

Graft Copolymerization of Acrylamide onto Konjac Glucomannan via Inverse Emulsion Polymerization and Its Thickening Properties

Dating Tian,¹ Hong-Quan Xie²

¹School of Chemical and Environmental Engineering, Hubei Institute for Nationalities, Enshi 44500, People's Republic of China

²Department of Chemistry, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China

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ABSTRACT: The graft copolymerization of acrylamide onto konjac glucomannan (KGM) was studied with inverse emulsion polymerization to obtain an effective thickener. The effects of the initiator concentration, emulsifier concentration, comonomer concentration, reaction temperature, and reaction time on the graft copolymerization were investigated. The results showed that the polymerization system retained good stability, and the graft efficiency of

the graft copolymerization was almost 95% under optimum conditions. Moreover, both the water solubility and thickening properties of the KGM were improved evidently by grafting with polyacrylamide. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3122–3127, 2008

Key words: biopolymers; graft copolymers; polysaccharides

INTRODUCTION

As important biological polymers, polysaccharides play unique roles in the evolutionary process of living things and have attracted much interest by researchers from chemistry, physics, biology, and medicine during the past decade.^{1–8} Konjac glucomannan (KGM) is a kind of polysaccharide containing β -1,4-glucoside linkages of β -D-glucose and β -D-mannose in a molar ratio of approximately 2 : 3. Because of its many functional properties, such as absorption, water retentivity, film formation, thickening, and gelation, it has been applied extensively in food, medicine, chemical engineering, agriculture, oil, textiles, and other related fields. KGM is a kind of good natural thickener that can be used in the textile industry for its good water retentivity. However, because KGM has bad properties, such as a low solubility, bad stability of hydrosol, and lazy flow, the utilization of KGM as a kind of auxiliary additive (i.e., thickener) in printing and dyeing in the textile

industry has many restrictions. The grafting polymerization of water-soluble commoners such as acrylamide (AM) onto KGM is a good way to improve its thickening properties. However, there have been two crippling problems in this research.^{9,10} On the one hand, the use of cerium(IV) salt as initiator during the graft copolymerization may lead to too high of a cost for this method to be extensively applied in industry. On the other hand, the traditional graft copolymerization of KGM, which is carried out by aqueous solution polymerization, shows low solid levels of polymer because the KGM exhibits a very high viscosity (η) in the aqueous solution, and the products must be treated by complicated posttreatment, such as settling, drying, and shivering.⁹ Moreover, those products are powders, which are not convenient for use in latex paint systems.

As is well known, an inverse emulsion polymerization system can retain good stability and high solid levels of polymers and a low η and quick rate of dispersion.^{11,12} However, there is no report on the graft copolymerization of KGM with vinyl monomers via inverse emulsion polymerization. This study dealt with the graft copolymerization of KGM–AM by inverse emulsion polymerization with azobisisobutyronitrile (AIBN) as an initiator, followed by azeotropic distillation to obtain a water in oil (W/O) type latex which could be directly used in latex paint systems, as well as a study of its thickening properties.

Correspondence to: D. Tian (tiandating@163.com).

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EXPERIMENTAL

Materials

Konjac glucomannan (KGM), supplied by Hongye KGM Co. (Enshi, People's Republic of China) was purified with ethanol and then dried under reduced pressure until it reached a constant weight. AM (Chemically Pure, Shanghai Chemical Reagent Co., Shanghai, China) was recrystallized with benzene before use. Span 80 (sorbitan monooleate) was a laboratory reagent. Other reagents were chemically pure and were used as received without further treatment.

Inverse emulsion polymerization

An oil phase containing paraffin oil (20 mL) as a high-boiling-point solvent and xylene (120 mL) as a low-boiling-point solvent, Span 80 (9 g) as an emulsifier, and AIBN (0.37 g) as an initiator were added to a reactor containing a stirrer, an oil/water separator, a condenser tube, and a thermometer. An aqueous solution (100 mL) of KGM (25 g) mixed with AM (26.65 g) was added to the oil phase. After emulsification with stirring at a speed of 800–1000 rpm for 20–30 min, polymerization was initiated by heating in a N₂ atmosphere with stirring at speed of 200–300 rpm. Polymerization was carried out at a certain temperature for several hours, followed by azeotropic distillation under a reduced pressure to remove water and xylene, and, thus, the thickener product of a W/O type latex was obtained.

