YING HAI LIU[*)], YANXIANG LI, LANYING YANG, YUANWEI LIU, LIBIN BAI

Hebei University
College of Chemistry and Environmental Science
Baoding, 071002, People's Republic of China

Graft copolymerization of methyl acrylate onto sodium alginate initiated by potassium diperiodatocuprate(III)

Summary — A novel redox system, potassium diperiodatocuprate(III) (DPC) — sodium alginate (SA), was employed to initiate the graft copolymerization of methyl acrylate (MA) onto SA in alkali medium. The effects of reaction variables, such as the initiator concentration, the ratio of monomer and SA, SA backbone concentration, as well as temperature and time, were investigated, and the grafting conditions were optimized. Graft copolymers with both high grafting efficiency and high part of grafting were obtained, which indicated that DPC-SA redox system is an efficient initiator for this graft copolymerization. The structures and the thermal stability of SA and SA-*g*-PMA were characterized by scanning electron microscope (SEM), infrared spectroscopy (IR) and thermogravimetric analysis (TGA). A mechanism is proposed to explain the generation of radicals and the initiation.

Key words: potassium diperiodatocuprate(III), sodium alginate, methyl acrylate, redox initiator, graft copolymerization, mechanizm.

Algin or alginate is a gelatinous substance produced by brown algae, and is used in a wide range of food, leather, pharmaceutical, and industrial applications. Because it is one of the few hydrocolloids that are capable of both thickening and gelling water, algin offers many useful properties, such as viscosity control, stabilization of suspensions, emulsions and foams, improved freeze or thaw stability, film formation, rheology control, *etc*. Algin has so many useful properties and is very "user and consumer friendly", since it is renewable, biodegradable, vegetable and wholly safe by all known tests [1]. But it is prone to enzymatic degradation and suffers from limitation in fabrication, which limited its application in some fields, for example in controlled release technology [2].

Grafting is a well-established and powerful method to develop natural and synthetic polymer hybrid materials. Among chemical initiation methods, redox-initiated grafting offers advantages since, in the presence of redox system, grafting can be carried out under milder conditions and side reactions are minimized. So far, grafting of vinyl monomers onto alginate has been carried out using ceric(IV) ions [3—7], persulfate [8], redox pair of persulfate with urea [9] or thiourea [10], hydrogen peroxide [11], hydrogen peroxide coupled with ferrous [12] or ascorbic acid [13], *et al*. Among these initiators, ceric(IV) ions were employed most extensively due to the higher extent of grafting compared to the other systems. But the high price and acid reactant medium limited its broad application.

Nowadays, the basic theoretical research and application of supernormal valence transitional metals have attracted considerable attention. Recent years, we have also obtained some achievements on the homopolymerization and graft copolymerization of vinyl monomers initiated by supernormal valence transition-metals, such as diperiodatocuprate(III) (DPC) [14—16], diperiodatoargentate(III) [17—18] or diperiodatonickelate(IV) [19—22]. It has been demonstrated that DPC is an efficient and cheap initiator.

In this paper, graft copolymerization of methyl acrylate (MA) onto sodium alginate (SA) has been investigated in details, using DPC-SA redox pair as initiator and in alkaline medium. It is superior to ceric ion due to the solubility of SA in water and insolubility of SA in acid aqueous solution, which further resulted in the higher grafting efficiency. At the same time, some structures and properties of graft copolymers were characterized by SEM, IR and TGA. A tentative mechanism is proposed to explain the formation of radicals and the initiation.

[*)] To whom all correspondence should be addressed; e-mail: candyzsp@sina.com

EXPERIMENTAL

Materials

Sodium alginate, natural compound (viscosity: 1.05—1.15 Pa · s), obtained from Damao Chemical Reagent Station, was washed with acetone to remove any adhering impurities before use and then dried under reduced pressure.

