Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

WATER-SOLUBLE AMPHOLYTIC GRAFTED POLYSACCHARIDES. II. SYNTHESIS AND CHARACTERIZATION OF GRAFT TERPOLYMERS OF STARCH WITH ACRYLAMIDE AND [2-(METHACRYLOYLOX)] ETHYL DIMETHYL (3-SULFOPROPYL) AMMONIUM HYDROXIDE

Zi-Heng Hu[a]; Li-Meng Zhang[abc]
[a] Institute of Polymer Science, School of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou, P.R. China [b] Zhongshan University, Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, Guangzhou, P.R. China [c] Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY, U.S.A.

To cite this Article Hu, Zi-Heng and Zhang, Li-Meng(2002) 'WATER-SOLUBLE AMPHOLYTIC GRAFTED POLYSACCHARIDES. II. SYNTHESIS AND CHARACTERIZATION OF GRAFT TERPOLYMERS OF STARCH WITH ACRYLAMIDE AND [2-(METHACRYLOYLOX)] ETHYL DIMETHYL (3-SULFOPROPYL) AMMONIUM HYDROXIDE', Journal of Macromolecular Science, Part A, 39: 5, 419 — 430

To link to this Article: DOI: 10.1081/MA-120003964

URL: http://dx.doi.org/10.1081/MA-120003964

J. MACROMOL. SCI.—PURE APPL. CHEM., A39(5), 419–430 (2002)

WATER-SOLUBLE AMPHOLYTIC GRAFTED POLYSACCHARIDES. II. SYNTHESIS AND CHARACTERIZATION OF GRAFT TERPOLYMERS OF STARCH WITH ACRYLAMIDE AND [2-(METHACRYLOYLOX)] ETHYL DIMETHYL (3-SULFOPROPYL) AMMONIUM HYDROXIDE

Zi-Heng Hu[1] and Li-Ming Zhang[1,2,*]

[1]Institute of Polymer Science, School of Chemistry
and Chemical Engineering, and
[2]Key Laboratory for Polymeric Composite and Functional
Materials of Ministry of Education, Zhongshan
University, Guangzhou, 510275, P.R. China

ABSTRACT

Water-soluble ampholytic grafted polysaccharides, namely the graft terpolymers of starch with acrylamide (AM) and [2-(methacryloylox) ethyl] dimethyl (3-sulfopropyl) ammonium hydroxide (DMAPS), were synthesized in aqueous solutions using an ammonium ceric nitrate/acid redox system as the initiator. The effects of various factors such as temperature, pH of reaction medium, and initiator concentration, and the amounts of AM, DMAPS, and starch on the graft percentage and monomer graft conversion were studied. IR analysis identified the existence of the grafting. For the selected grafted starch, the composition was determined based on the elemental analysis, and the thermal stability was characterized by thermogravimetric analysis, as well, the corresponding degradation activation energy and kinetic order were calculated. The

---

*Corresponding author. Current address: Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY 11794-3400. E-mail: lmzhang@sbchem.sunysb.edu

relationship between the reduced viscosity of the graft terpolymers in aqueous NaCl solution and the solution pH was also investigated.

Key Words: Grafted Polysaccharides; Polyamphotlyte; Zwitterionic monomer; Starch; Graft Terpolymers

INTRODUCTION

The grafting of hydrophilic monomers onto polysaccharides has been the subject of extensive investigation.[1−14] The resulting water-soluble grafted polysaccharides may have many different applications and may hold industrial promise for the future. To date, there are many studies dealing with the grafting of a neutral monomer, an anionic or cationic monomer and their mixed system on polysaccharides, but very little work has been done on the grafting of a Zwitterionic monomer or its binary mixture on polysaccharides.