Evaluation of the graft efficiency (GE) and content of polyacrylamide (PAM) in the graft copolymers

The products obtained were precipitated out with alcohol and washed with acetone and then dried *in vacuo* at 50–60°C for 2 days. The weighed solid particles were extracted with a mixture of glycol and glacial acetic acid (volume ratio = 6 : 4)^{11,13} in a Soxhlet extractor for 30 h to remove the homopolymers. The extract was precipitated out with methanol, washed with alcohol, and then dried *in vacuo* for 24 h, followed by accurate weighing to obtain the weight of homopolymers in the graft polymers.

The total amount of PAM in the graft copolymers was determined by the following sequence: 2 g of graft copolymers were refluxed with 200 mL of a 1 mol/L H₂SO₄ solution for 2 h to remove the KGM, filtered, washed with alcohol, dried under a reduced pressure for 24 h, and then weighed accurately.

GE was calculated with the following equation:

$$\text{GE (\%)} = \frac{w_1 - w_0}{w_1} \times 100\%$$

where w_0 is the weight of the homopolymers in the graft copolymers and w_1 is the total weight of PAM in the graft copolymers.

The weight percentage of PAM in the graft copolymers (ω_{PAM}) was calculated with the following equation:

$$\omega_{\text{PAM}} = \frac{w_1 - w_0}{w_2} \times 100\%$$

where w_2 is the weight of the graft copolymers.

η and viscosity index (VI)¹⁴

η of the thickener was determined by a NDJ-1 rotating viscometer (Shanghai, China) with a rotating speed of 6 rpm after the polymer dispersion containing about 50% polymer was dispersed by stirring in water to make a 1.0% solution.

The thixotropic properties of the thickener were characterized by VI, which was defined as the ratio of the viscosity at a rotation speed of 60 rpm (η_{60}) and the viscosity at a rotation speed of 6 rpm (η_6), as shown in the following equation:

$$\text{VI} = \frac{\eta_{60}}{\eta_6}$$

Preserved η (%)¹⁴

The electrolytic resistance of the thickener was determined by the measurement of the η of a 1% dispersion in water after the addition of NaCl to make a 0.05% NaCl concentration at rotation speed of 6 rpm. Preservation of η against electrolyte was calculated as follows:

$$\begin{aligned} \text{Preserved } \eta (\%) &= \frac{\eta \text{ of 1\% dispersion containing NaCl}}{\eta \text{ of 1\% dispersion}} \times 100\% \end{aligned}$$

IR analysis

IR spectra of the sample were taken by Avatar 370 of Thermo Nicolet at wave numbers from 4000 to 400 cm⁻¹ with the KBr disc method.

RESULTS AND DISCUSSION

Effect of the amount of initiator on the graft copolymerization

Figure 1 shows the influence of the content of AIBN based on the oil phase as the initiator on the graft copolymerization when other reaction conditions were fixed. With increasing amount of AIBN, GE exhibited a maximum value at 1.5 mmol/L. This phenomenon may be attributed to the following reason: On the one hand, with the increase in initiator concentration, the number of free radicals generated in the system increased greatly, which favored the graft copolymerization and led to an increasing GE.

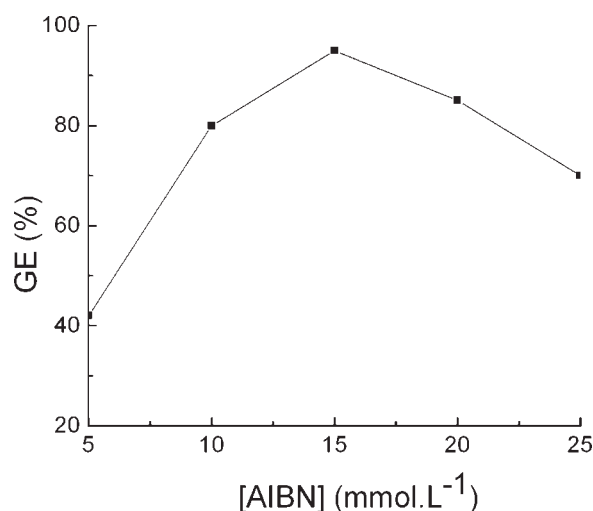


Figure 1 Effect of the amount of initiator on the graft copolymerization ($\omega_{\text{Span 80}} = 6 \text{ wt } \%$, $[\text{AM}] = 1.5 \text{ mol/L}$, temperature = 60°C , time = 4 h, oil/water volume ratio = 1.5 : 1).

On the other hand, when the initiator concentration was too high, the large amount of AIBN in the system produced excess radicals, and the homopolymerization of AM occurred, which resulted in a decrease in GE.

