Microwave-assisted Synthesis of Maleated Rosin-cassava Starch Ester

DUAN Wen-gui

DUAN Wen-gui, FANG Hua-xiang, MA Huan-ge, LI Guang-hua, CEN Bo

(College of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China)

Abstract: Maleated rosin-cassava starch esters (MRCSE) of different degree of substitution (D_S) were synthesized by O-acylation of cassava starch with maleopimaric acid chloride (MPA-Cl) under microwave irradiation. By single factor experimentation, the optimal conditions for the synthesis of MRCSE were obtained as follows: cassava starch 0.5 g, MPA-Cl 3.4 g, reaction time 1.5 h, reaction temperature 110 ℃, microwave power 700 W, pyridine amount 25 mL, activation time of cassava starch 1.5 h, and molar ratio 1∶1 (maleated rosin chloride to the hydroxyl group per *D*-glucose unit). The resulted MRCSE was characterized by means of FT-IR, NMR, XRD, and elemental analysis. Also, the effect of reaction conditions on the D_S of MRCSE has been studied. The intrinsic viscosity and solubility of MRCSE with D_S value of 0.170 were measured. The results showed that the modified starch esters have lower intrinsic viscosity and better solubility than the raw cassava starch, especially water-solubility, indicating that MRCSE is a novel water-soluble starch derivative.

Key words: maleated rosin; cassava starch; maleated rosin-cassava starch ester; microwave irradiation

CLC number: TQ351 **Document code**: A **Article ID**: 0253 - 2417(2009)05 - 0016 - 07

马来松香木薯淀粉酯的微波合成

段文贵, 方华祥, 马欢歌, 李光华, 岑 波

(广西大学 化学化工学院, 广西 南宁 530004)

摘 要:在微波辐照下,通过木薯淀粉与马来松香酰氯(MPA-Cl)的 O-酰化反应合成了不同取代度的马来松香木薯淀粉酯(MRCSE),利用 FT-IR、NMR、X 射线衍射(XRD)和元素分析对 MRCSE 进行了表征。探讨了反应条件对 MRCSE 取代度的影响,通过单因素试验得出最佳合成工艺条件为:木薯淀粉 0.5 g,MPA-Cl 3.4 g,吡啶体积 25 mL,淀粉活化时间 1.5 h,反应温度 110 ℃,功率 700 W,反应时间 1.5 h,物质的量比 1∶1(马来松香酰氯-葡萄糖单元中羟基数)。并测试了 D_S 为 0.170 的 MRCSE 的特性黏度和溶解性能。结果表明,与原料木薯淀粉相比,MRCSE 的特性黏度降低、溶解性能变好,尤其可溶于冷水,即 MRCSE 是一种新型水溶性淀粉衍生物。

关键词:马来松香;木薯淀粉;马来松香木薯淀粉酯;微波辐射

Starch is one of the richest, the most cost-effective and important renewable natural polymer. However, native starch is insoluble in water and most organic solvents due to its crystalline nature[1], which limits its wide applications. So, starch is usually modified by chemical reaction at its hydroxyl groups to improve its properties such as solubility, hydrophilicity, porosity, functionality, formability, and mechanical strength. One of the common chemical modification of starch is esterification[2-4]. Recently, many researchers have reported the preparation of modified starch using acetate, succinate and maleic anhydride, and their hydrophilicities were improved[5-6]. Maize and potato starch esters were prepared by the reaction with acid anhydride using pyridine as catalyst and dimethylformamide as solvent under heterogeneous reaction conditions[7-9]. In