Methyl acrylate, from Tianjin Huadong Chemical Reagent Station, was washed successively with aqueous sodium hydroxide solution and distilled water, and then dried over anhydrous sodium sulfate and distilled under reduced pressure.

Diperiodatocuprate(III) was synthesized according to the reported procedure [23]. Namely, the following substrates: $CuSO_4 \cdot 5H_2O$ (5.53 g), KIO_4 (6.80 g), and KOH (9.0 g) were added to about 250 mL of water. The mixture was shaken thoroughly and heated on a hot plate. In about 20 min the boiling mixture turned intensely red and the boiling was continued for another 20 min more for the completion of the reaction. The mixture was then cooled, filtered through sintered glass crucible (G-4) and diluted to 250 mL with doubly distilled water. The concentration of DPC was measured by its absorption at λ = 414 nm using Shimadzu UV-265 spectrophotometer (Japan). The concentration of base DPC was calculated as 0.025 M.

The other solvents were all of analytical reagents grades and used as received.

Graft copolymerization

In a typical experiment, the graft copolymerization was carried out as follows: a required amount of sodium alginate was dissolved completely in water in a 50 mL conical flask, and the required amount of aqueous potassium hydroxide solution and aqueous acetic acid solution were added to maintain the same alkalinity in the reaction system. The flask was stoppered and deaerated sufficiently by sparging with nitrogen and were equilibrated at required temperature with constant stirring. Then MA was injected, followed by DPC aqueous solution, and the total volume of the reaction mixture was made up to 28 mL with distilled water. After required reaction time, the mixture was cooled and neutralized by aqueous acetic acid solution and then it was poured into excess of methanol to precipitate the crude copolymer. The precipitated product was filtered through weighted sintered glass funnel filter, washed to neutral with methanol and dried to a constant weight under vacuum at 60 °C. The homopolymer of methyl acrylate (PMA) was removed from the crude graft copolymer by exhaustive Soxhlet extraction with acetone for 48 hours. The final copolymer was then dried to a constant weight under vacuum. The above process was repeated for the different temperature (20—60 °C), time, monomer concentration, initiator concentration (0.4—1.4 mol/L) as well as SA backbone concentration (0.15—0.40 g).

Different concentrations of initiator would cause the change of pH value of the reaction system, which results in the variation of grafting parameters accordingly. However, in pH range from 10 to 13 in this work, we found pH influence was not evident. In order to keep pH value invariable, we have added the required amount of potassium hydroxide solution and acetic acid solution into the reaction system before injecting the monomer and initiator.

Methods

The grafting parameters, such as total conversion (*C*), grafting efficiency (*GE*) and percentage of grafting (*PG*) were defined and calculated as follows:

C % = (total weight of PMA/weight of MA charged) · 100 %

GE % = (weight of PMA grafted/total weight of PMA used) · 100 %

PG % = (weight of PMA grafted/weight of SA) · 100 %.

Scanning electron microscope AMKAY-1000B was used to observe the morphologies of SA and SA-*g*-PMA.

FT-IR spectra of the pure SA and SA-*g*-PMA (after exhaustive Soxhlet extraction with acetone were recorded using FTS-40 spectrometer (BIO RAD Co. U.S.A.), using potassium bromide pellets technique.

Thermogravimetric analyses (TGA) of ungrafted and grafted SA were carried out using Shimadzu apparatus (DGC-40 DTA-TG) at a heating rate of 10 °C/min in a static air atmosphere.

RESULTS AND DISCUSSION

Effects of grafting parameters

DPC concentration

As it is shown in Fig. 1, when the total volume, the ratio of MA/SA as well as reaction temperature, time and pH are kept invariably, by varying DPC concentrations, *C* (curve 1) and *PG* (curve 3) increase significantly first, reach a maximum value, and then decrease slightly. The initial increasing trend may be due to the fact that in this concentration range, DPC attacks the characteristic group (-OH) of SA backbone directly, and creates a great deal of grafting sites, which will initiate the grafting in the presence of MA. As a result, *C* and *PG* grow sharply. However, an excess of DPC will accelerate the oxidation of radicals by DPC and the propagating chain will be terminated. Whereas *GE* (curve 2) keeps at a high level and almost unchanged at first and afterwards declines slightly. The decline of *GE* may be due to the enhanced chance of the transfer reaction to monomer.