Effect of the amount of emulsifier used on the graft copolymerization

The emulsifier used in the inverse emulsion polymerization was Span 80, a surfactant of W/O type. Figure 2 indicates the dependence of weight percentage of Span 80 ($\omega_{\text{Span 80}}$) (w/w based on the oil phase) on GE. GE values rose rapidly and reached an optimum value and then decreased slightly. As is well known, in inverse polymerization, the water phase forms an interior phase, and the oil phase forms an external phase. The polymerization occurs in the W/O type micelles. When the amount of emulsifier used is too low, the polymerization system is not stable, and demulsification occurs easily. As the amount of Span 80 increased, the number of micelles grew rapidly, which greatly increased GE. However, when the amount of Span 80 reached a certain value, the number of micelles did not increase and instead became constant. Moreover, the chance of occurring chain-transfer reactions increased accordingly because Span 80 contained many active types of hydrogen. Thus, the GE values reached a maximum and then decreased slightly.

Effect of the oil/water volume ratio on the graft copolymerization

The influence of the oil/water volume ratio on the graft copolymerization was studied. As shown in

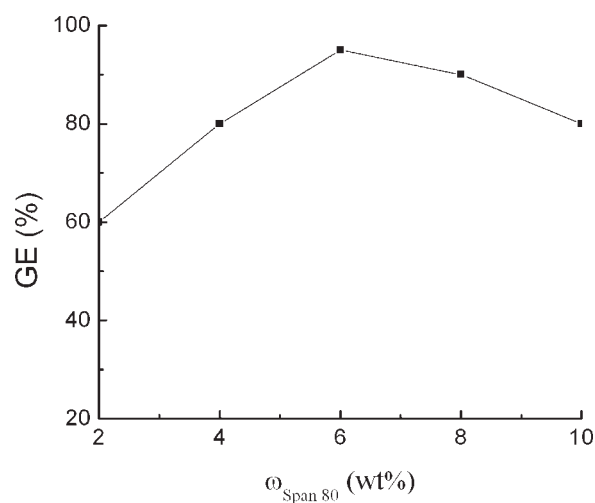


Figure 2 Effect of the amount of emulsifier used on the graft copolymerization ($[\text{AIBN}] = 15 \text{ mmol/L}$, $[\text{AM}] = 1.5 \text{ mol/L}$, temperature = 60°C , time = 4 h, oil/water volume ratio = 1.5 : 1).

Figure 3, GE exhibited a maximum value at 1.5 : 1. In the inverse emulsion polymerization, oil was continuous phase, which played the role of a dispersing water phase and carried off heat. When the oil content was low, the aqueous particles were comparatively larger, and the surface area of contact between the initiator in the oil phase and the monomer and KGM in the aqueous phase was small. When the oil content became comparatively high, the heat of polymerization could be easily eliminated, and the surface area of contact between AIBN and AM and KGM became larger. Thus, GE increased when the oil/water volume ratio increased from 1.0 to 1.5. However, when excess oil was used, the aqueous droplets dispersed in the oil phase were quite small,

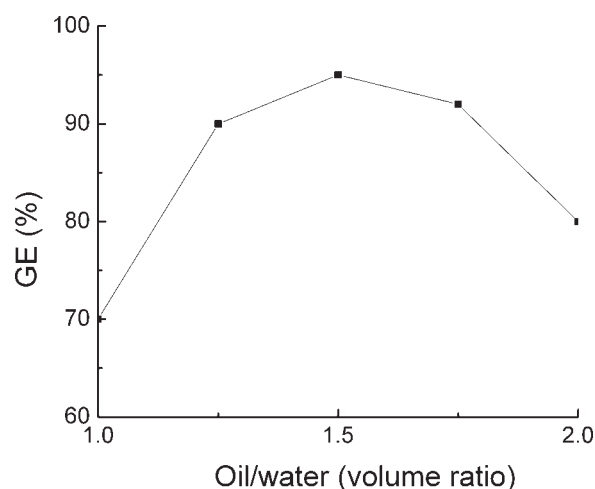


Figure 3 Effect of the oil/water volume ratio on the graft copolymerization ($[\text{AIBN}] = 15 \text{ mmol/L}$, $\omega_{\text{Span 80}} = 6 \text{ wt } \%$, $[\text{AM}] = 1.5 \text{ mol/L}$, temperature = 60°C , time = 4 h).

