Graft Copolymerization of Methyl Acrylate onto Chitosan Initiated by Potassium Diperiodatoargentate (III)

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ABSTRACT: A novel efficient redox system—potassium diperiodatoargentate [Ag(III)]-chitosan—was employed to initiate the graft copolymerization of methyl acrylate (MA) onto chitosan in aqueous alkali solution. The effects of reaction variables such as monomer concentration, initiator concentration, reaction time, and temperature were investigated and the grafting conditions were optimized. The structures and the thermal stability of chitosan and chitosan-*g*-PMA were characterized by infrared spectroscopy (IR) and thermogravimetric analysis (TGA). The solubility of chitosan-*g*-PMA in some mixed solvent was tested. The graft copolymer was shown to be an effective compatibilizer in blends of poly(vinyl chloride) (PVC) and chitosan. Finally, a mechanism is proposed to explain the formation of radicals and the initiation. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 799–804, 2006

Key words: potassium diperiodatoargentate [Ag(III)]; chitosan-*g*-PMA graft copolymer; blending

INTRODUCTION

Chitosan, obtained from chitin (poly-β-(1→4)-*N*-acetyl-$_D$-glucosamine) through deacetylation using strong aqueous alkali solution, is a more versatile form of this polysaccharide, which is the second most abundant natural polymer on earth after cellulose. Grafting various vinyl monomers onto its backbone is a promising method for the preparation of new materials, because the potential and multiple applications of this versatile material can be increased and its chemical and physical properties can be improved greatly. Many graft copolymers of chitosan and vinyl monomers were synthesized and evaluated as flocculant, paper strengthener, drug-releaser, absorbent resin, and so on.[1–7]

The basic theoretical research and application of supernormal valence transition-metals in chemical fields nowadays resulted some achievements in vinyl monomer polymerization and graft copolymerization using supernormal valence transition-metal, such as Mn(VII), Cr(VI), Ni(IV), Cu(III),V(V), Ce(IV), and so forth.[8–11] So far, there are few reports on graft copolymerization of vinyl monomer onto chitosan using potassium diperiodatoargentate [Ag(III)]-chitosan redox system as initiator. Normally, it is believed that the mechanism of oxidation by Ag(III) is a two-electron-transfer process without radicals, and Ag(III) cannot initiate polymerization of vinyl monomer.[12,13] However, in our previous studies, potassium diperiodatoargentate (III) (DPA) formed the potential redox initiation system with various reducing agents and was shown to be an effective initiator in both homopolymerization[14,15] and graft copolymerization.[16–19] A two-step single-electron-transfer process is well established to explain the formation of radicals and the initiation on the reduction of DPA.

In the present study, DPA was successfully employed as oxidant and chitosan as reductant to make up the redox system to initiate the graft copolymerization of methyl acrylate (MA) onto chitosan backbone. The combined effects of the principal reaction variables on the copolymerization were investigated, and the structures and properties of the grafted products were characterized by Fourier transfer infrared spectroscopy (IR) and thermogravimetric analysis (TGA). A two-step single-electron-transfer mechanism is proposed to explain the production of radicals and the initiation.

EXPERIMENTAL

Materials

The sample of pure chitosan was obtained as a gift from Yuhuan County Chemical Plant Zhejiang Province. Its degree of deacetylation is ≥82% and the molecular weight 2.0×10^5 –3.0×10^5.

Chitosan was ground[18] to powder (>60 mesh) from flats and dried under vacuum at room temperature.

MA, from Beijing Yili Company (Beijing, China), was washed successively with aqueous sodium hydroxide solution and distilled water to get rid of the inhibitor. Then, it was dried over anhydrous sodium sulfate and distilled under vacuum. The middle fraction was used. The DPA solution was synthesized and standardized according to the reported procedure.[20] The other reagents and solvent (analytical grade) were used without any further purification. MA and DPA solution were placed in the refrigerator during the experiment.