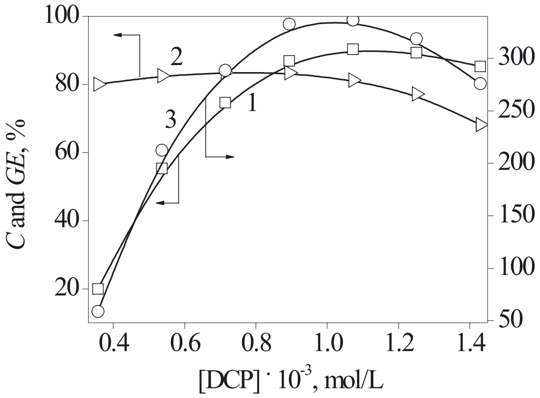


Fig. 1. Effect of DPC concentration ([DPC]) on grafting parameters: 1 — conversion (C), 2 — grafting efficiency (GE), 3 — percentage of grafting (PG) [m_{SA} = 0.25 g, MA/SA (weight) = 4.59, T = 25 °C, t = 35 min]

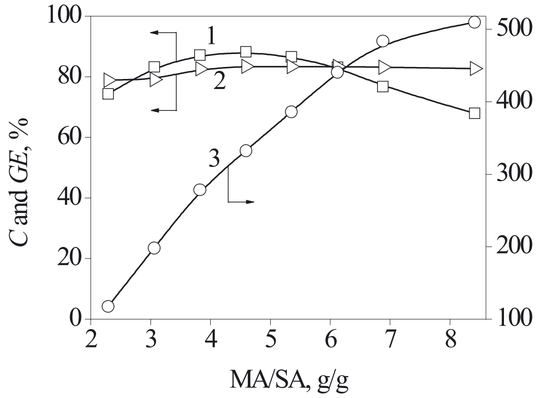


Fig. 2. Effect of MA/SA weight ratio on grafting parameters; for curves symbols see Fig. 1. ([DPC] = 0.89 · 10^{-3} mol/L, m_{SA} = 0.25 g, T = 25 °C, t = 35 min)

Monomer/sodium alginate ratio

The effect of MA/SA ratio on graft copolymerization is depicted in Fig. 2. It is observed from this figure that *C* (curve 1) and *PG* (curve 3) increase initially with the increasing MA/SA ratio, but beyond MA/SA = 4.59, *PG* increases continuously, while *C* decreases. At the same time, *GE* (curve 2) increases at the beginning and thereafter keeps constant. The initial increasing trend of all the grafting parameters may be ascribed to the surface activity and self-emulsifying properties of SA and SA-*g*-PMA, which assist in the higher availability of monomer molecules to the growing chains and active sites of SA. The following decreasing trend of *C* (curve 1) may be due to too large ratio of MA and DPC, namely, DPC is relative deficient to the superabundant of MA. Hence, though the absolute amount of grafted polymer increases, as evidenced by the increase in *PG* all the time, whereas it decreases relative to the fast increase in MA.

Backbone concentration

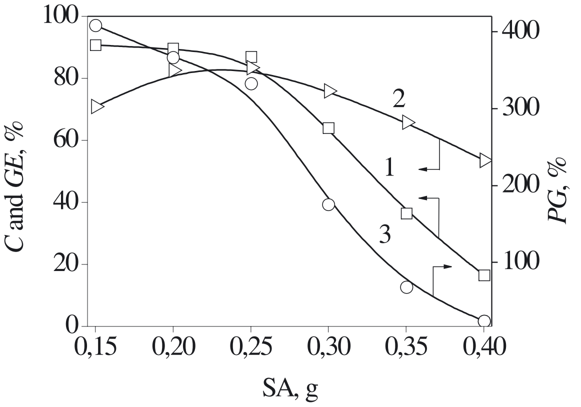


Fig. 3. Effect of SA concentration on grafting parameters; for curves symbols see Fig. 1. ([DPC] = 0.89 · 10^{-3} mol/L, MA/SA (weight) = 4.59, T = 25 °C, t = 35 min)