收稿日期:2008 - 11 - 14
基金项目:广西科学基金资助项目(桂科自 0640005);广西林产化学品开发与应用重点实验室开放基金资助项目(GXFC08-04)
作者简介:段文贵(1964 -),男,广西资源人,教授,博士,博士生导师,主要从事天然资源化学和有机合成研究;
E-mail:wgduan@ gxu. edu. cn。

addition, the synthesis of the higher fatty acid starch esters (C_8-C_{18}) was also reported by the reaction with fatty acid chlorides (C_8-C_{18}) using N,N-dimethylacetamide/lithium chloride as solvent under homogeneous reaction conditions, and higher D_S values products were obtained[10-11]. However, the report on the preparation of starch derivatives using rosin (including modified rosin) as esterification reagents is rare up to now. Rosin is a natural, renewable, and rich resource in the world. Maleated rosin is one of the modified rosin with a carboxyl group and an anhydride group in the molecule. Thus, maleated rosin may be introduced to starch molecules through esterification using its acyl chloride as intermediate[12]. However, acyl chloride group in maleopimaric acid chloride (MPA-Cl) is attached to a tertiary carbon and a bulky three-ring phenanthrene skeleton, and esterification at hydroxyl groups in starch molecules will be very difficult under conventional heating condition. Recently, there is increasing interest in microwave heating as a method to facilitate reactions. Some researchers have reported the rapid preparation of starch maleates half-esters with D_S up to 0.25 and the synthesis of disproportionated rosin- polyethylene glycol-maleic acid ester under microwave irradiation[13]. In this research, maleated rosin-cassava starch esters (MRCSE) were synthesized by esterification of starch with MPA-Cl using microwave irradiation. MPA-Cl was obtained via consecutive reaction of rosin with maleic anhydride and reaction of maleopimaric acid anhydride (MPA) with $SOCl_2$. The influencing factors of esterification were investigated. The degree of substitution was determined by elemental analysis, and the structure of MRCSE was characterized by means of FT-IR, ^{1}H NMR, ^{13}C NMR and XRD. Also, solubility and intrinsic viscosity of MRCSE were measured.

1 Experimental

1.1 Materials and equipments

Cassava starch was kindly supplied by Guangxi Agricultural Reclamation Group, China, and was dried overnight at 105 ℃. Raw rosin (acid value 169.8 mg/g) was purchased from Wuzhou Pine Chemicals Co., Ltd., China. $SOCl_2$, DMF, pyridine, methanol and acetone were purchased from Chengdu Kelong Chemical Reagent Co.,China, and were all used as received. A Xianghu microwave-induced synthesis/extraction apparatus (XH-100B), produced by Beijing Xianghu Science and Technology Development Co., Ltd., China, was employed for esterification of cassava starch.

1.2 Characterization

Elemental analysis was performed using PE2400 Ⅱ element analyzer (Perkin Elmer Instruments Co., Ltd., USA), and D_S values of starch esters were calculated from carbon content. FT-IR spectra were recorded in the range of wave numbers 4000-400 cm^{-1} using Nicolet Nexus 470 FT-IR spectrometer (Nicolet Co., Ltd., USA). ^{13}C NMR and ^{1}H NMR spectra were recorded on AVANCE AV 500 MHz spectrometer (Bruker Corporation, Switzerland, DMSO-d_6 as solvent). X-ray diffraction (XRD) patterns were obtained by Rigaku D/max 2 500 V (Rigaku Corporation, Japan).

1.3 Synthesis of MRCSE under microwave irradiation

Maleopimaric acid (MPA) and maleopimaric acid chloride (MPA-Cl) starting from rosin were prepared according to the literature procedure[12]. Synthetic route of maleated rosin-cassava starch ester (MRCSE) was shown in Fig. 1.

Esterification of starch with MPA-Cl was carried out in two steps, namely, the activation of cassava starch and the esterification of starch with MPA-Cl under microwave irradiation. The procedures are as follows: anhydrous cassava starch 0.5 g [approximately 3 mmol of anhydrous glucose units (AGU), molecular weight of AGU is 162] and 15 mL pyridine were added into a three-neck round flask. Then, under stirring, the three-neck flask was placed in a microwave reactor, setting microwave irradiation time (2 h), temperature

(115 ℃), power (800 W). After microwave irradiation and cooling the flask, DMF (10 mL) solution of MPA-Cl(3.4 g) was added in to the flask. Microwave program was run immediately under magnetic stirring, setting microwave irradiation time (1.5 h), temperature (110 ℃), power (700 W). After reaction, 100 mL methanol was added gradually to the reaction mixture under stirring, and precipitate was isolated. Then, the precipitate (MRCSE) was filtered, washed three times with anhydrous methanol (20 mL) and dried under vacuum at 70 ℃ to obtain a fine yellow powder.