Graft copolymerization and treatment of copolymer

Graft copolymerization was carried out in a 50-mL four-necked flask equipped with thermometer, condenser, stirrer, and gas inlet. In a typical reaction, 0.3 g chitosan powder was added with constant stirring under nitrogen. The required amount of monomer was added, followed by Ag(III) aqueous solution and the total volume was made up to 20 mL with distilled water. The graft copolymerization was performed at different temperature, monomer concentration, initiator concentration, and reaction time. After completion of reaction, the reaction mixture was cooled and neutralized by aqueous hydrochloric acid solution. It was poured into ethanol and the precipitated material was filtered through weighted sintered glass funnel and washed over several times with ethanol. The crude graft copolymer was dried to a constant weight under vacuum at 60°C. The homopolymer was removed from the crude graft copolymer by exhaustive Soxhlet extraction with acetone for 48 h. The final graft copolymer was dried at 60°C to a constant weight under vacuum.

Measurements

Chitosan-g-PMA was characterized by IR analysis using an FTS-40 spectrophotometer in potassium bromide The TGA of chitosan (4.71 mg) and the copolymers (3.95 mg) were carried out on a Shimadzu apparatus DGC-40 DTA-TG in atmospheric oxygen at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Grafting percentage (G%), efficiency percentage (E%), and the total conversion (C%) were defined and calculated as follows:

$$G\ (\%) = (\text{Weight of PMA grafted}/$$
$$\text{weight of chitosan}) \times 100\%$$
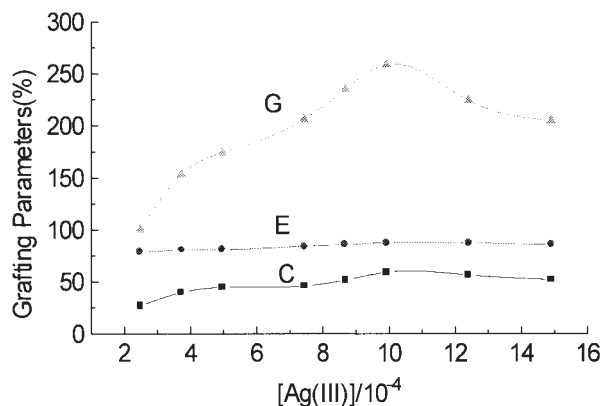
Figure 1 The effect of [Ag(III)] on grafting parameters. MA, 1.5 mL; temp., 35°C; time, 1h.

$$E\ (\%) = (\text{Weight of PMA grafted}/$$
$$\text{total weight of PMA}) \times 100\%$$

$$C\ (\%) = (\text{Total weight of PMA}/$$
$$\text{weight of MA charged}) \times 100\%$$

Effect of initiator concentration

Keeping other the variable fixed, the effect of Ag(III) concentration grafting is shown in Figure 1. The concentration of Ag(III) affects E% little, whereas G% and C% increase with the increase of Ag(III) concentration initially. This is because Ag(III) attacks on the characteristic group (—NH₂) of chitosan backbone directly generating macroradicals that can be originated to initiate the graft copolymerization of chitosan and MA. However, at higher concentration of the initiator, the active sites for grafting may be increased on the chitosan backbone, but since Ag(III) is able to participate in the termination reaction and the chance of chain transfer reaction to monomer is enhanced. There is a decrease in G% and C%, consequently.

Effect of the ratio of monomer/chitosan

The influence of the ratio of MA/chitosan on the grafting is shown in Figure 2. It was observed that the grafting parameters reach a maximum when MA/chitosan ratio was 5.8, and then the values fall gradually as the ratio increases further. Because of the limited solubility of MA in the reaction medium, when the ratio of MA/chitosan is lower, the probability of interaction of chitosan and MA is little so that both C% and G% decrease. With an increase in the ratio of MA to chitosan, self-emulsification of chitosan-g-PMA results into absorption of more monomers on the chitosan surface, which considerably enhances the rate of the grafting reaction, therefore, C% and G% increase
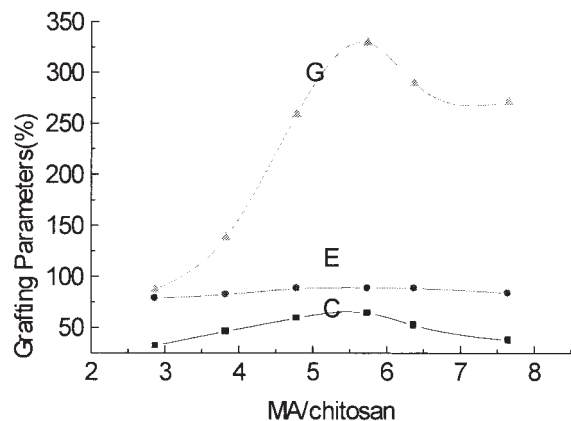
Figure 2 The effect of MA/chitosan on grafting parameters. Temp., 35°C; [Ag(III)] = 9.92 × 10^{-4} mol/L, time, 1 h.