As it can be seen from Fig. 3, *C* (curve 1) and *PG* (curve 3) decrease steadily with the increased SA concentration. However, *GE* (curve 2) increases at first and thereafter declines. It may be explained that an increase in backbone concentration can make more monomers and initiators easily approachable to the surface of SA and produce more grafted side chains which cause *GE* increase. The decreasing trend of all the parameters may be explained as follows: firstly, the high viscosity of the reaction system makes the diffusion of both monomer and DPC to SA difficult, thus the rate of grafting will be hindered greatly. Besides, the difficulty of DPC diffusion leads to a higher local DPC concentration, which makes the rate of termination accelerate due to the reaction between the propagating chain radicals and primary radicals as well as the oxidation of the radicals by DPC. In addition, the decrease in MA/SA ratio is also on account of the decrease in *PG*. Similar observations have also been reported in the case of ceric-induced grafting of ethyl acrylate onto sodium alginate [3].

Temperature

As it is shown in Fig. 4, *C* (curve 1) and *PG* (curve 3) increase at the beginning up to 30 °C and decrease to

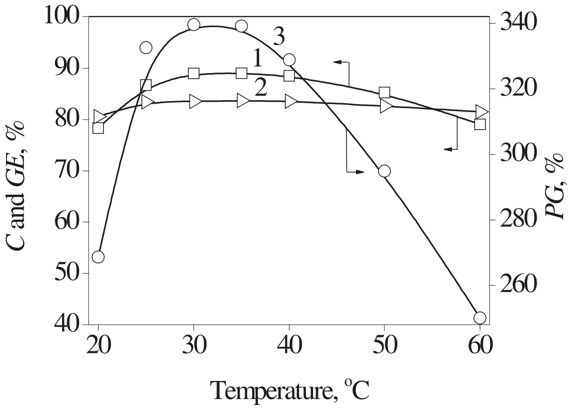


Fig. 4. Effect of temperature on grafting parameters; for curves symbols see Fig. 1. ([DPC] = 0.89 · 10^{-3} mol/L, MA/SA (weight) = 4.59, m_{SA} = 0.25 g, t = 35 min)

some extent with further temperature increase up to 60 °C. However, *GE* (curve 2) keeps almost unchanged in the range studied. The initial improvement in *C* and *PG* may be due to the higher rate of dissociation of initiator, enhanced ionization of SA (which attracts more DPC) as well as the quickened diffusion and mobility of the monomer molecules from the aqueous phase to the backbone with the increase in temperature. The decline of *C* and *PG* with further increased temperature can be ascribed both to the enhanced radical termination reaction *via* oxidation by DPC and to increased chance of chain transfer reaction.

Time

Figure 5 illustrates the influence of reaction time on grafting parameters. It is clear from the figure that during first 15 min an induction period occurs, caused probably by the presence of some amount of impurities in SA. After this time *GE* (curve 2) keeps unchanged during the course of the reaction, whereas both *C* (curve 1) and *PG* (curve 3) increase steadily with the reaction time prolonged up to 35 min, and then maintain a *plateau*, which is in consistent with the general rule of conventional radical polymerization. So, the optimized reaction time is 35 min.