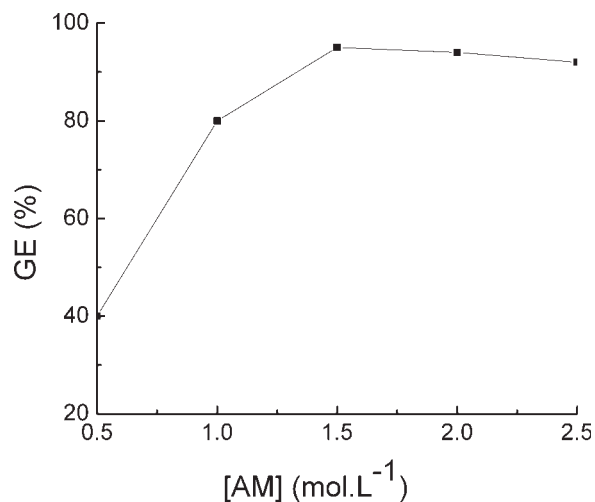


Figure 4 Effect of the concentration of AM on the graft copolymerization ([AIBN] = 15 mmol/L, $\omega_{\text{Span 80}}$ = 6 wt %, temperature = 60°C, time = 4 h, oil/water volume ratio = 1.5 : 1).

which may have caused a low GE because too much surface area may have enhanced the homopolymerization of AM, which thus lowered GE. Therefore, the optimum oil/water volume ratio in this system was 1.5 : 1.

Effect of the amount of AM on the graft copolymerization

Figure 4 shows the influence of AM content (on the basis of total volume) on the graft copolymerization. When [AM] was less than 1.5 mol/L, GE increased quickly with increasing [AM]. However, when [AM] was higher than 1.5 mol/L, GE decreased slowly. Of course, in the range of a certain content, increasing the concentration of monomers increased the number of monomer molecules initiated by each radical, and GE increased rapidly. However, when the concentration of monomer reached a certain extent, the homopolymerization competing with the graft copolymerization probably increased, so GE did not increase any more and tended to level off.

Effect of the reaction temperature on the graft copolymerization

Figure 5 shows the effect of the reaction temperature on the graft copolymerization. GE exhibited a maximum value at 60°C. On the one hand, with increasing temperature, the radical formation rate increased, and the rate of chain propagation also increased. The increase in GE may have been due to the increase of KGM free volume, which caused the exposure of active points and the shifting of molecule segments. As temperature increased above 60°C, the decrease in GE may have been due to the

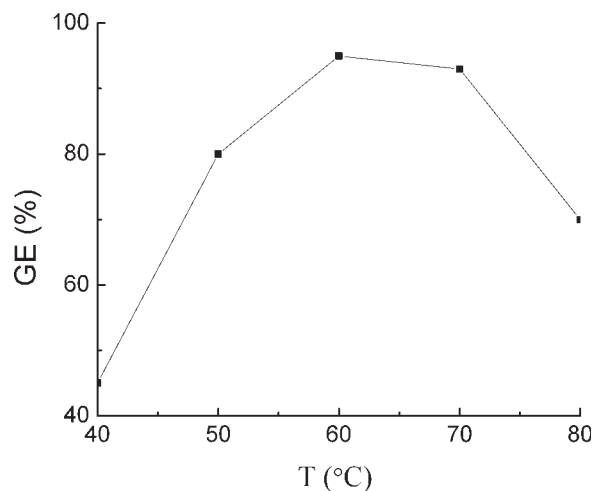


Figure 5 Effect of the reaction temperature (T) on the graft copolymerization ([AIBN] = 15 mmol/L, $\omega_{\text{Span 80}}$ = 6 wt %, [AM] = 1.5 mol/L, time = 4 h, oil/water volume ratio = 1.5 : 1).

increase of termination reactions and side reaction rates.

Effect of the reaction time on the graft copolymerization

Reaction time played a significant role in GE, as shown in Figure 6. GE exhibited a maximum value at 4 h. At the beginning of the reaction, the rate of reaction increased when the amount of AM was high. So GE increased with increasing reaction times. However, with too long a reaction time, the amounts of both AM and radicals decreased, and moreover, side reactions, such as the hydrolysis of KGM, might have occurred, which decreased GE.