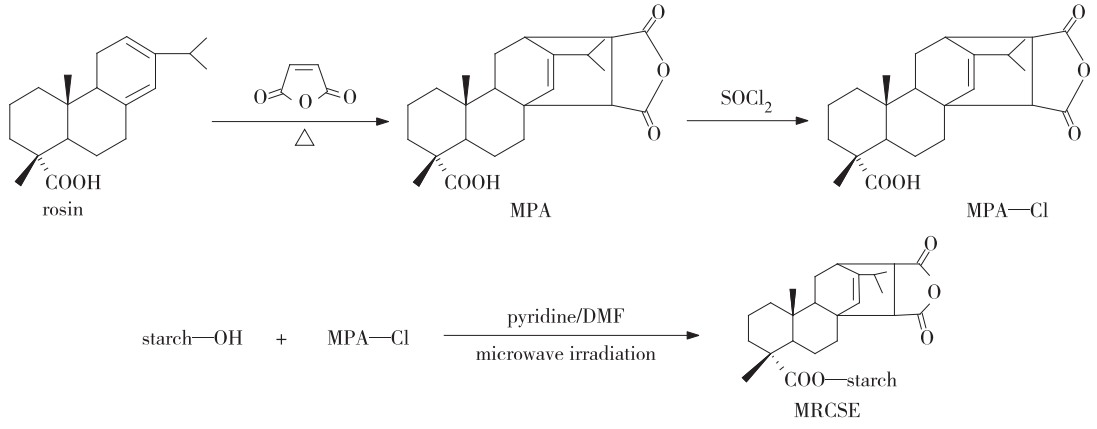

Fig. 1 Synthetic route of maleated rosin-cassava starch ester (MRCSE)

1.4 Determination of the degree of substitution (D_S)

The D_S for a starch derivative is defined as the number of hydroxyl groups (OH) substituted per *D*-glucopranosyl structural unit of the starch polymer. Since each *D*-glucose unit possesses three reactive hydroxyl groups, the maximum value of D_S is 3. The unreacted maleopimaric acid chloride (MPA-Cl)) in the reaction mixture was separated from the product by dissolving in methanol[11].

1.5 Determination of solubility and intrinsic viscosity

Solubility of MRCSE was measured at 5 % (g/mL) concentration in different organic solvents at room temperature. Intrinsic viscosities of native starch and MRCSE were determined in dimethyl sulfoxide (DMSO). Native cassava starch or MRCSE (0.25 g) was dissolved in DMSO (5 mL) and time of flow were measured in triplicate at 25 ℃ using an Ubbelohde type 1836-A viscometer at varying concentrations by diluting *in situ*[4].

2 Results and discussion

2.1 Synthesis of MRCSE

In our previous study, it was found that, under conventional heating , acyl chloride group in disproportionated rosin chloride is very difficult to react with hydroxyl groups in starch molecules owing to the obvious steric hindrance of acyl chloride group attached to a tertiary carbon and a bulky three-ring phenanthrene skeleton. Microwave irradiation has been demonstrated to have advantage over conventional heating for starch modification reactions[13]. DMF and pyridine are good solvents for the reaction system under microwave irradiation, because they can absorb microwave radiation very well to heat up rapidly. On the other hand, there are inter- and intramolecular hydrogen bondings among hydroxyl groups in starch molecules, so that the reaction activity of hydroxyl groups is lower. Therefore, before esterification reaction, it is needed to destroy hydrogen bondings of the native cassava starch to activate hydroxyl groups. Subsequently, MRCSE was synthesized by esterification of starch with MPA-Cl under microwave irradiation.