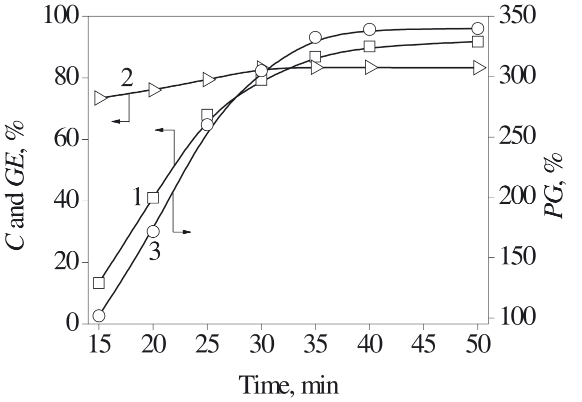


Fig. 5. Effect of time on grafting parameters; for measurements parameters see Fig. 4 and curves symbols see Fig. 1

Characteristic of grafted copolymer

Scanning Electron Microscopy

It is obvious from SEM micrographs (Fig. 6) that the surface of pure SA is very rough and not smooth, whereas the surface of SA-*g*-PMA gets to be smoother and has almost turned entirely, which may be due to the incorporation of PMA onto SA backbone.

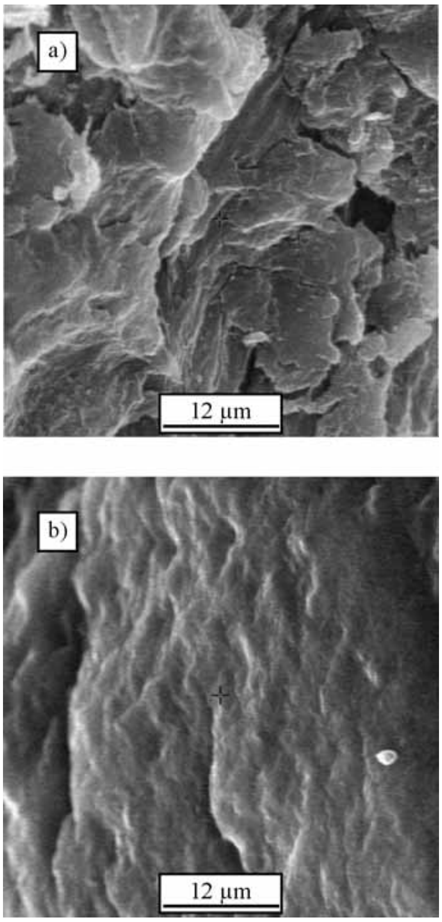


Fig. 6. SEM micrographs of SA (a) and SA-g-PMA (b)

IR Spectroscopy

As shown in Fig. 7, in the spectrum of SA [spectrum a], the characteristic peaks exist. The absorption bands around 1613 cm^{-1} and 3414 cm^{-1}, attributed to stretching vibration bands of carboxylate and of hydroxyl groups, respectively can be observed. Spectrum of the graft copolymer [spectrum b], besides retainning the above-mentioned bands of pure SA, shows an additional stronger absorption band at 1737 cm^{-1}, characteristic absorption of ester carbonyl groups in PMA of the copolymer, which confirmed the formation of SA-*g*-PMA effectively [16, 24, 25]. In the IR spectra there was observed also the variation of the intensities of the bands 3420 cm^{-1} — partly due to the presence of the hydroxyl groups and partly maybe from the absorbed moisture.

Thermal analysis

From our TGA investigations it is evident that pure SA shows a weight loss in three stages. The first stage ranges from 44.1 °C to 188 °C and shows about 6.27 % weight loss. This may correspond to the loss of residual or absorbed moisture. No such inflexions in this range of temperature are observed in TGA curve of SA-*g*-PMA. This reveals that graft copolymer is resistant to moisture absorption owing to the incorporation of hydrophobic PMA chain. The second stage at SA destruction, referred as pyrolysis, starts at 188.0 °C and continues up to 516.0 °C, during which there is 52.08 % weight loss due to the degradation of macromolecular chain. The initial step of SA-*g*-PMA degradation starts before 308.0 °C (about 20.25 % weight loss) and may be caused by the