In a previous study,[15,16] we had grafted a carboxybetaine-type zwitterionic monomer, 2-(2-methacryloethyldimethylammonio) ethanoate, onto hydroxymethyl cellulose and found that the resulting grafted polysaccharides have an obvious advantage in thickening the salt-containing drilling fluids for oilfield due to the antipolyelectrolyte behavior of carboxybetaine groups in the side chains. In this paper, we report the synthesis and characterization of new water-soluble grafted polysaccharides from the graft terpolymers of starch with acrylamide (AM) and the sulfobetaine-type zwitterionic monomers [2-(methacryloylox)ethyl]dimethyl(3-sulfopropyl) ammonium hydroxide (DMAPS).

EXPERIMENTAL

Materials

Potato starch (commercial grade) was purified by washing with 80% alcohol and dried at 105°C before use. The sulfobetaine-type zwitterionic DMAPS (purchased from Aldrich Chemical Company, Inc), AM (chemical grade), and cerium ammonium nitrate (CAN; chemical grade) were used without further purification.

Graft Copolymerization

The grafting reactions were carried out under nitrogen in a 250 mL four-necked flask equipped with stirrer, thermometer, and reflux condenser. A definite amount of starch was dissolved in distilled water at 90°C with stirring, and N_2 was bubbled through. After 30 minutes, the solution of initiator

(CAN) was added to the reaction system. After 10 minutes, the monomers (AM + DMAPS) were added together with H_2SO_4 which was used to adjust the pH of the solution. The graft copolymerization was run in a thermostatic water bath at the required temperature for 5 hours. The resulting product was precipitated in ethanol. In order to remove possible homopolymers or copolymers during the grafting reaction, the precipitate was also extracted with mixed solvents (acetic acid:glycol = 60:40) in a Soxhlet extractor for 3 times, because the solvent system can easily dissolve the homopolymers (PAM or PDMAPS) from AM or DMAPS and their copolymers [Poly(AM–DMAPS)] as shown by a separate study on PAM, PDMAPS and Poly(AM–DMAPS). Finally, the purified product was dried in vacuum at 40°C to constant weight. The grafting percentage (G%) and the monomer grafting conversion (C%) were calculated as follows:

$$G\% = (W_2 - W_0) \times 100/W_0$$
$$C\% = (W_2 - W_0) \times 100/W_1$$

where W_0, W_1 and W_2 denote the weights of the starch, total monomers, and the purified product, respectively.

Characterization

The IR analysis of the graft copolymer was carried out by using a Nicolet model 205 spectrophotometer (KBr). The composition of the graft copolymer was determined based on the elemental analysis. The intrinsic viscosity of the graft copolymer in NaCl solutions of different concentrations was investigated at 30°C by a Ubbelohde viscometer. The thermal stability of the graft copolymer was determined by thermogravimetric analysis (TGA).

RESULTS AND DISCUSSION

Effect of pH of Reaction Medium

Table 1 illustrates the effect of pH medium on the G% and C%. At the range of pH 1.0 ~ 1.5, the G% and C% attain maxima. This might be because a lower pH of the reaction system is unfavorable to the generation of the free radicals, as shown in the following equilibrium:

$$Ce^{4+} + St{-}H \rightleftharpoons Ce^{3+} + St\bullet + H^+$$

while at higher pH, the initiator decomposes fast to result in an increase of the rate of termination reaction than the rate of propagation.

Table 1. Effect of pH Medium on the Grafting

pH	G%	C%
0.5	199	66.6
1.0	278	92.5
1.5	287	95.7
2.0	260	86.5
2.5	203	67.6
3.0	156	52.0

Conditions: [starch] = 2 g/dL; [AM] = 3 g/dL; [DMAPS] = 3 g/dL; [CAN] = 5.0×10^{-3} mol/L; 40°C; 5 h.

