects of molecular weight of living polymers on the grafting onto chitosan powder and solubility of polymer-grafted chitosan in several solvents are also discussed.

EXPERIMENTAL

Chitosan

Chitosan was obtained from Tokyo Kasei Kogyo Co., Ltd., Japan, and used without further purifi-

cation. The preparation of chitosan powder was achieved by reprecipitation by adding alkali solution into HCl solution of chitosan.¹⁰ A typical example is as follows. Into a 500-mL flask, 3.0 g of chitosan and 300 mL of ion-exchange water were charged. Then the chitosan was dissolved by adding 30.0 mL of 0.5N HCl into the mixture under stirring with a magnetic stirrer. Insoluble materials were removed by filtration through a sintered glass filter, and pH of the filtrate was brought to about 5 by the dropwise addition of 10N NaOH under vigorous stirring. Finally, the pH was adjusted to 9 by the addition of 0.1N NaOH. The chitosan powder was precipitated by centrifugation at 5.0×10^3 rpm. The precipitate obtained was dispersed in ion-exchange water, and the dispersion was allowed to centrifuge at 5.0×10^3 rpm. The chitosan precipitated was dispersed again in ion-exchange water and centrifuged. The procedures were repeated until supernatant solution became free from alkali. Washed chitosan was resuspended in acetonitrile and dried *in vacuo* at room temperature.

Monomer and Reagents

Isobutyl vinyl ether (IBVE) was washed with 5% alkaline aqueous solution and water, dried over potassium hydroxide, refluxed over sodium, and distilled just before use. MeOZO obtained from Aldrich Chemical Co. was dried over calcium hydride and distilled just before use.

Hydrogen chloride (anhydrous, 1.0M solution in diethylether) and zinc chloride (1.0M solution in diethylether) were obtained from Aldrich

Chemical Co., which were diluted with toluene (10.0 mmol L^{-1}) (0.20 mol L^{-1}) and stored in ampules at -30°C . Methyl *p*-toluenesulfonate (MeOTs) was obtained from Tokyo Kasei Kogyo Co., Ltd., and used without further purification.

Toluene was washed with concentrated sulfuric acid, alkaline aqueous solution, and pure water; dried over calcium chloride; refluxed over sodium; and distilled. Acetonitrile was dried over calcium hydride, distilled over diphosphorous pentoxide, and distilled over calcium hydride.

Living Cationic Polymerization of IBVE and MeOZO

The preparation of living poly(IBVE) cation was carried out by the cationic polymerization of IBVE using HCl/ZnCl₂ initiating system according to the method of Higashimura and Sawamoto and coworkers.^{11,12} 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 ZnCl₂ solution into 8.0 mL of IBVE solution (0.50 mol L^{-1} in toluene) containing 1.0 mL of HCl solution. The polymerization was conducted at 0°C , and the conversion, which was determined from residual IBVE concentration by gas chromatography, reached 100% after 1 h.

The living poly(MeOZO) cation was prepared by the cationic ring-opening polymerization of MeOZO by the use of MeOTs as an initiator according to the method of Saegusa et al.^{13,14} Into a 100-mL flask, equipped with a three-way stopcock, containing 120 mmol of MeOZO and 15.0 mL of acetonitrile, 6.6 mmol of MeOTs were added via a syringe. The polymerization was conducted at 80°C for 20 h under dry nitrogen and, at that time, the conversion was 100%.

Quenching of the Living Polymer Cation

The quenching of living poly(IBVE) and poly(MeOZO) cation was achieved by the addition of 5.0 mL of 10% ammoniacal methanol after 1 and 4 h, respectively, at which the conversions of IBVE and MeOZO were 100%.⁸

Reaction of Chitosan Powder with Living Polymer Cation

Into a 100-mL flask containing 0.10 g of chitosan powder, 10.0 mL toluene solution ($8.0 \times 10^{-5} \text{ mol L}^{-1}$) of living poly(IBVE) cation were added in a

glove box under dry nitrogen. The flask was sealed, and the mixture was stirred with a magnetic stirrer at 0°C . After a fixed time, the reaction was terminated by the addition of methanol. For the grafting reaction of poly(MeOZO) cation, 26.0 mL of polymer solution (0.25 mol L^{-1} in acetonitrile) were allowed to react with 0.10 g of chitosan powder.