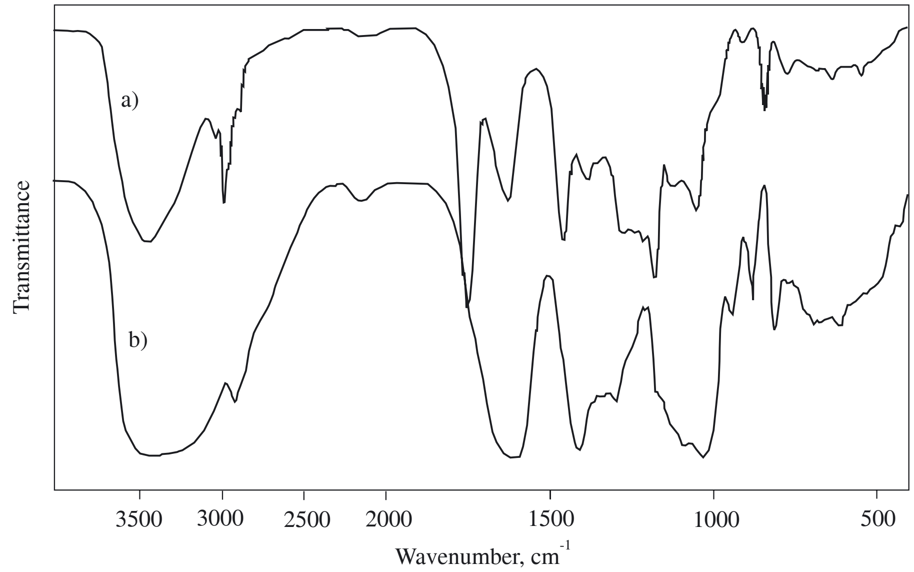
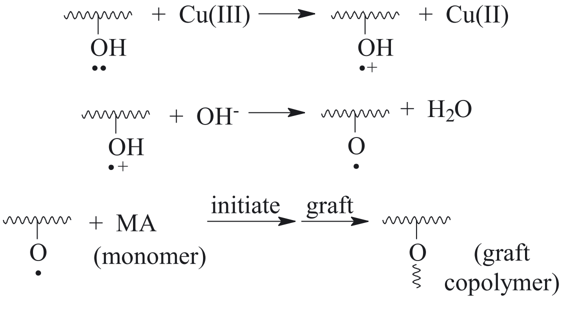


Fig. 7. Infrared spectra of SA (a) and SA-g-PMA (b)

degradation of some ungrafted SA. The second step at this product destruction — between 308.0 °C and 507.9 °C, with about 49.38 % weight loss — is attributed to the degradation of the grafted copolymer. During the last stage (>500 °C) of SA and the graft copolymer degradation weight losses are 16.32 % and 16.86 % respectively and are a result of carbonization. In addition, it is also evident from TGA curve that the temperature at 50 % weight loss of grafted copolymer is 349.8 °C *i.e.*, higher than that of pure SA (316.1 °C), which means that grafting improves the thermal stability of SA.

Initiation mechanism of grafting reaction

SEM, IR spectra and TGA results show that PMA has been grafted onto SA. Infrared spectra analysis can also be used to prove the grafting sites by the variation in the intensity of the -OH absorption band. It was found that this intensity in the spectrum of SA-*g*-PMA is weakened, which indicates that the grafted chains are linked through the hydroxyl groups. So, we propose a tentative initiation mechanism based on a single-electron-transfer process of DPC (Scheme A).



Scheme A. Mechanism of grafting reaction of MA onto SA initiated by DCP

CONCLUSIONS

Graft copolymerization of MA onto SA in an aqueous alkaline medium initiated by DPC can be carried out successfully. As a result of our work, graft copolymers SA-*g*-PMA with high graft efficiency and grafting percentage have been obtained. DPC-SA system is found to be an efficient redox initiator for this graft copolymerization. DPC obtained from $CuSO_4 \cdot 5H_2O$ is cheaper than other initiators, which is favorable to facilitate its application. The graft reaction proceeds at a mild temperature and in alkali aqueous medium.

