Study on Synthesis of Hydrophobically Associated Cationic Starch

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Abstract: Hydrophobically associated cationic starch (HACS) was synthesized by inverse suspension polymerization, in which the continuous phase was cyclohexane, dispersant was Span 80-Tween 80 and initiator was redox initiator. Effects of dispersant, reaction temperature and time on soluble properties and the grafting properties were discussed. The grafted product was characterized with IR and X-ray diffraction. The experiment results showed that copolymerization can be proceeded rapidly at low temperature, and the optimum reaction condition was as follows: ratio of $m(St) : m(AM) : m(DMDACC) : m(OA)$ 4 : 7.4 : 1.5 : 0.6, content of initiator 3.1 mmol/L, grafting temperature 30 ℃, reaction time 3 h. The monomer conversions is 92.6 %, grafting rate is 53.8 % and viscosity-average relative molecular weight (M_V) is 3.26×10^6.

Key words: hydrophobically associated cationic starch; graft copolymerization; inverse suspension polymerization

疏 水 缔 合 阳 离 子 淀 粉 的 合 成 研 究

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摘 要: 本研究以环己烷为连续相, Span 80/Tween 80 为分散剂, 采用氧化还原引发体系, 通过反相悬浮聚合技术, 合成疏水缔合阳离子淀粉接枝共聚物。研究了反应温度, 引发剂用量, 反应时间对接枝性能的影响及溶解性能。并用 IR、X 衍射对共聚物进行了表征。结果表明: 采用氧化还原引发剂可使聚合反应低温快速进行, 在 $m(St) : m(AM) : m(DMDACC) : m(OA)$ 为 4 : 7.4 : 1.5 : 0.6 时, 引发剂用量 3.1 mmol/L, 30 ℃ 反应 3 h, 单体转化率 92.6 %, 接枝率 53.8 %, 粘均相对分子质量 (M_V) 3.26 × 10^{6}。

关键词: 疏水缔合阳离子淀粉; 接枝共聚反应; 反相悬浮聚合

Hydrophobically associated cationic starch (HACS) is a hydrophobically associated water-soluble polymer, which possesses a hydrophilic macromolecular chain associated hydrophobically with a small amount of hydrophobic groups. It has salt-thickening behavior, temperature resistance, shear-thinning behavior and surface activity, with great practical potential of application in many fields such as oil/gas exploitation, wastewater and sludge treatment, coatings, biological drugs and engineering materials for projects[1-3], especially in treatment of oil-bearing wastewater due to its hydrophobic groups favorable to dissolve oil.

According to statistics, the annual output of natural starch-containing carbohydrate reaches 500 billion tons which is far more than other organic matters. Carbohydrate is the richest organic resource that human may use. Its research and application have been the focus of world attention. Starch molecule has a large quantity of hydroxyl groups and the nature of starch can be changed by esterification, etherification, oxidation and cross-linking reaction of these hydroxyl groups. Graft copolymerization of starch and ethylene monomer is an

important way of its chemical modification.

Inverse suspension polymerization, started in the 1990s, has solved the problems of heat transfer and agitation of aqueous solution in synthesis process of polymerization. Compared to starch graft copolymerization, inverse suspension polymerization has temperate reaction conditions and less by-reactions[4]. It is also reported that inverse suspension polymerization has been used to prepare starch graft copolymer[5-6]. No literature, however, has reported inverse suspension polymerization used to synthesize graft copolymer of HACS, using mixture of potassium persulfate and sodium bisulfate as initiator[7].

This article describes how inverse suspension polymerization is employed to synthesize graft copolymer of hydrophobically associated cationic, using cyclohexane as continuous phase and Span 80-Tween 80 as emulsifier. It also deplores influences of dispersant, reaction time and reaction temperature on conversion rate of monomer, grafting rate of starch and grafting efficiency. The graft copolymer was characterized with IR and X-ray diffraction.

1　Experimental

1.1　Materials

Starch is from Tianjin Zhenda Chemical Industry Ltd. Octadecyl acrylate (OA) is made from solid superacid as catalyst by melt esterification[8]. Acrylamide is used without further purification, from Beijing Oriental Chemical Industry Ltd. Dimethyl diallyal ammonium chloride (DMDAAC): industrial grade, 60 % aqueous solution, products of Shanghai Plant of Agents, filtered and purified by extraction for 3 times with absolute ether and cyclohexane before it is used. Potassium persulfate is reagent grade, product of Shanghai Second Plant of Agents, recrystallized with water, dried and stored for use. Cyclohexane is reagent grade chemical, product of Shanghai Second Plant of Agents. Span 80 and Tween 80 are reagent grade, products of Dalian Plant of Agents.