The effect of activation time on the D_S of MRCSE has been studied. The reaction conditions were as follows: activation conditions: microwave power 600 W, temp. 120 ℃; esterification conditions: molar ratio

(MPA-Cl to hydroxyl group in starch) 1, pyridine 25 mL, microwave power 700 W, temp. 110 ℃, time 1.5 h. When activation time increased from 0.5 to 1.5 h, D_S increased from 0.116 to 0.170, then D_S slightly decreased even under longer activation time, which indicated that D_S reached its optimal value at activation time of 1.5 h. Since there are strong inter-and intramolecular hydrogen bondings among hydroxyl groups in native starch molecules, it is essential to activate the starch sufficiently at first.

In following experiments, 1.5 h of activation time was used to the synthesis of MRCSE, and the effect of esterification conditions on D_S was investigated. The esterification conditions include reaction time, reaction temperature, microwave power, volume of pyridine, and molar ratio of MPA-Cl to the hydroxyl groups in starch, and the results are shown in Table 1.

As seen from Table 1, D_S increased first with increased reaction temperature (samples 1,2,3 and 4) and time (samples 5, 6, 7 and 8). At elevated reaction temperature and longer reaction time, the acyl chloride may collide and react with hydroxyl groups sufficiently, resulting in higher D_S. However, when reaction temperature and time were above 110 ℃ and 1.5 h, respectively, there was no further increase of D_S, which may be attributed to the hydrolysis of MRCSE products. Thus, reaction temperature 110 ℃ and time 1.5 h were employed for the following synthesis of MRCSE.

Table 1　Results of esterification of starch with MPA-Cl[1)]

samples	temperature/℃	time/h	pyridine/mL	molar ratio value	microwave power/W	D_S of MRCSE
1	100	1	15	0.33	500	0.112
2	110	1	15	0.33	500	0.121
3	120	1	15	0.33	500	0.119
4	130	1	15	0.33	500	0.112
5	110	1	15	0.33	500	0.121
6	110	1.5	15	0.33	500	0.124
7	110	2	15	0.33	500	0.118
8	110	2.5	15	0.33	500	0.116
9	110	1.5	15	0.33	500	0.124
10	110	1.5	25	0.33	500	0.138
11	110	1.5	35	0.33	500	0.129
12	110	1.5	45	0.33	500	0.113
13	110	1.5	25	0.33	500	0.138
14	110	1.5	25	0.5	500	0.152
15	110	1.5	25	1	500	0.156
16	110	1.5	25	2	500	0.154
17	110	1.5	25	1	500	0.156
18	110	1.5	25	1	600	0.165
19	110	1.5	25	1	700	0.170
20	110	1.5	25	1	800	0.128

1) activation time 1.5 h

It is also very important to control the amount of pyridine and molar ratio (MPA-Cl/OH) in this reaction system. Samples 9, 10, 11 and 12 showed the effect of pyridine amount on D_S from 15 to 45 mL. With the increase of amount of pyridine, D_S increased rapidly at first and then decreased. It is concluded that the esterification can not be catalyzed and activated sufficiently by a lower amount of pyridine, but excessive pyridine probably leads to dilution of the reaction system and increase of side reactions due to absorbance of excessive microwave.

The effect of molar ratio (MPA-Cl/OH) on D_S is shown on samples 13, 14, 15 and 16. When the molar ratio of reactants was 1∶1, D_S reached 0.156. The increase of reaction efficiency with molar ratio is due to the greater availability of acyl chloride molecules to contact with cassava starch at higher concentration. As MPA-Cl is too much, however, the dispersion of starch in the reaction system may be affected, leading to the decrease of D_S.

In this reaction system, microwave power is also an important parameter. As shown on samples 17, 18, 19 and 20, 700 W of microwave power resulted in D_S up to 0.17. When microwave power increased, the heating efficiency was improved to accelerate the esterification. However, the reaction temperature would increase too fast under larger microwave power, leading to some side reactions. Therefore, 700 W of microwave power was considered to be appropriate for esterification.