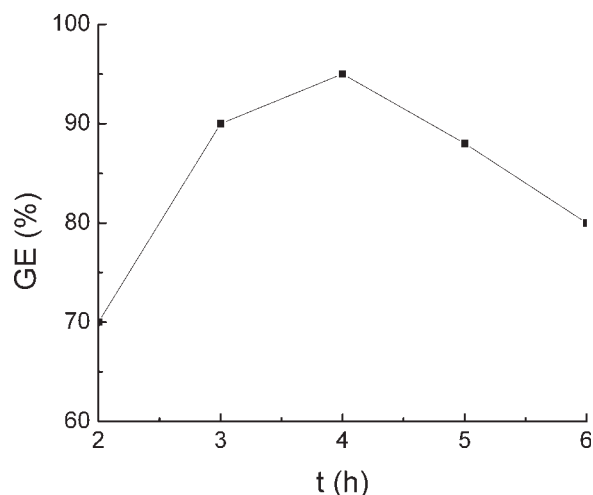


Figure 6 Effect of the reaction time (t) on the graft copolymerization ([AIBN] = 15 mmol/L, $\omega_{\text{Span 80}}$ = 6 wt %, [AM] = 1.5 mol/L, temperature = 60°C, oil/water volume ratio = 1.5 : 1).

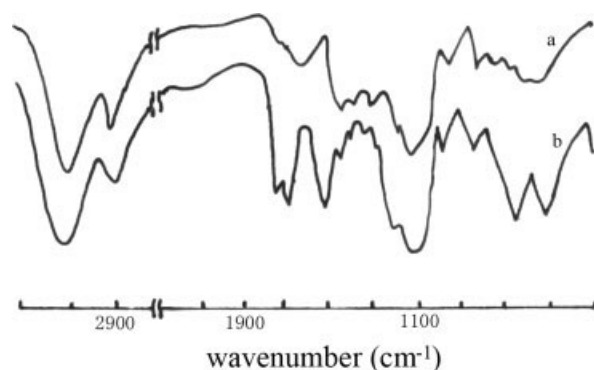


Figure 7 FTIR analyses of the samples: (a) KGM and (b) KGM-g-PAM.

Fourier transform infrared (FTIR) analyses of the samples

Figure 7 shows the FTIR spectra of KGM-g-PAM and KGM. The results show that KGM-g-PAM exhibited two stretching absorption peaks at 1670 and 1640 cm^{-1} , which are two characteristic absorption peaks of $-\text{CO}-\text{NH}_2-$ (the former is the stretching vibration peak of $-\text{CO}$, and the latter is the deformation vibration absorption peak of $-\text{NH}_2$). Those bands were not present in the KGM spectrum, which confirmed that AM was grafted onto KGM.

Effect of PAM in the graft copolymers on the water solubility and thickening properties

Although KGM is a type of natural thickener, it shows bad water solubility and cannot be used as a thickener directly. However, both the water solubility and thickening properties were greatly improved with increasing content of PAM in the products, as shown in Table I. The hydrophilicity of the polymers increased with the introduction of water-soluble monomers such as AM into the polymer chains. The increase in solution η resulted from the extension of the polymer chain because more free water could easily enter into the segments; thus, the thickening properties were improved.

Meanwhile, VI, which reflected the thixotropic properties of the thickener, exhibited a decreasing tendency. This implied that the thixotropic proper-

TABLE I
Effect of ω_{PAM} on the Water Solubility and Thickening Properties of the Graft Copolymer

ω_{PAM}	$\eta \times 10^{-4}$ (mPa s)	VI	Preserved η (%)	Water solubility
0	4.4	0.35	97.0	Partially soluble
18.4	5.5	0.30	97.0	Partially soluble
35.2	6.8	0.27	97.0	Soluble
41.0	8.8	0.20	95.0	Easily dissolved
46.0	9.0	0.18	94.2	Easily dissolved

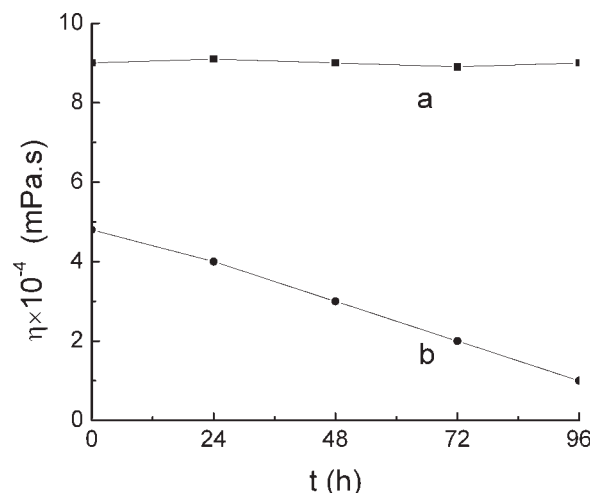


Figure 8 Effect of the storage time (t) on the change in the aqueous η of (a) KGM-g-PAM and (b) KGM.

ties were closely related to the thickening properties. Usually, the better a thickener is, the lower VI is, or the better the thixotropic properties are. This fact has a positive significance on the practical application.