1.2　Copolymer synthesis

Place a three-neck round-bottom flask with agitator, dropping funnel and gas-guiding tube in constant temperature bath; add quantitatively cyclohexane, Span 80, Tween 80 and OA; intrude nitrogen for 30 min, sufficiently emulsified; add 70 ℃ pasted and cooled (to reaction temperature) starch and stir for 20 min; add an appropriate amount of $K_2S_2O_8 \cdot NaHSO_3$. Fifteen min later, first drip half of the required dosage of DMDAAC and then drip the mixed aqueous solution of remaining DMDAAC an AM at a definite rate. React for 3 h at 30 ℃. Precipitate it with 95 % ethanol, wash for 3–4 times and dry for 4 h in 60 ℃ vacuum drier to obtain raw product.

Add different proportions of OA and prepare a series of HACS with different OA contents.

1.3　Treatment of product

Weigh raw graft product quantitatively into an extractor and extract with acetone for 24 h. Remove copolymer and dry at 60 ℃ under vacuum to constant weight, to obtain pure graft copolymer.

1.4　Structural characterization

Tablet the pure graft copolymer with potassium bromide and measure its infrared absorption spectrum with FT-IR 1730 infrared spectrometer. Characterize the copolymer with X-ray diffraction .

1.5　Determination of reaction rate of graft copolymerization

Determine the remaining monomer concentration by potassium bromide-potassium bromate method at different reaction temperatures. Calculate polymerization reaction rate R_P as per monomer consumption at definite reaction time.

For determinations of monomer conversions, graft rate and graft efficiency, refer to reference[5]. For

determinations of limiting viscosity number, M_V cationic degree and solubility time refer to references[6,9–10].

2　Conclusion and discussion

2.1　Influences of hydrophobic monomer dosage on dissolubility and M_V

As seen in Table 1, after introducing hydrophobic group into polymer molecular chain, water solubility decreases and limiting viscosity number and M_V also decrease. The higher the hydrophobic group content in polymer molecular chain is, the lower the M_V is.

Table 1　Influences of hydrophobic monomer dosage on dissolubility and M_V

PSOAMDAS	$m(St)$: $m(AM)$: $m(DMDACC)$: $m(OA)$	monomer conversion/%	grafting rate/%	dissolution time/min	limiting viscosity number/($mL \cdot g^{-1}$)	M_V
0	4 : 8 : 1.5 : 0	94.2	56.8	24	717.33	4.32×10^6
1	4 : 7.8 : 1.5 : 0.2	93.6	55.6	91	681.21	3.99×10^6
2	4 : 7.6 : 1.5 : 0.4	92.4	55.3	152	624.63	3.50×10^6
3	4 : 7.4 : 1.5 : 0.6	92.4	53.8	226	596.43	3.26×10^6
4	4 : 7.2 : 1.5 : 0.8	92.8	52.5	334	511.72	2.57×10^6
5	4 : 7.0 : 1.5 : 1.0	92.1	51.6	560	423.62	1.92×10^6

It can be seen in Table 2, after cationic monomer DMDACC has been introduced into polymer molecular chain, cationic activity increases, M_V and monomer conversion rate decrease and water solubility increases.

Table 2　Influence of DMDAAC dosage on cationic degree

PSOAMDAS	$m(St)$: $m(AM)$: $m(DMDACC)$: $m(OA)$	monomer conversion/%	grafting rate/%	solubility time/min	limiting viscosity number/($mL \cdot g^{-1}$)	M_V	cationic degree /%
6	4 : 8 : 0 : 0.6	93.7	59.8	176	577.45	3.11×10^6	0
7	4 : 8 : 1 : 0.6	92.5	57.7	140	548.63	2.88×10^6	6.9
8	4 : 8 : 2 : 0.6	91.9	56.3	132	524.92	2.69×10^6	10.6
9	4 : 8 : 3 : 0.6	91.1	54.8	123	496.58	2.47×10^6	13.7
10	4 : 8 : 4 : 0.6	90.1	52.4	117	463.22	2.21×10^6	15.4

2.2　Influence of reaction temperature on grafting performance

The influences of changing reaction temperature at ratio of $m(St)$: $m(AM)$: $m(DMDACC)$: $m(OA)$ 4 : 7.4 : 1.5 : 0.6, content of initiator 3.1 mmol/L, on monomer conversion rate, grafting rate and grafting efficiency are studied. The result is shown in Fig. 1.