gradually. The decline of parameters at higher MA/chitosan ratio may be explained as follows: The strengthened adsorption of monomer onto chitosan will interfere with the approach of Ag(III) to chitosan, which is necessary to produce grafting sites to initiate grafting. With the reactant volume fixed, the increase in monomer means lower magnitude of solvent, which results in the decrease of monomer in water. With the MA increased, the chain transfer reaction to monomer tends to proceed more easily. All these result grafting parameters to decrease gradually.

Effect of the temperature

At the fixed concentration of Ag(III), and the amount of chitosan/MA, the graft copolymerization was carried out at different temperatures ranging from 20°C to 50°C. The relationship between temperature and the grafting parameters is shown in Figure 3. Grafting parameters increase at first and then both G% and E% decrease. The enhancement of the parameters may be
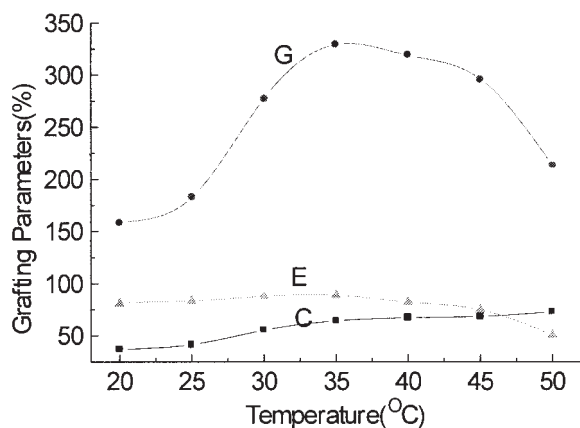
Figure 3 The effect of temperature on grafting parameters. [Ag(III)] = 9.92 × 10^{-4} mol/L, MA, 2.6 mL, time, 1 h.
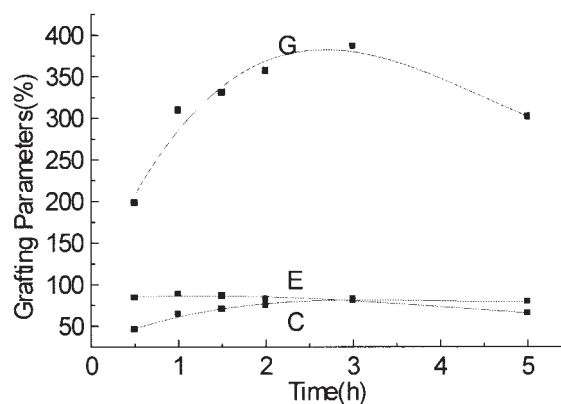
Figure 4 The effect of reaction time on grafting parameters. MA, 1.8 mL; [Ag(III)] = 9.92 × 10^{-4} mol/L; temp., 40°C.

due to the increase in the rate of the production of active free radicals, which increases the rate of initiation and propagation of the polymer chains. The decrease in E% and G% at higher temperature may be due to the enhanced rate, both of chains transfer to monomer, and of termination of growing grafted chains. The optimum temperature for maximum grafting is 35°C.

Effect of reaction time

To analyze the effect of reaction time on grafting parameters, the graft copolymerization was carried out at different time intervals, keeping all other conditions constant. As shown in Figure 4, the grafting parameters increase steadily with the reaction time up to 3 h and thereafter decrease slightly. The increasing trend has clearly indicated that Ag(III) could keep its activity for a period of time. With the time, new graft chains form on active sites on the chitosan backbone. However, Ag(III) was almost consumed after 3 h, which resulted in the slightly decreased trend.