However, the preserved η to the initial η against 0.05% NaCl changed little. This fact indicated that the grafting monomer used in this system was a kind of nonionic monomer and was not sensitive to electrolyte. Therefore, the products had good electrolyte resistance.

Effect of the storage time on the change in the aqueous η values of KGM and KGM-g-PAM

Figure 8 shows the effect of storage time on the change in the aqueous η values of KGM and KGM-g-PAM. The η of KGM hydrosol exhibited bad stability, which decreased evidently after 24 h. This implied that the unmodified KGM had bad water solubility, and the bound water exuded from the networks of macromolecules gradually because of phase separation after a long time. Moreover, the hydrosol system collapsed almost completely, and the η values were too low to be measured by the rotating viscometer. However, for the modified KGM-g-PAM, both the capability of bounding water and the water retentivity were improved greatly because a hydrophilic monomer, AM, was grafted onto the KGM polymer, which completely formed hydrogen bonds with H_2O within three dimensions. Thus, the hydrosol of KGM-g-PAM showed a stability of η and almost did not change after several days, which would be profitable in practical application.

CONCLUSIONS

The graft copolymerization of KGM with AM via inverse emulsion polymerization was carried out

successfully with AIBN as an initiator, Span 80 as an emulsifier, paraffin oil as a high-boiling-point oil, and xylene as a low-boiling-point oil, followed by azeotropic distillation to obtain a W/O type latex. The optimum reaction conditions in this system were as follows: [AIBN] = 15 mmol/L, $\omega_{\text{Span 80}} = 6$ wt %, [AM] = 1.5 mol/L, temperature = 60°C, time = 4 h, and oil/water volume ratio = 1.5 : 1. The W/O type latex can be used directly in latex paint systems, and there is no need for the preparation of a powder. The solid level of polymer in this system (ca. 20%) was higher than that in aqueous solution polymerization (usually under 10%). Both the water solubility and the thickening properties of the products were improved greatly with increasing content of PAM in the products. The thixotropic properties of modified KGM were better than those of the unmodified KGM. Moreover, the hydrosol of the synthesized KGM-g-PAM showed good stability of η and good electrolyte resistance and could be used as a new kind of thickener.

References

1. Tye, R. G. *Food Technol* 1991, 45, 82.
2. Kishida, N.; Okimasu, S. *Agric Biol Chem* 1987, 42, 669.
3. Tian, D.; Hu, W.; Zheng, Z.; Liu, H.; Xie, H. Q. *J Appl Polym Sci* 2006, 100, 1323.
4. Yang, G.; Huang, Q. L.; Zhang, L. N.; Zhou, J. P.; Gao, S. J. *J Appl Polym Sci* 2004, 92, 77.
5. Liu, Z. L.; Hu, H.; Zhuo, R. X. *J Polym Sci Part A: Polym Chem* 2004, 42, 4370.
6. Shinsaku, K.; Shigetomo, T.; Naruhiro, H. *Food Hydrocolloids* 2002, 16, 289.
7. Ratcliffe, I.; Williams, P. A.; Viebke, C.; Meadows, J. *Biomacromolecules* 2005, 6, 1977.
8. Oomizu, S.; Onishi, N.; Suzuki, H.; Ueda, K.; Mochizuki, M.; Morimoto, K.; Kawamoto, S.; Ono, K.; Kameyoshi, Y.; Hide, M. *Clin Exp Allergy* 2006, 36, 102.
9. Tian, D.; Shi, B.; Wang, F.; Xie, H. Q. *J Funct Polym* 2003, 16, 251.
10. Zhang, Y.; Yan, X.; Xu, Y. *J Central China Normal Univ (Nat Sci)* 1996, 30, 309.
11. Lu, S.; Lin, T.; Cao, D. *Starch* 2003, 55, 222.
12. Yenjer, S. *Eur. Pat.* 216091 (1987).
13. Wang, Z.; Liu, Z. *J Wuhan Univ Technol-Mater Sci Ed* 2006, 21, 83.
14. Xie, H. Q.; Tian, D.; Guo, J. S. *Angew Makromol Chem* 1998, 259, 7.