Effect of Initiator Concentration

Figure 1 shows the effect of CAN concentration on the grafting. The G% and C% initially increase with the increase of CAN concentration from 0.001 to 0.006 mol/L, then these grafting parameters decrease gradually with the further increase of CAN concentration. The increase of the G% and C% first may be attributed to the increasing number of free radicals on the starch backbone on which the monomers can be grafted. The decline in G% and

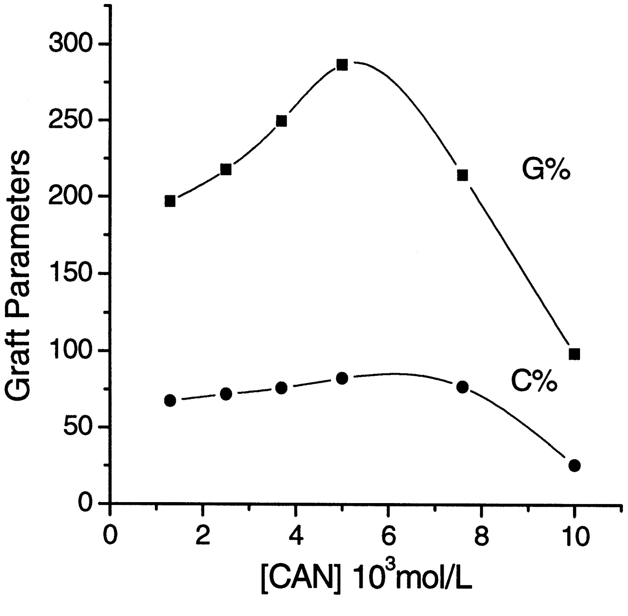

Figure 1. The effect of CAN concentration on the grafting. Conditions: [starch] = 2 g/dL; [AM] = 3 g/dL; [DMAPS] = 3 g/dL; pH 2; 40°C; 5 h.

C% at higher CAN concentration (>0.006 mol/L) may be due to the termination of the growing grafted chain by excess CAN.

Effect of Temperature

The effect of reaction temperature on the grafting is shown in Fig. 2. It can be noted that the G% reaches a maximum of 287% at an optimum temperature of 40°C and then decreases with the further increase of temperature. A similar change was observed for the C%. The increase in G% up to 40°C may be due to the higher diffusion rate of monomer molecules to starch backbone. The decrease in G% and C% beyond 40°C may result from the faster rate of the termination reaction of free radicals on the grafted chains.

Effect of Starch Amount

Table 2 shows the effect of the starch amount on the G% and C%. At the starch concentration of 20 g/L, the G% and C% reach the maximum and then decrease steadily with the further increase of starch amount. This is because the high starch concentration makes the solution sticky, which is unfavorable for the diffusion of the reactants and initiator.

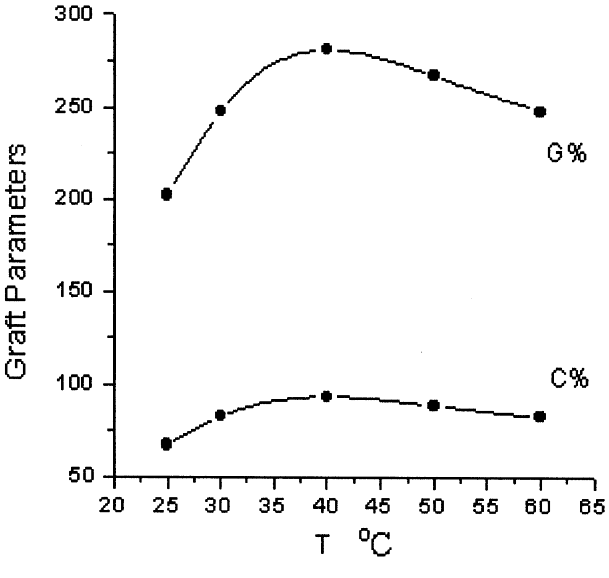

Figure 2. The effect of temperature on grafting. Conditions: [starch] = 2 g/dL; [AM] = 3 g/dL; [DMAPS] = 3 g/dL; [CAN] = 5.0×10^{-3} mol/L; pH 2; 5 h.