Percentage of Grafting

The chitosan powder obtained from the above reactions was dispersed in a good solvent for polymer [THF for poly(IBVE) and methanol for poly(MeOZO)], and the system was centrifuged at $5.0 \times 10^3 \text{ rpm}$. The precipitated chitosan powder was dispersed in THF or methanol and centrifuged again. These procedures were repeated several times. Then ungrafted polymer was extracted with a good solvent of polymer using a Soxhlet apparatus until no more polymer could be extracted in the solvent. After the above procedure, the polymer-grafted chitosan powder was dried *in vacuo* at 50°C and weighed. The percentage of grafting was

$$\text{Grafting (\%)} = \frac{\text{Polymer grafted (g)}}{\text{Chitosan powder used (g)}} \times 100$$

The amount of polymer grafted onto the chitosan was determined from the difference in weight of chitosan powder before and after the reaction.

Determination of Infrared Spectrum

The infrared (IR) spectrum of polymer-grafted chitosan powder was recorded on a Hitachi Infrared Spectrophotometer Model 270-30 using a KBr pellet.

Determination of Molecular Weight

The molecular weight and molecular weight distribution of poly(IBVE) and poly(MeOZO) were determined by gel permeation chromatography (GPC) using a polystyrene standard. For GPC measurements, CCPD instrument (TOSOH) equipped with a polystyrene gel column (TSK-GEL G3000HHR) was used.

Solubility of Polymer-Grafted Chitosan

Polymer-grafted chitosan was dispersed in 15 mL of solvent and allowed to stand at room tempera-

Table I Grafting Reaction of Living Poly(IBVE) Cations with Chitosan Powder at Room Temperature

Polymer	Reaction	$\overline{M}_n \times 10^{-3}$	Grafting (%)
Poly(IBVE) ^a	Quenched	5.0	4.2
Poly(IBVE) ^a	Living	5.0	44.0
Poly(MeOZO) ^b	Quenched	2.2	0.5
Poly(MeOZO) ^b	Living	2.2	24.5

^a Chitosan, 0.10 g; poly(IBVE), 1.2 mmol.

^b Chitosan, 0.10 g; poly(MeOZO), 5.0 mmol.

ture. After a definite time, insoluble materials were removed by filtration through a sintered glass filter and dried *in vacuo* at 50°C and weighed.

Determination of Viscosity

The viscosity of soluble part of poly(MeOZO)-grafted chitosan in water was determined by a rotation viscometer. For viscometer, a Tokyo Keiki BL-type viscometer was used.

RESULTS AND DISCUSSION

Grafting of Living Polymer Cations with Chitosan Powder

The preparation of end-capped poly(IBVE) has been conducted by the reaction of living poly(IBVE) cation with nucleophiles.¹⁵⁻¹⁷ As mentioned above, chitosan powder has primary amino groups. Therefore, the grafting of poly(IBVE) onto chitosan powder by the termination of the living polymer cation with amino groups on chitosan powder was investigated in heterogeneous system. The preparation of chitosan powder was achieved by reprecipitation according to the method of Yabuki et al.¹⁰

Living poly(IBVE) was generated by using HCl-ZnCl₂ initiator system in toluene according to the method of Higashimura and Sawamoto and coworkers.^{11,12} The molecular weight distribution of this living polymer was very narrow ($M_w/M_n = 1.10$), and the number-average molecular weight (M_n) agreed with the theoretical value.

The grafting reaction of living poly(IBVE) cation ($M_n = 5.0 \times 10^3$) with chitosan powder was carried out at room temperature under several conditions. The results are summarized in Table I.

Living poly(IBVE) was found to be grafted easily onto the chitosan powder by the termination of living polymer cation with amino groups of chitosan. On the contrary, the polymer scarcely reacted with chitosan powder after quenching with ammoniacal methanol. A small amount of quenched polymer remained on chitosan powder even after extraction with a good solvent for polymer. This may be due to physical adsorption of polymer by chitosan powder.

In addition, the living poly(MeOZO) cation is also very sensitive to nucleophiles, such as amines.¹⁸ Therefore, the grafting of poly(MeOZO) cations onto chitosan powder was investigated. Living poly(MeOZO) was prepared by the cationic ring-opening polymerization of MeOZO using MeOTs as a catalyst.^{13,14} The molecular weight distribution of the living polymer was also very narrow ($M_w/M_n = 1.10$), and the number-average molecular weight (M_n) agreed with the theoretical value.