IR spectroscopy

The grafting was confirmed by comparing the IR spectra of chitosan with that of the grafted product (Fig. 5). The main difference observed is the presence of carbonyl stretching vibration absorption band at 1729 cm^{-1} in the IR spectra of the graft copolymer, which corresponds to the carbonyl group of PMA chains. Moreover, absorption bands at 827 cm^{-1} and 760 cm^{-1} are observed because of the rocking absorption of methylene groups in PMA. The N—H bending vibration bands of the copolymer at 1660 cm^{-1} (I) and 1560 cm^{-1} (II) become different compared with that of pure chitosan. So it could be proposed that Ag(III) may react with amino group in chitosan to originate macroradicals first and then initiate MA grafting polymer-
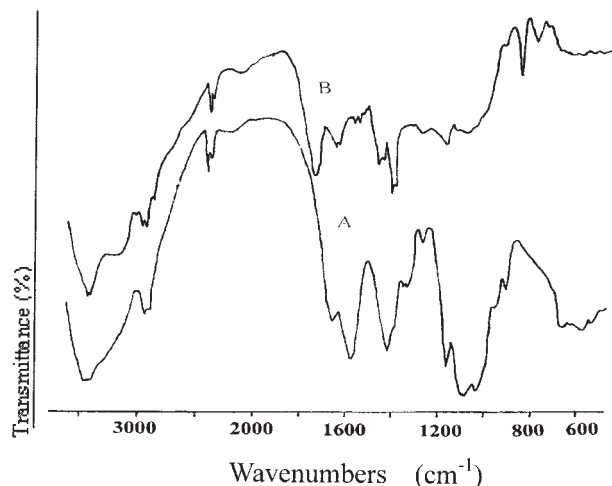
Figure 5 IR spectra of chitosan (A) and chitosan-g-PMA (B).

ization. It is clear that chitosan and MA are able to produce the graft copolymer with Ag(III)-chitosan as the initiator.

Thermal analysis

TGA of pure chitosan and the grafted copolymer is shown in Figure 6. The TGA of chitosan (A) shows a weight loss in two stages. The first stage ranges between 30°C and 105°C and shows about 7.96% loss in weight. This may be corresponding to the loss of adsorbed and bound water. The second stage of weight loss starts at 210°C and that continues up to 404°C during which there was 45.1% of weight loss due to the degradation of chitosan, whereas the TGA of the grafted product (B) is different from it. It is observed the latter has three stages of distinct weight loss between 20°C and 620°C. The first stage ranges between 30°C and 100°C with 2.53% of the adsorbed and bound water weight loss. The second stage of weight loss starts at 184°C and that continues up to 341°C during which there was 20.9% of weight loss due to the degradation of ungrafted chitosan. There is 51.3% weight loss in the third stage from 341°C to 450°C that contributes to the decomposition of chitosan-g-PMA. So, it is evident that grafting MA onto chitosan could enhance the stability of pure chitosan at higher temperature.

Solubility test

The solubility test of chitosan-g-PMA was also carried out. The grafted products are insoluble in some mixed solvents. However, the graft copolymers swell in solvents tested, such as glacial acetic acid: 1% acetic acid (1:1), 1% acetic acid: ethanol(1:1), 1% acetic acid: acetone(1:1), 1% acetic acid: acetone (2:1), and so forth.

Test of blending

PVC (2 g), 0.1 g chitosan, and 0.05 g chitosan-g-PMA ($G\%$ = 258.8%) were stirred completely in dichloromethane for 1 h. A film of chitosan/chitosan-g-PMA/PVC was obtained by casting the solution onto a glass surface. The solvent was allowed to evaporate under atmospheric pressure at 30°C for 2 days and in vacuum at 50°C for 24 h. A film of chitosan/PVC blends was prepared similarly. The external and sectional SEM micrographs of two films mentioned earlier showed that the addition of graft copolymer made the interface of two kinds of polymer indistinct (Fig. 7). The cast film of PVC and chitosan containing the graft copolymer is homogeneous and reasonably transparent for miscible system, while the film of chitosan/PVC is heterogeneous and distinctly opaque, indicating immiscibility.[21] So the graft copolymer is an efficient way of improving the compatibility of chitosan and PVC. Chitosan-g-PMA has a good practical foreground in the synthesis of degradable plastics.