2.2 FT-IR analysis of MRCSE

FT-IR spectra of native starch and MRCSE with D_S of 0.156 (sample 15) are shown in Fig. 2. The spectrum of native starch (Fig. 2(a)) shows —OH peak at 3421 cm^{-1}[11]; —C—O— characteristic peaks in glucose ring and glucosidic linkage at 1159, 1082 and 1014 cm^{-1}[4]. Also, peaks at 861, 765 and 575 cm^{-1} were attributed to the stretching vibrations of the whole glucose ring; the peak at 1638 cm^{-1} presumably originated from tightly bound water in the starch[14]; the peak at 2923 cm^{-1} is the characteristic of C—H stretches associated with the ring methine hydrogen atoms. From FT-IR spectrum of MPA-Cl (Fig. 2(c)), peaks at 1842 and 1782 cm^{-1} were attributed to C═O peaks in the anhydride group, which is consistent with the literature[12].

In the spectrum (Fig. 2(b)) of MRCSE, in addition to the characteristic peaks of native cassava starch, some new peaks of MRCSE appeared. The peak at 1719 cm^{-1} was corresponded to C═O peak in the ester groups from starch ester, and peaks at 1840 and 1781 cm^{-1} were attributed to the C═O peaks in the anhydride group from maleated rosin molecule. From IR spectra, it is confirmed that MRCSE was successfully synthesized under microwave irradiation.

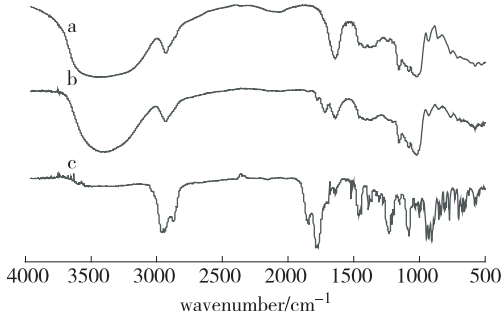

Fig. 2 IR spectra of the native cassava starch (a), MRCSE (b) and MPA-Cl (c)

2.3 ^{1}H NMR and ^{13}C NMR analysis of MRCSE

In order to verify further whether MRCSE was synthesized, MRCSE (sample 19) was characterized by ^{1}H NMR and ^{13}C NMR spectra as shown in Fig. 3. Compared with ^{1}H NMR and ^{13}C NMR spectra of native cassava starch[3,15], the new proton signals at δ 1.07, 1.25 and 2.07 in ^{1}H NMR spectrum are assigned to protons of CH_3, CH_2 and CH in maleated rosin; ^{13}C NMR spectrum shows the characteristic signals at δ 31 and 34, indicating the presence of CH_3 and CH_2 in maleated rosin. The signals at δ 126.68, 144 and the signal at δ 163.38 are attributed to the carbon atoms of double bond and anhydride, respectively. The most importance was the occurrence of the signal at δ 178.45 assigned to carbonyl carbon atom in ester group of MRCSE.

Obviously, the results from the ^{1}H NMR and ^{13}C NMR spectra also confirmed that the MRCSE was synthesized.