Table 2. Effect of Starch Concentration on the Grafting

[Starch] (g/dL)	G%	C%
1	194	64.8
2	287	95.7
4	205	68.2
6	163	54.3

Conditions: [AM] = 3 g/dL; [DMAPS] = 3 g/dL; [CAN] = 5.0×10^{-3} mol/L; pH 2; 40°C; 5 h.

Effect of Monomer Amounts

Table 3 shows the effect of the amounts of AM and DMAPS on the G% and C%. The grafting parameters increase with the increase of AM amount when keeping the amount of DMAPS constant (Table 3, No. 1 ~ 4). A similar change of the G% and C% can be seen for the increase of DMAPS amount, while keeping the AM amounts constant (Table 3, No. 2, 6, 7). The increase in G% and C% may result from the greater availability of the monomers in the proximity of starch macroradicals. When the weight of total monomers is unchanged, the increase in the ratio of AM and DMAPS results in the increase of the G% and C% (Table 3, No. 4, 5, 7), showing that AM is easier to be grafted onto the starch than DMAPS.

IR Analysis

The IR spectrum of the graft terpolymer showed not only the characteristic absorption bands of starch but also the characteristic bands

Table 3. Effect of Monomer Ratio on the Grafting

No.	[AM] (g/dL)	[DMAPS] (g/dL)	G%	C%
1	0	2	24.3	24.3
2	2	2	69.4	34.7
3	3	2	169	67.4
4	4	2	246	82.0
5	3	3	187	62.3
6	2	3	116	46.3
7	2	4	155	51.8

Conditions: [starch] = 2 g/dL; [CAN] = 5.0×10^{-3} mol/L; 40°C; 5 h.

of $-CONH_2$ (1673 cm^{-1}) and $-SO_3^-$ (1041 cm^{-1}) indicating that the graft terpolymer contained the chain structure of AM and DMAPS.

Composition of Graft Terpolymers

Based on elemental analysis, the composition of the graft terpolymers was determined as follows:

$$(6X_{St} + 11X_D + 3X_A) : (X_D + X_A) : X_D = X_C : X_N : X_S \tag{1}$$

$$X_{St} + X_D + X_A = 100\% \tag{2}$$

where X_{St}, X_D and X_A are the molar percents (mol%) of the starch, DMAPS and AM in the graft terpolymer, respectively, and X_C, X_N and X_S denote the molar percents (mol%) of element C, N and S in the graft terpolymer.

Then, X_{St}, X_D and X_A can be calculated by Eqs. 3, 4, and 5, as follows:

$$X_{St} = (X_C - 3X_N - 8X_S)/(X_C + 3X_N - 8X_S) \tag{3}$$

$$X_D = 6X_S/(X_C + 3X_N - 8X_S) \tag{4}$$

$$X_A = 6(X_N - X_S)/(X_C + 3X_N - 8X_S) \tag{5}$$

The results are listed in Table 4.

Dependence of Viscosity of Graft Terpolymer on pH in NaCl Solution

The reduced viscosity of graft terpolymers, which were dissolved in 0.1 mol/L and 0.3 mol/L NaCl at different pH, is shown in Fig. 3. At the pH of 7, all curves show minima indicating that the samples have the isoelectric points. At the isoelectric point (pH = 7), the positive charge and negative charge become almost equal along a polymer chain leading to the coiling structure of the polymer chain, thus resulting in the minimum viscosity. At a pH lower than the isoelectric point, the positive charge is more than the negative charge because of the shielding of the H^+ ion to the negative charge,

Table 4. The Compositions of the Graft Copolymers Obtained by Elemental Analysis

No.	X_C (%)	X_N (%)	X_S (%)	X_{St} (%)	X_D (%)	X_A (%)
4	83	13	4.1	12	27	61
5	84	12	3.8	20	25	55

Nos. 4. 5 were the samples listed in Table 3.