The initiation mechanism of grafting reaction

IR spectroscopy and TGA confirmed that the MA has been grafted onto chitosan. It is verified once more that the process Ag(III) → Ag(I) belongs to the two-step single-electron-transfer mechanism.[16] The IR spectrum above has revealed that the N—H zigzag vibration bands of the graft copolymer at 1660 cm^{-1} (I), 1560 cm^{-1} (II) compared with that of pure chitosan display the different characteristics. So, it could be proposed that Ag(III) react with amino group in chitosan to generate macroradicals first and then initiate MA grafting. The initiation mechanism, referencing to the related papers,[16–19] may be shown in Scheme 1.
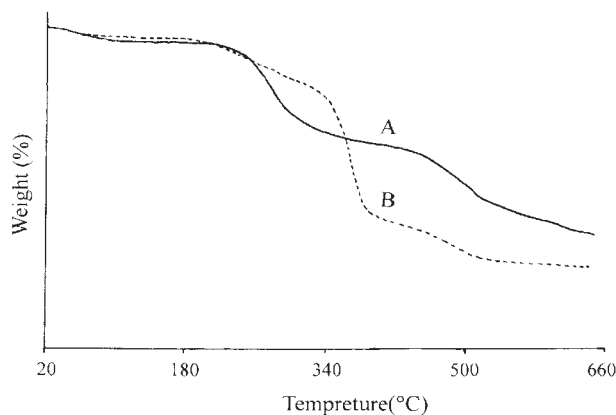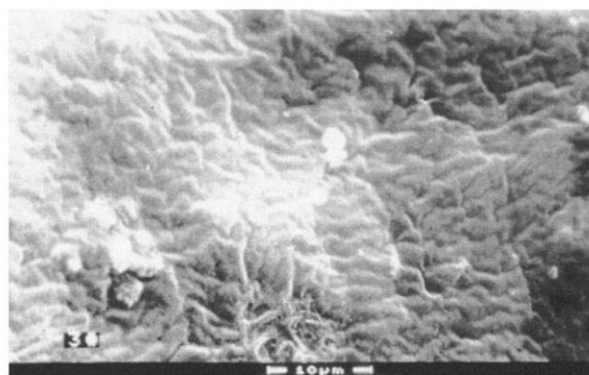

Figure 6 Thermogravimetric analysis (TGA) of pure chitosan (A) and the grafted copolymer (B).
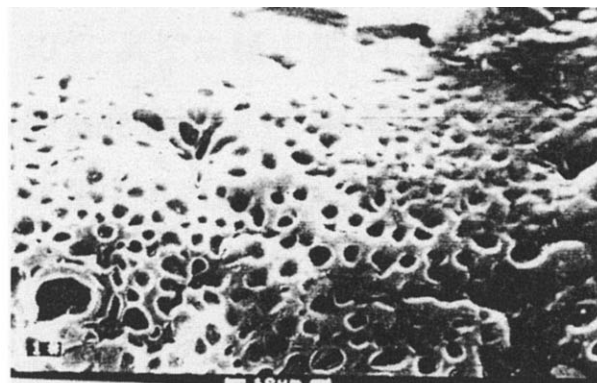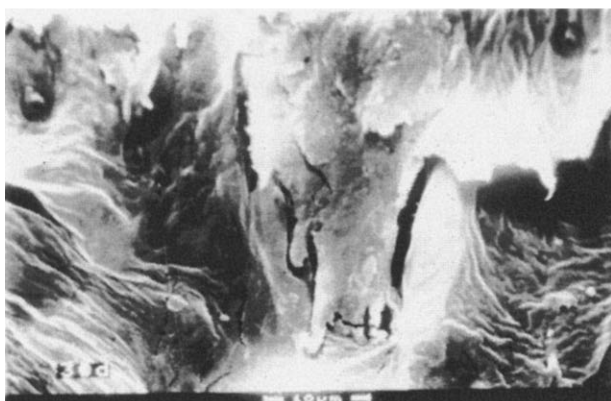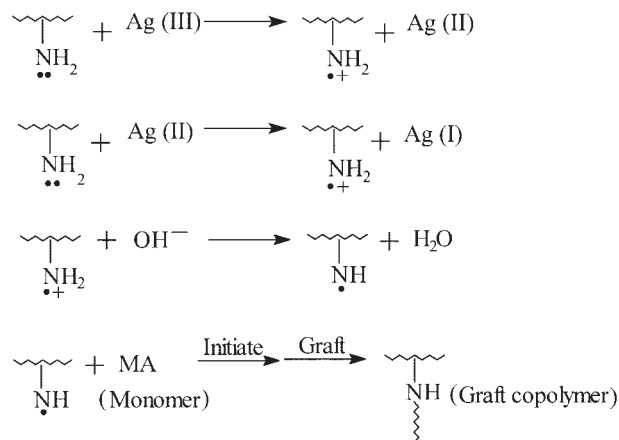
A

B

C

D

Scheme 1

CONCLUSIONS

The feasibility of grafting MA onto chitosan by using Ag(III)-chitosan as the redox initiator has been demonstrated by this work. The grafted products can enhance the thermal stability of pure chitosan and swell in many mixed solvents tested. Changes of morphology between chitosan/PVC blends and chitosan/chitosan-*g*-PMA/PVC blends were obvious. Chitosan-*g*-PMA may improve the compatibility of two phases of chitosan and PVC.