It can be seen in Fig. 1, that with the reaction temperature rising, monomer conversion rate, grafting rate and grafting efficiency increase and reach the maximum value at 30 ℃. However, when temperature continues rising, monomer conversion rate, grafting rate and grafting efficiency begin to decrease. This is mainly because continuous rise of reaction temperature will result in: 1) promoting monomers diffusion to the grafting position; 2) speeding up decomposition rate of initiator; 3) increasing initiation and propagation rate of chain; 4) increasing termination rate of chain; 5) increasing homopolymerization rate of monomer and 6) increasing polymerization rate initiated by heating monomer. Among these factors, 1)–(3) raise

— ○ — monomer conversion rate;
— □ — grafting rate;　— △ — grafting efficiency

Fig. 1　Influence of reaction temperature on grafting performance

grafting rate and grafting efficiency, but 5) and 6) reduce grafting rate and grafting efficiency. When temperature is below 30 ℃, 1)–3) play the main role. With temperature going up, grafting rate and grafting efficiency increase. When temperature is above 30 ℃, 4)–6) play the main role, making grafting rate and grafting
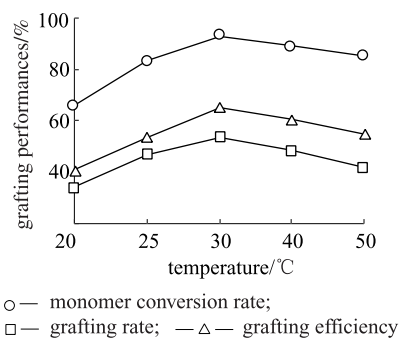
efficiency a descending tendency. This is the reason why figure shows the grafting conversion rate, grafting rate and grafting efficiency of monomer are the highest at 30 ℃.

With other reaction conditions unchanged, determine reaction rate at different temperatures through Arrhenius Equation.

$$R_P = A \exp(-E_a/RT)$$

For the above equation, take logarithm to obtain $\lg R_P = \lg A - (E_a/2.303R)/T$ and make a plot of $\lg R_p$ against $1/T$. The result is shown in linear correlation. Calculate apparent activation energy of graft copolymerization reaction according to the slope of straight line.

$$E_a = 24.76 \text{ kJ/mol}$$

When monocomponent potassium persulfate is used for initiation of polymerization, it must be heated to over 60 ℃. So, polymerization reaction can be quickly completed at low temperature when redox initiator is used.

2.3　Influence of initiator dosage on grafting performance

With concentration of initiator changed at ratio of $m(St):m(AM):m(DMDACC):m(OA)$ 4 : 7.4 : 1.5 : 0.6, grafting temperature 30 ℃, influences on monomer conversion rate, grafting rate and grafting efficiency are studied. The result is shown in Fig. 2.

Taking the monomer content as reference, when redox initiator consisted of $K_2S_2O_8/NaHSO_3$ is used, monomer conversion rate, grafting rate and grafting efficiency are increased while concentrated of initiator is increasing. When dosage of initiator is 3.1 mmol/L, values of monomer conversion rate, grafting rate and grafting efficiency reach their maximum. If the initiator dosage is greater than 3.1 mmol/L monomer content, monomer conversion rate, grafting rate and grafting efficiency of synthesized hydrophobically associated cationic starch (HACS) decrease. During the study, we also found that, if initiator dosage is greater than 4.1 mmol/L monomer content, it is easy to implode, forming blocky gel. The main reason is that, with the increase of the low initiator content, the number of free radical, in the system is increased so that the active centers of grafting reaction due to the reaction of initiator and starch increase. In addition, active centers in the monomer also increase, reaction of chain-growth speeds up and the grafting reaction polymer increases, the monomer conversion rate, grafting rate and grafting efficiency are eventually enhanced. When initiator dosage is more than 3.1 mmol/L, concentration of free radicals produced in the reaction system is too high, the probability of collision increases, which speeds up not only the reaction of chain growth but also the reaction of chain termination. Under this circumstances, implosion occurs easily, even no products can be made. Thus, with the monomer mass as reference, the appropriate initiator dosage is 3.1 mmol/L.

2.4　Influence of reaction time on grafting performance

The influences of changing reaction time at ratio of $m(St):m(AM):m(DMDACC):m(OA)$ 4 : 7.4 : 1.5 : 0.6, content of initiator 3.1 mmol/L, on monomer conversion rate, grafting rate and grafting efficiency are studied. The result is shown in Fig. 3.