The grafting reaction of living poly(MeOZO) cation ($M_n = 2.2 \times 10^3$) with chitosan powder was carried out at room temperature under several conditions. The results are also shown in Table I. As shown in Table I, poly(MeOZO) was also grafted onto the chitosan powder by the termination of the corresponding living polymer cation with amino groups of chitosan.

Based on the above results, it is concluded that the living poly(IBVE) and living poly(MeOZO) cations successfully reacted with surface amino groups of chitosan powder and poly(IBVE) or poly(MeOZO) with narrow molecular weight distribution and well-defined molecular weight was grafted onto the chitosan powder as shown in Schemes 1 and 2.

IR Spectra of Polymer-Grafted Chitosan Powder

Figure 1 shows IR spectra of untreated chitosan powder and poly(MeOZO)-grafted chitosan powder obtained from the above grafting reaction. IR spectrum of poly(MeOZO)-grafted chitosan powder shows new absorptions at 570, 686, 818, 1010, 1034, and 1124 cm⁻¹, which are characteristic of poly(MeOZO). Based on the above results, it is concluded that living poly(MeOZO) cations can be successfully reacted with amino groups of chitosan powder.

Effect of Reaction Time on the Grafting

Figures 2 and 3 show the relationship between percentage of grafting onto chitosan powder and

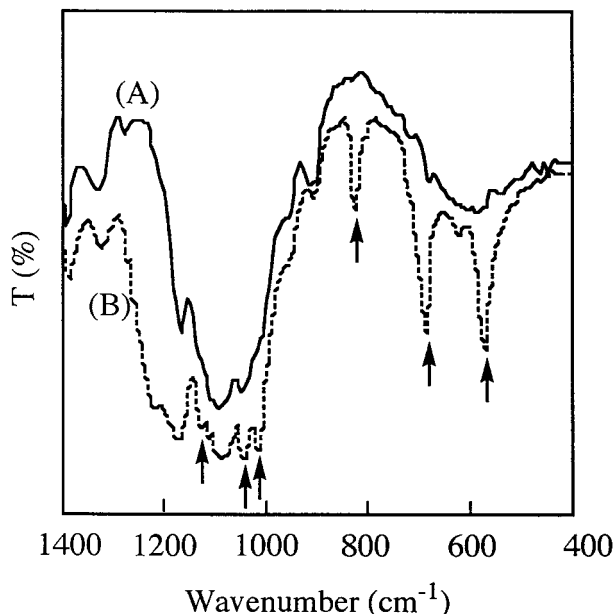


Figure 1 IR spectra of (A) untreated and (B) poly(MeOZO)-grafted chitosan.

reaction time in the grafting of poly(IBVE) and poly(MeOZO), respectively. As shown in Figures 2 and 3, the reaction rate was very small. The percentage of grafting increased with progress of the reaction and reached a constant value after 4 days. This may be due to the fact that the reaction

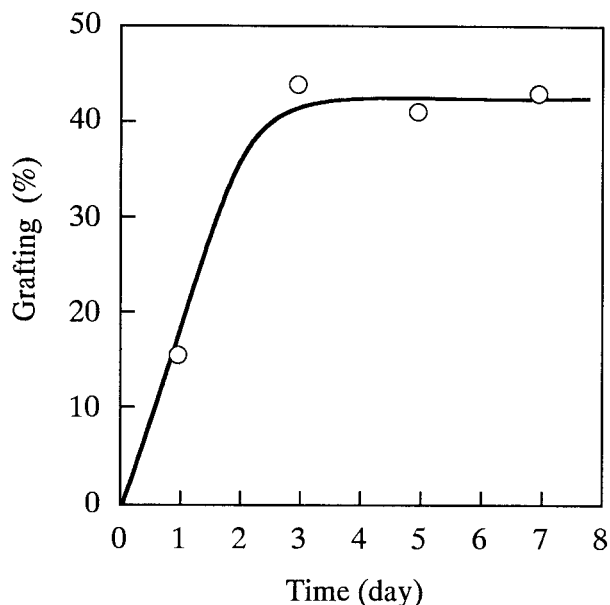


Figure 2 Effects of reaction time on the grafting of the poly(IBVE) onto chitosan: chitosan, 0.10 g; living poly(IBVE) cation (8.0×10^{-5} mol L⁻¹ in toluene), 10.0 mL; 0°C.