Under the experimental conditions, graft copolymer with high graft efficiency and grafting percentage using Ag(III)-chitosan system as initiator has been obtained. Ag(III)-chitosan is concluded to be an efficient redox initiator for the graft copolymerization. The two-step single-electron-transfer mechanism proposed in redox process is a modification to traditional mechanism. Moreover, because the activation energy of the reaction employing Ag(III)-chitosan as initiator is low, the graft copolymerization is possible at a mild temperature (35°C), compared with other initiators. So, Ag(III)-chitosan as initiator is thought to be practical and has a good foreground.

Figure 7 SEM micrographs of chitosan/PVC blends and that of chitosan/chitosan-*g*-PMA/PVC blends. (A) External SEM photographs of the film of chitosan/PVC blends; (B) Sectional SEM photographs of the film of chitosan/PVC blends; (C) External SEM photographs of the film of chitosan/chitosan-*g*-PMA/PVC blends; (D) Sectional SEM photographs of the film of chitosan/chitosan-*g*-PMA/PVC blends.

References

1. Shantha, K. L.; Bala, U.; Rao, K. P. Eur Polym Mater 1995, 31, 377.
2. Kim, K. H.; Kim, K. S.; Kim, Y. B. Pollimo 1987, 11, 261.
3. Ouchi, T.; Banba, T. J Macromol Sci Chem 1991, A28, 959.
4. Kim, C. H.; Jo, S.-K.; Kong, O. K. 1995, 6, 267.
5. Saito, H.; Wu, X. D. Macromol Rapid Commun 1997, 18, 547.
6. Kang, D. W.; Choi, H. R.; Kweon, D. K. J Appl Polym Sci 1999, 73, 469.
7. Chern, C.-S.; Lee, C.-K. J Polym Sci Part A: Polym Chem 1999, 37, 1489.
8. Gao, J.; Yu, J.; Wang, W.; Chang, L.; Tian, R. J Macromol Sci Pure Appl Chem 1998, A35, 483.
9. Liu, Y.; Liu, Z.; Zhang, Y.; Deng, K. J Macromol Sci Pure Appl Chem 2002, A39, 129.
10. Liu, Y.; Liu, Z.; Zhang, Y.; Deng, K. J Appl Polym Sci 2003, 89, 2283.
11. Liu, Y.; Liu, Z.; Zhang, Y. Chem J Internet 2002, 046027pe.
12. Kirschenbaum, L. J Inorg Nucl Chem 1976, 38, 881.
13. Rao, J. P.; Sethuram, B.; Ram, N. Indian J Chem 1981, 20a, 733.
14. Liu, Y. H.; Song, M. F.; Hou, R. S. Chem J Chin Univ 1992, 13, 1151.
15. Song, X. R.; Liu, Y. H.; Feng, X. F.; Zhang, H. M. J Hebei Univ 1996, 16, 32.
16. Liu, Y. H.; Zhang, J. S.; Li, W. P.; Deng, K. L. Polym Mater Sci Eng 2002, 18, 161.
17. Song, X. R.; Liu, Y. H.; Liu, W. H.; Liu, C. H. Y.; Ren, G. P. Polym Mater Sci Eng 1999, 15, 162.
18. Liu, Y. H.; Shang, Y. J.; Yu, T. L.; Fan, Z. T. J Hebei Univ 1997, 17, 30.
19. Liu, Y. H.; Liu, W. H.; Zhao, M.; Meng, J. G. Acta Polym Sinica 1997, 5, 597.
20. Balikungeri, A.; Pelletier, M.; Monnier, D. Inorganica Chimca Acta 1997, 5, 557.
21. Aoi, K.; Takasu, A.; Okada, M. Macromolecules 1997, 30, 6134.