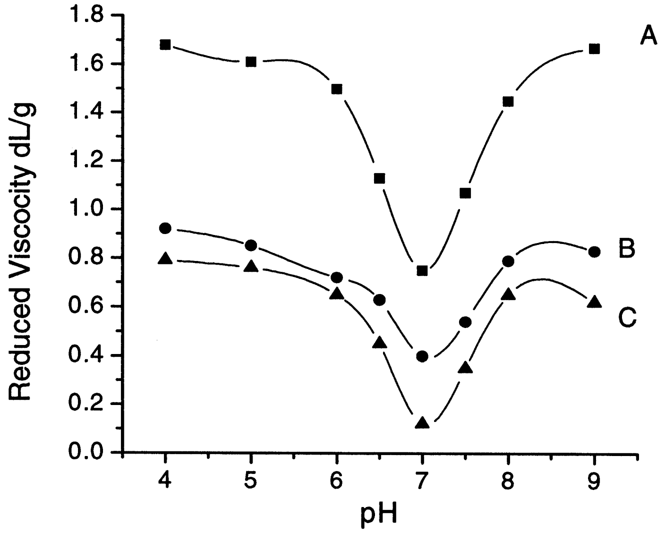

Figure 3. Reduced viscosities of the graft copolymers in NaCl solution in different pH. Conditions: (A) Table 3, No.5 in 0.3 mol/L NaCl; (B) Table 3, No.5 in 0.1 mol/L NaCl; (C) Table 3, No. 4 in 0.1 mol/L NaCl.

while at the higher pH, the negative charge is more than the positive charge for the shielding of the OH^- ion. The presence of a net charge (or the electrostatic repulsion) in the polymer chain makes the chain adopt an extended structure, leading to higher viscosity. It can also be noted that the concentrations of NaCl don't change the isoelectric point, but the reduced viscosity of the polymer solution increases with increasing NaCl concentration, showing the antipolyelectrolyte behavior. This is because the intramolecular ionic attraction in the polymer chain can be suppressed at higher ionic strength.

Thermal Stability of Graft Terpolymer

The TGA curves for the thermal degradation of a 5-mg graft copolymer with the grafting percentage of 169% at various heating rates in air atmosphere are shown in Fig. 4. From Fig. 4, it is clear that three degradation stages are observed. The first stage is due to the loss of the adsorbed moisture, while the second stage of the degradation is due to the degradation of the starch main chain and the ester of DMAPS chain. The third stage is due to the further degradation of the graft chain. It can be seen in Table 5 that the temperatures at the start of intense degradation (T_{start}), the maximum peak at the two stages (T_{m1}, T_{m2}), and 50% wt loss ($T_{50\%}$) increase with an increase in the heating rate.

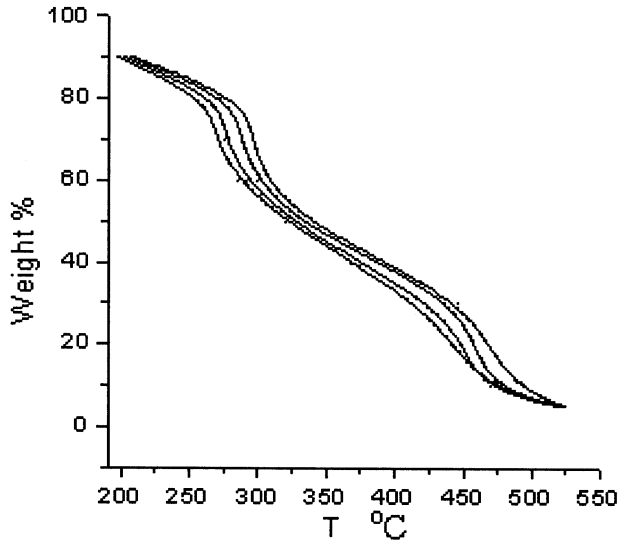

Figure 4. The TGA curves of CGAD at various heating rate. The curves from left to right: 5, 10, 20, and 40°C/min.