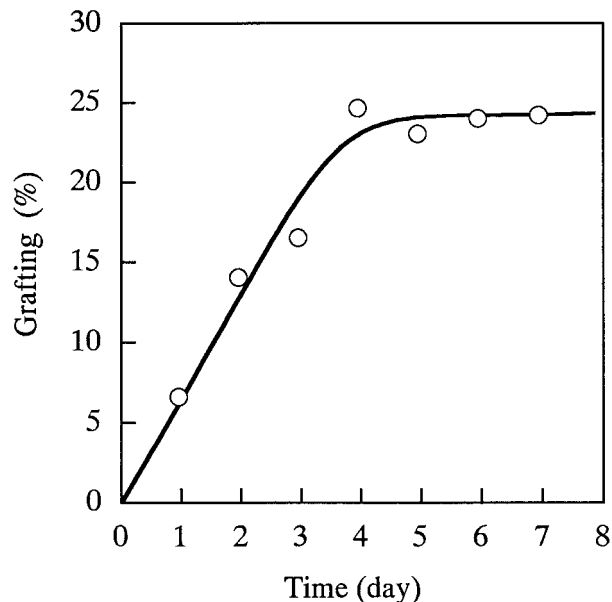


Figure 3 Effects of reaction time on the grafting of the poly(MeOZO) onto chitosan: chitosan, 0.10 g; living poly(MeOZO) cation (0.25 mol L⁻¹ in acetonitrile), 26.0 mL; 80°C.

of polymers with amino groups of chitosan powder proceeded from surface to the inner part with progress of the grafting reaction because the crystalline structure of chitosan is gradually broken by the grafting of polymer.

Effect of Molecular Weight of Living Polymer on the Grafting

The effect of molecular weight of living poly(IBVE) cation on the grafting reaction with chitosan powder was examined. The results are shown in Figure 4.

The percentage of grafting increased with increasing molecular weight of living poly(IBVE), but the mole number of grafted poly(IBVE) chain decreased with increasing molecular weight. The same tendency was observed in the grafting reaction of surface reactive groups on the carbon black with amino- or hydroxyl-terminated functional polymers¹⁹⁻²² and in the grafting by the reaction of living polymer cation with nucleophilic groups on silica and carbon black surfaces.^{8,9}

Furthermore, the effect of molecular weight of living poly(MeOZO) on the grafting reaction with chitosan powder was also investigated (Fig. 5). As with poly(IBVE) grafting onto chitosan, the percentage of poly(MeOZO) grafting onto chito-

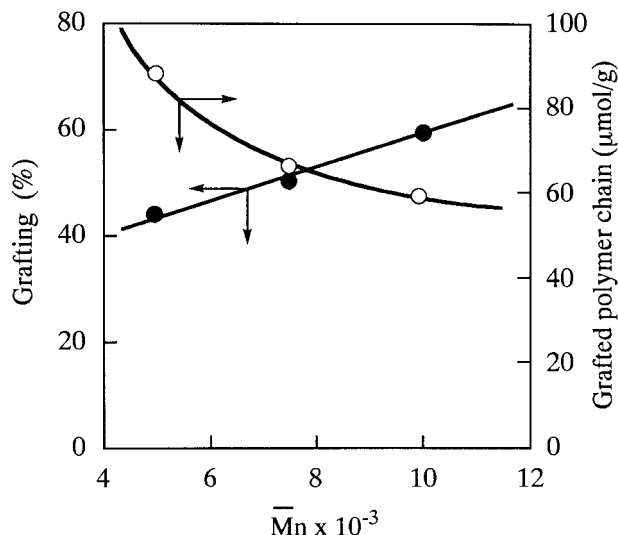


Figure 4 Effects of molecular weight of living poly-(IBVE) cation on grafting onto chitosan: chitosan, 0.10 g; living poly-(IBVE) cation ($8.0 \times 10^{-5} \text{ mol L}^{-1}$ in toluene), 10.0 mL; 0°C ; 1 h.

san powder decreased with increasing molecular weight of living poly(MeOZO) cation.