In the early stage of reaction, monomer conversion rate, grafting rate and grafting efficiency of mon-
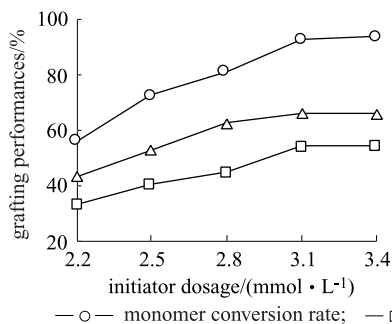

—○— monomer conversion rate;　—□— grafting rate;　—△— grafting efficiency

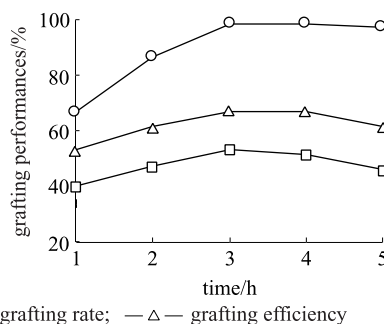**Fig. 2　Influence of initiator dosage on grafting performance**

Fig. 3　Influence of reaction time on grafting performance

omer increase with the reaction time extending. However, in the later stage of reaction, grafting rate increase slowly and grafting efficiency arises the highest value and soon afterwards, present a descending tendency. All these show that in the early stage of reaction, there are many grafting active regions, concentrations of monomer and free radicals are high, chemical route of reaction holds a leading post and grafting reaction goes fast. When reaction time is extended, monomer conversion rate, grafting rate and grafting efficiency of monomer will increase rapidly with prolonging of the reaction time. With the reaction going on, physical route of diffusion and collision of reacting molecules hold a leading post in place of chemical route[12]. In this case, chain propagation is diffusion controlled, the efficiency of initiator decreases signi-ficantly, most free radicals produced by initiator decomposition are consumed by its elementary reaction with dehydrated glucose on large starch molecular chain of the system, and active points of starch free radicals are completely saturated. Polymerization rate decreases gradually and very slowly. Continuous prolonging of reaction time will have no much influence on the reaction. For HACS synthesized by inverse suspension polymerization, the appropriate reaction time is 3 h.

2.5 Characterization of graft copolymerization

2.5.1 Infrared spectra   From the spectra we can see that absorption peak at 3024 cm^{-1} is the stretching vibration absorption of methyl carbon-hydrogen bond of quaternary ammonium group. The absorption peaks at 1481 and 1479 cm^{-1} separately are the stretching vibration absorption of methyl carbon-nitrogen bond of quaternary ammonium group; the absorption peak at 1690 cm^{-1} is the carbonyl stretching vibration absorption, the absorption peak at 1120 cm^{-1} is the C—O—C symmetric stretching vibration absorption of ester group; such absorption peaks, however, cannot be found in the infrared spectrum of starch. All these show that the product is a grafting copolymer and AM/OA/DMDAAC are grafted into the molecular chain of starch and also demonstrates that the separating method and synthesis process are practicable.

2.5.2 X-ray diffraction   Starch has acute diffraction peaks near 17°, 20° in 2θ, indicating that starch has a certain crystallinity. X-ray diffraction diagram of graft copolymer shows a diffuse peak near 23° in 2θ, indicating that PSOAMDA copolymer is an amorphous one. After starch is graft copolymerized with AM/OA/DMDAAC, the state of aggregation of original starch has been changed, indicating that graft copolymerization has taken place between AM/OA/DMDAAC and starch. The result is shown in Fig.4.
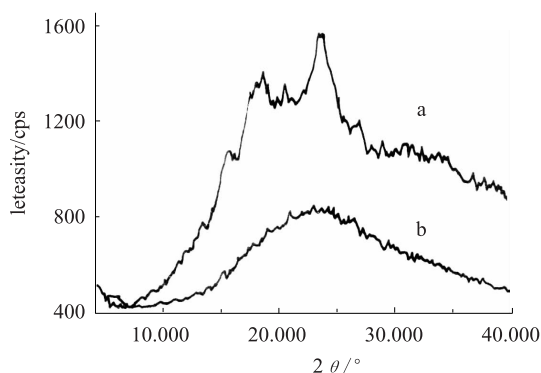

Fig.4 X-ray diffraction of starch (a) and PSOAM-DA (b)

3   Conclusion

3.1   In the molecular chain of polymer, with increase of OA, water solubility decreases and M_V decreases. The higher hydrophobic group content in polymer molecular chain is, the lower the M_V is. After DMDAAC is increased, cationic degree increases, M_V and monomer conversion rate decrease and water solubility increases.

3.2   When redox initiator is used to initiate, the graft copolymerization of starch and AM, DMDAAC, OA can take place quickly at a low temperature. The apparent activation energy: $E_a = 24.76$ kJ/mol.

3.3   HACS was synthesized by inverse suspension polymerization. When the continuous phase was cyclohexane, dispersant was Span 80-Tween 80 and initiator is $K_2S_2O_8/NaHSO_3$ at 3.1 mmol/L, graft temperature 30 ℃, reaction time 3 h, monomer conversions is 92.6 %, grafting rate is 53.8 %, grafting efficiency is 65.4 % and M_V is 3.26×10^6.

3.4 The data from IR and X-ray diffraction show that AM/OA/DMDAAC is grafted into starch chain and also demonstrates that the separating method and synthesis process are practicable.

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