The activation energy for a given weight fraction (W%) and the kinetic order of the degradation can be determined by Ozawa's method [7]:

$$\mathrm{Log\,B} + 0.457\,\mathrm{E/RT} = \mathrm{K} \tag{6}$$

$$\mathrm{Log}\left|(1-\mathrm{C})^{1-\mathrm{n}} - 1\right| = \mathrm{Log\,B}\ (\mathrm{n} \neq 1) \tag{7}$$

$$\mathrm{Log}\,|\mathrm{Ln}(1-\mathrm{C})| = \mathrm{Log\,B}\ (\mathrm{n} = 1). \tag{8}$$

$$\mathrm{C} = 1 - \mathrm{W/W_0} \tag{9}$$

where B is the heating rate (°C/min), T is the temperature (K), K is a constant, E is the activation energy, R is the ideal gas constant, n is the reaction order, and W_0 and W represent the initial weight and weight at any time.

Table 5. Heat Stability of the Graft Copolymer at Various Heating Rates in Air

Heating Rate (°C/min)	T_{start} (°C)	T_{m1} (°C)	T_{m2} (°C)	$T_{50\%}$ (°C)
5	186	267	443	321
10	203	275	451	325
20	206	285	459	330
40	209	293	469	337

According to Eq. 6, the activation energy of degradation can be determined from the slope of the linear relationship between Log B and 1/T, as shown in Fig. 5; the activation energies corresponding to the second and third stages have been calculated as follows:

$$\Delta E_2 = 111.0\,\mathrm{kJ/mol}\ \text{(the second stage)}$$
$$\Delta E_3 = 94.7\,\mathrm{kJ/mol}\ \text{(the third stage)}$$

The Log Ln(1 − C)| plotted against the logarithm of the heating rate (B) in an air atmosphere is shown in Fig. 6. The good linear relationship obtained means that the kinetic order is 1 for the thermal degradation of the graft terpolymers.

CONCLUSION

Water-soluble ampholytic grafted polysaccharide from the graft terpolymer of potato starch with AM and DMAPS was synthesized by using CAN as the initiator and was ascertained by IR. The effects of various factors on the grafting were studied. Its composition was calculated based on elemental analysis. The reduced viscosity of the graft terpolymer in aqueous NaCl attains its minimum at the isoelectric point, and the minimum value of the

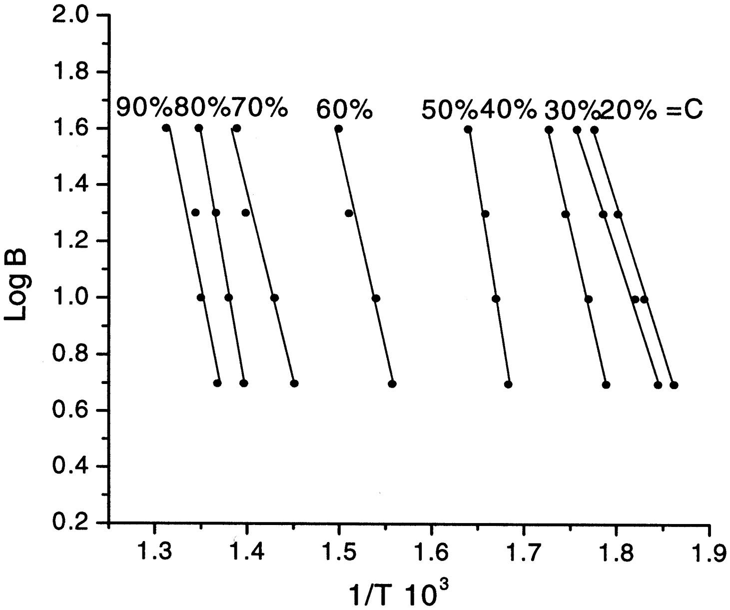

Figure 5. The plots of logarithms of heating rate B vs. 1/T in air atmosphere.