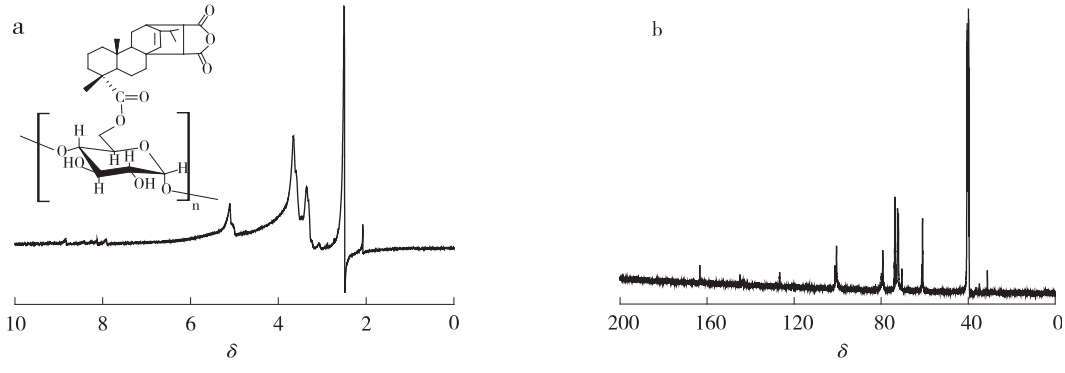

Fig. 3 ^{1}H NMR (a) and ^{13}C NMR (b) spectra of the MRCSE

2.4 X-ray diffraction analysis of MRCSE

The change of starch structure before and after modification was investigated by means of X-ray diffraction as shown in Fig. 4. Native cassava starch sample (Fig. 4(a)) shows distinct crystalline peaks at 15, 17, 18 and 23 ° which are in agreement with A-type pattern of cereal starch. However, only one broad peak around 20 ° was detected for MRCSE (Fig. 4(b)), implying obvious decrease of the crystallinity after modification, because esterification occurred both in the amorphous region and the crystalline region, which destroyed the crystalline form of cassava starch[16-17] and indicated that maleated-rosin was introduced into the starch.

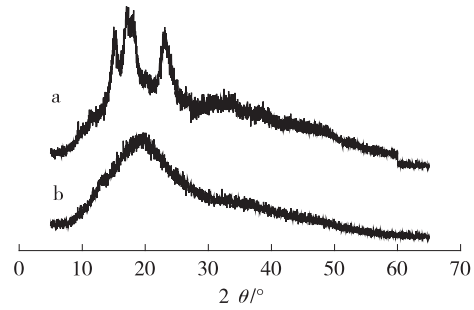

Fig. 4 X-Ray diffraction patterns of cassava starch(a) and MRCSE(b)

2.5 Solubility and intrinsic viscosity of MRCSE

Native cassava starch is very difficult to dissolve in common organic solvent owing to the strong inter- and intramolecular hydrogen bondings. It may be predicted that solubility properties will be changed via introducing the hydrophilic anhydride groups into cassava starch. Table 2 shows the solubility of MRCSE with different D_S. Starch esters (MRCSE) were soluble or partially soluble in strong polar solvents such as DMSO and water, but slightly soluble or even insoluble in non-polar or weak polar solvents such as toluene, benzene and pyridine, which indicate that solubility of cassava starch was well improved after modification. The reason may be attributed to the destruction of inter- and intramolecular hydrogen bonds and crystalline regions of cassava starch by introducing bulky rosin group and hydrophilic anhydride group.

Table 2 Solubility of MRCSE

solvents	solubility		solvents	solubility	
	D_S 0.151	D_S 0.137		D_S 0.151	D_S 0.137
H_2O	soluble	partially soluble	acetone	insoluble	insoluble
DMSO	soluble	soluble	isopropanol	insoluble	insoluble
CH_3OH	insoluble	insoluble	THF	soluble	partially soluble
$CHCl_3$	insoluble	insoluble	pyridine	partially soluble	slightly soluble
DMA	soluble	partially soluble	ethyl acetate	insoluble	insoluble
DMF	soluble	insoluble	dioxane	partially soluble	slightly soluble
CCl_4	insoluble	insoluble	ethanol	insoluble	insoluble
toluene	insoluble	insoluble	dichloromethane	insoluble	insoluble
benzene	insoluble	insoluble	petroleum ether	insoluble	insoluble

The intrinsic viscosities of MRCSE with 0.1 and 0.17 of D_S were 15.23 and 9.61 dL/g, respectively. These values were all much lower than that of native cassava starch (78.00 dL/g). The reason may be related to the fact that modification reaction resulted in not only the esterification of the hydroxyl groups in starch and their solubilities increased, but also depolymerization of polymer chains at high temperature under microwave irradiation for a long time[13].