This may be due to amino groups of chitosan powder being shielded by neighboring grafted polymer chains. This effect was enhanced with an increase of molecular weights of the living polymers.

Solubility of Polymer-Grafted Chitosan Powder

Solubility of poly(IBVE)-grafted and poly-(MeOZO)-grafted chitosan powder in several sol-

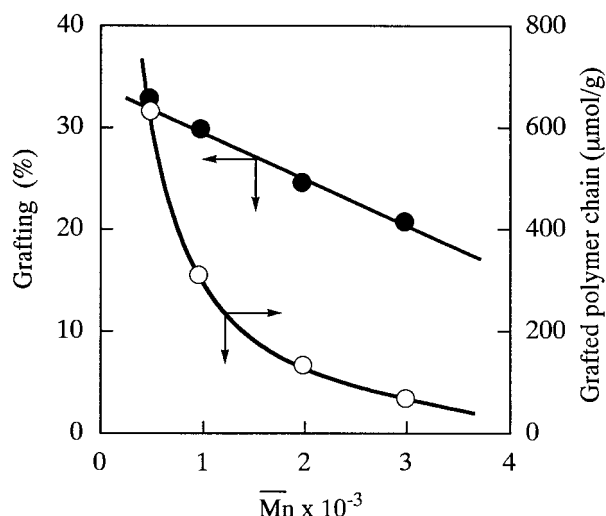


Figure 5 Effects of molecular weight of living poly-(MeOZO) cation on grafting onto chitosan: chitosan, 0.10 g; living poly-(MeOZO) cation (0.25 mol L^{-1} in acetonitrile), 26.0 mL; 80°C ; 10 h.

Table II Solubility of Chitosan, Poly(MeOZO)-grafted Chitosan, and Poly(IVBE)-Grafted Chitosan at Room Temperature

Solvent	Chitosan	Poly(MeOZO)-Grafted Chitosan ^a	Poly(IVBE)-Grafted Chitosan ^b
MeOH	×	×	×
CH ₃ CN	×	×	×
CHCl ₃	×	×	×
THF	×	×	×
H ₂ O	×	○	×

○, soluble; ×, insoluble.

^a Grafting, 24.5%.

^b Grafting, 44.0%.

vents was compared with that of untreated chitosan powder. The results are shown in Table II. Although, untreated and poly-(IBVE)-grafted chitosan powder was insoluble in all solvents, poly-(MeOZO)-grafted chitosan powder (grafting = 24.5%) was soluble in water, and no insoluble part was observed.

Table III shows the effect of the percentage of grafting on the solubility of poly-(MeOZO)-grafted chitosan powder in water. As shown in Table III, the soluble part of poly-(MeOZO)-grafted chitosan powder in water increased with an increasing percentage of grafting. The water-soluble part of the chitosan powder was confirmed to be poly-(MeOZO)-grafted chitosan powder by IR spectra. On the other hand, the insoluble part in water was ungrafted chitosan.

These results indicate that grafting reaction of living polymer cation with chitosan powder proceeds from surface amino groups to inner amino groups of powder with progress of the grafting reaction.

Table III Effect of the Percentage of Grafting on the Solubility and Viscosity of Poly(MeOZO)-Grafted Chitosan

Grafting (%)	Soluble Part (%)	Insoluble (%)	Viscosity (mPa s^{-1}) ^a
0	0.0	100.0	—
5.3	9.7	90.3	20.4
9.8	49.8	50.2	55.1
12.9	72.2	27.8	100.5
14.4	100.0	0.0	191.8
24.5	100.0	0.0	234.6

^a Aqueous solution, 0.2 wt %; 25°C .

The viscosity of soluble part of poly(MeOZO)-grafted chitosan in water are also shown in Table III. The viscosity was found to have increased with the increasing percentage of grafting.

CONCLUSIONS

1. Poly(IBVE) and poly(MeOZO) with controlled molecular weight and narrow molecular weight distribution were readily grafted onto chitosan powder in heterogeneous system by the reaction of the corresponding living polymer cation with amino groups of chitosan.
2. The mole number of grafted polymer chains decreased with the increasing molecular weight of the living polymer cation.
3. By grafting of poly(MeOZO) onto chitosan, the chitosan became soluble in water.

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