The proof of grafting was obtained from IR analysis. Based on TGA results, it was found that the grafted SA was more thermally stable than ungrafted one, which may broaden the range of SA applications. The morphology was also changed greatly after grafting. Further work on this problem is in progress.

REFERENCES

1. Mcneely W. H., Pettitt D. J.: "Industrial gums", Academic, New York—London 1973.
2. Philipp B., Bock W., Schierbaum F.: *J. Polym. Sci., Polym. Symp.* 1979, **66**, 83.
3. Shah S. B., Patel C. P., Trivedi H. C.: *Angew Makromol. Chem.* 1994, **214**, 75.
4. Shah S. B., Patel C. P., Trivedi H. C.: *Carbohydr. Polym.* 1995, **26**, No 1, 61.
5. Shah S. B., Patel C. P., Trivedi H. C.: *High Perform Polym.* 1992, **4**, No 3, 151.
6. Vijayakumar M. T., Reddy C. R., Joseph K. T.: *Eur. Polym. J.* 1985, **21**, 415.
7. Shah S. B., Patel C. P., Trivedi H. C.: *High Perform Polym.* 1994, **6**, No 3, 193.
8. Radhakrishnan N., Lakshminarayana Y., Devi S. U., Srinivasan K. S. V.: *J. Macromol. Sci., Pure Appl. Chem.* 1994, **A31**, 581.

9. Wu G. S., Hou S. Z., Chen Y. Q.: *Yingyong Huaxue* 1993, **10**, No 1, 51.
10. Wu G. S., Li S. Z., Wu Z. P.: *Shiyou Huagong* 1995, **24**, No 11, 793.
11. Blair H. S., Lai K. M.: *Polymer* 1982, **23**, 1838.
12. Shah S. B., Patel C. P., Trivedi H. C.: *J. Appl. Polym. Sci.* 1994, **51**, 1421.
13. Wang S. X., Sun H. W., Liu Y. H.: *Ziran Kexueban* 1996, **16**, No 2, 24.
14. Liu Y. H., Song X. R., Shi H. M., Xu L. L.: *Chem. J. Chinese U.* 1990, **11**, 328.
15. Liu Y. H., Liu W. H., Yu T. L., Fan Zh. T., Wang F. L.: *J. Mol. Sci.* 1997, **13**, No 1, 41.
16. Liu Y. H., Zhang J. S., Li W. P.: *J. Hebei U.* 2001, **21**, No 1, 57.
17. Liu Y. H., Liu W. H., Zhao M., Meng J. G.: *Acta Polym. Sin.* 1997, No 5, 597.
18. Liu Y. H., Song M. F., Hou R. S.: *Chem. J. Chinese U.* 1992, **13**, 1151.
19. Shang Y. J., Liu Y. H., Deng K. L., Li W. P.: *J. Hebei U.* 1999, **19**, No 4, 356.
20. Liu Y. H., Shang Y. J., Li W. P., Wang Z., Deng K. L.: *Acta Polym. Sin.* 2000, No 2, 235.
21. Liu Y. H., Li W. P., Deng K. L.: *J. Appl. Polym. Sci.* 2001, **82**, 2636.
22. Liu Y. H., Liu Z. H., Zhang J. S., Deng K. L.: *J. Macromol. Sci.-Pure* 2002, **A39**, 129.
23. Jaiswal P. K., Yadava K. L.: *Indian J. Chem.* 1973, No 11, 837.
24. Liu Y. H., Zhang J. S., Li W. P., Deng K. L.: *Polym. Mat. Sci. Eng.* 2002, **18**, 161.
25. Liu Y. H., Lin X. H., Deng K. L. *et. al.*: *J. Macromol. Sci.-Pure* 2003, **A40**, 211.

Received 20 II 2004.