3 Conclusion

Maleated rosin-cassava starch esters (MRCSE) with different degree of substitution were synthesized by O-acylation of cassava starch with malepimeric acid chloride (MPA-Cl) under microwave irradiation. It is confirmed that MRCSE was successfully synthesized by means of FT-IR, NMR, XRD, and elemental analysis. The maximum degree of substitution (D_S = 0.170) was obtained under activation time of starch 1.5 h and esterification conditions of reaction time 1.5 h, reaction temperature 110 ℃, microwave power 700 W,

pyridine 25 mL, and molar ratio 1∶1. Compared with native cassava starch, intrinsic viscosity of MRCSE was much lower, and its solubility was well improved especially in water, which indicate that MRCSE is a new water-soluble starch derivative.

References:

[1]张燕萍. 变性淀粉制造与应用[M]. 北京:化学工业出版社,2003:269.
[2]ABURTO J, ALRIC I, BORREDON E. Preparation of long-chain esters of starch using fatty acid chlorides in the absence of an organic solvent [J]. Starch/Starke, 1999, 51(4): 132-135.
[3]ABURTO J, ALRIC I, THIEBAUD S, et al. Synthesis, characterization, and biodegradability of fatty-acid esters of amylose and starch[J]. Journal of Applied Polymer Science, 1999, 74: 1440-1451.
[4]FANG J M, FOWLER P A, SAYERS C, et al. The chemical modification of a rang of starches under aqueous reaction conditions[J]. Carbohydrate Polymers, 2004, 55(3): 283-289.
[5]PRAFUL N B, REKHA S S. Studies on the optimization of preparation of succinate derivatives from corn and amaranth starches[J]. Carbohydrate Polymers, 2002, 47(3): 277-283.
[6]RUNCANG S, SUN X C. Succinoylation of sago starch in the N, N-dimethylacetamide/lithium chloride system[J]. Carbohydrate Polymers, 2002, 47(4): 323-330.
[7]SAGAR A D, MERILL E W. Properties of fatty-acid esters of starch[J]. Journal of Applied Polymer Science, 1995, 58(9): 1647-1656.
[8]ABURTO J, THIEBAUD S, ALRIC I, et al. Properties of octanoated starch and its blends with polyethylene[J]. Carbohydrate Polymers, 1997, 34(1/2): 101-111.
[9]ABURTO J, HAMAILI H, MOUYSSET-BAZIARD G, et al. Free-solvent synthesis and properties of higher fatty esters of starch (Part II)[J]. Starch/Starke, 2000, 51(8/9): 302-307.
[10]HEINZE T, TALABA P, HEINZE U. Starch derivatives of high degree of functionalization(1). Effective, homogeneous synthesis of *p*-toluenesulfonyl (tosyl) starch with a new functionalization pattern[J]. Carbohydrate Polymers, 2000, 42(4): 411-420.
[11]FANG J M, FOWLER P A, TOMKINSON J, et al. The preparation and characterization of a series of chemically modified potato starches[J]. Carbohydrate Polymers, 2002, 47(3): 245-252.
[12]LEE J S, HONG S H. Synthesis of acrylic rosin derivatives and application as negative photoresist[J]. European Polymer Journal, 2002, 38: 387-392.
[13]BISWAS A, SHOGREN R L, KIM S, et al. Rapid preparation of starch maleate half-esters[J]. Carbohydrate Polymers, 2006, 64(4): 484-487.
[14]KACURAKOVA M, WILSON R H. Developments in mid-infrared FTIR spectroscopy of selected carbohydrates[J]. Carbohydrate Polymers, 2001, 44(4): 291-303.
[15]KAPUSNIAK J, SIEMION P. Thermal reactions of starch with long-chain unsaturated fatty acids(Part 2). Linoleic acid[J]. Journal of Food Engineering, 2007, 78: 323-332.
[16]WON C Y, CHU C C, YU T. Synthesis of starch-based drug carrier for the control/release of estrone homone[J]. Carbohydrate Polymers, 1997, 32(3/4): 239-244.
[17]ZHANG M, JU B Z, ZHANG S F, et al. Synthesis of cationic hydrolyzed starch with high D_S by dry process and use in salt-free dyeing[J]. Carbohydrate Polymers, 2007, 69(1): 123-129.