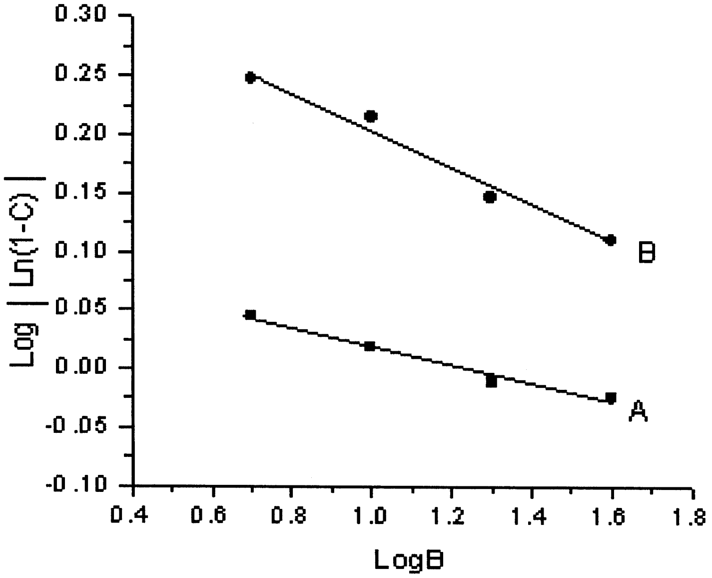

Figure 6. The relationship between Log|Ln(1 − C)| and Log B by Ozawa's method for n = 1 in air atmosphere: (A) 350°C (B) 400°C.

reduced viscosity is increased by the addition of NaCl. Thermal degradation of the graft copolymer shows that the degradation has 3 stages; their activation energies have been found as follows: $\Delta E_2 = 111\,kJ/mol$ (the second stage), $\Delta E_3 = 94.7\,kJ/mol$ (the third stage). The kinetic order of degradation is 1.

ACKNOWLEDGMENTS

The work is supported by the Natural Science Foundations of China (Grant 29804011) and Guangdong Province (Grant 960021) and by the Foundation for University Key Teacher by the Ministry of Education, China.

REFERENCES

1. Zhang, L.M. Macromol. Mater. Eng. **2001**, *286*, 267.
2. Zhang, L.M. Starch/Starke **2001**, *53*, 401.
3. Zhang, L.M.; Chen, D.Q. Starch/Starke **2001**, *53*, 311.
4. Nayak, B.P.; Singh, R.P.J. Appl. Polym. Sci. **2001**, *81*, 1776.
5. Singh, R.P.; Karmakar, G.P.; Rath, S.K., et al., Polym. Eng. Sci. **2000**, *40*, 46.
6. Zhang, L.M.; Tan, Y.B.; Li, Z.M. J. Appl. Polym. Sci. **2000**, *77*, 195.
7. Zhang, L.M.; Sun, B.W. J. Appl. Polym. Sci. **2000**, *74*, 3088.

8. Tan, Y.B.; Li, Z.M. J. Appl. Polm. Sci. **2000**, *76*, 305.
9. Zhang, L.M. Macromol. Mater. Eng. **2000**, *280* (7–8), 66.
10. Zhang, L.M.; Tan, Y.B.; Li, Z.M. Polym. Int. **2000**, *48*, 921.
11. Tan, Y.B.; Zhang, L.M.; Li, Z.M. J. Appl. Polym. Sci. **1998**, *69*, 879.
12. Yin, X.C.; Zhan, L.M.; Li, Z.M. J. Appl. Polym. Sci. **1998**, *70*, 921.
13. Zhang, J.; Zhang, L.M.; Li, Z.M. J. Appl. Polym. Sci. **2000**, *78*, 537.
14. Athawale, V.D.; Lele, V. Carbohyd. Polym. **2000**, *41*, 407.
15. Zhang, L.M.; Tan, Y.B.; Huang, S.J.; Chen, D.Q.; Li, Z.M. Journ. Mac. Sci.-Pure & Appl. Chem. **2000**, *A37*, 1247.
16. Zhang, L.M.; Tan, Y.B.; Li, Z.M. Carbohyd. Polym. **2001**, *44*, 255.

Received July 30, 2001
Revised November 20, 2001