

Microwave Irradiation Copolymerization of Superabsorbents from Cornstarch and Sodium Acrylate

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ABSTRACT: Sodium acrylate was grafted onto cornstarch by microwave irradiation to synthesize a superabsorbent, in which potassium persulfate (PPS) was used as the initiator and polyethyleneglycol diacrylate as the crosslinker. It was found that microwave irradiation could substantially accelerate the synthesis, without the need to remove O₂ or inhibitor. Catalyzed by *p*-toluene sulfonic acid, polyethyleneglycol was esterified with acrylate to synthesize the crosslinker. An orthogonal test of L₉(3⁴) was designed to study the effects of relevant factors on absorbency and yield of products, including microwave power, irradiation time, initiator

amount, and crosslinker content. Microwave power was believed to be the most significant factor affecting the swelling ratio and solubility of the product. Optimized experimental results showed that 10 min of microwave irradiation at 85–90 W could produce a cornstarch-based superabsorbent with a swelling ratio of 520–620 g/g in distilled water and solubility of 8.5–9.5 wt %. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 264–269, 2005

Key words: superabsorbent; microwave irradiation; copolymerization; swelling; synthesis

INTRODUCTION

Superabsorbents are polyelectrolytes with a low degree of crosslinking, which can absorb hundreds or thousands of times their own weight in water. This characteristic allows superabsorbents to be widely used in many fields, such as farming and forestry, horticulture, medicine, articles for hygiene, industry, biology, and environmental cleanup.

Currently, the common way to produce superabsorbents is through solution polymerization^{1–7} or inverse suspension polymerization,^{8–11} which requires long reaction times and large amounts of organic solvent as precipitator or dispersed phase that is difficult to dispose of later. Removal of inhibitor and purging with nitrogen are required as well.

Microwave irradiation can heat reactants selectively, directly, without thermal inertia, and without the involvement of a heat exchange medium. It has been found that a variety of organic reactions could be conducted efficiently in a few minutes in unsealed vessels at ambient pressure in unmodified microwave ovens by using selected organic solvents.¹² Jacob et al.¹³ studied the polymerizing reaction of methyl ac-

rylate initiated by microwave. Their results showed that the reaction rate increased from 138 to 275% compared with that of the conventional thermal cure. Lu et al.¹⁴ studied microwave radiation solid-state copolymerization of maleic anhydride (MAH) and maleate (MDE) and found that the yield increases when the monomer ratio is 1:1 because copolymerization is easy to be conducted under microwave radiation.

In this article, we report the application of microwave irradiation in preparing superabsorbents from acrylate acid and cornstarch, and investigation of the factors that affected the swelling ratio and solubility of superabsorbent products, such as microwave power, irradiation time, and composition of reactants.

EXPERIMENTAL

Materials

Acrylic acid (AA) was purified by distillation under reduced pressure to remove the inhibitor before use. Polyethyleneglycol diacrylate was prepared in our laboratory and used as the crosslinker in copolymerization. Other chemical agents were used as purchased without further purification. All solutions were prepared in distilled water.

Synthesis of polyethyleneglycol diacrylate

Polyethyleneglycol (600 g/mol) and acrylic acid were mixed in a three-neck flask at a molar ratio of 1 : 2.6 for

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15–20 min, after which *p*-toluene sulfonic acid (4 wt %), benzene (20 wt %), and quinol (0.5 wt %) were added to the reaction mixture. The reaction temperature was maintained at 80–85°C for 4–5 h until no additional water was distilled off. The reaction product was diluted with water to the concentration of 0.4 vol % and was used in experiments for preparing superabsorbents.

Synthesis of superabsorbents

Preparations of starch slurry and sodium acrylate were carried out separately in a thermostatic apparatus with magnetic stirrer. Sodium acrylate was prepared by dropping sodium hydroxide (10N) slowly into acrylic acid while stirring in a cool-water bath. In a 100-mL PTFE beaker, starch was mixed with a certain volume of crosslinker solution (0.4 vol %) and initiator solution (0.1 mol/L). Then sodium acrylate was added to the beaker and thoroughly mixed with the slurry in the water bath. Until the temperature of the mixture was about 30°C, the beaker was placed in a microwave oven at a certain location and was irradiated for a prescribed time. The microwave oven was a model WHLO7S-3 (Sanle General Electric Corp., Nanjing, China), with a microwave frequency of 2450 MHz and a power output from 0 to 700 W with continuous adjustment.

After a given time of irradiation, the product was removed from the microwave oven and immersed in ethanol for at least 4 h, then dried at 60°C for 12 h. All samples were triturated, ranging from 80 to 100 mesh, and dried in an oven at 60°C for at least one day before the tests.

Duplicable tests were applied to guarantee the reliability of the experiments, and the data were mean values of the experimental results.

Measurement of swelling ratio and solubility of superabsorbent

The weighed sample (W_{SAP}^0 , generally about 0.1 g) was immersed in 200 mL distilled water. When equilibrium was reached 4 h later, the excess water in the hydrogel–water mixture was filtered out through a nylon filter silk of 100 mesh. Then, the swollen gel (W_{GEL}) left behind was placed in a beaker of known weight (W_b) and the total weight ($W_{\text{GEL}} + W_b$) was measured. Subsequently, this beaker was dried in an oven at 60°C until the beaker weight ($W_{\text{SAP}}^1 + W_b$) was constant. From the difference of the weight ($W_{\text{SAP}}^0 - W_{\text{SAP}}^1$) of the sample, solubility of the superabsorbent can be calculated according to following formula:

$$\text{Solubility (\%)} = \frac{W_{\text{SAP}}^0 - W_{\text{SAP}}^1}{W_{\text{SAP}}^0} \times 100$$

The swelling ratio (Q) was calculated according to following formula:

$$Q = \frac{W_{\text{GEL}}}{W_{\text{SAP}}^1} = \frac{(W_{\text{GEL}} + W_b) - W_b}{W_{\text{SAP}}^1} \quad (\text{g/g})$$

RESULTS AND DISCUSSION

Orthogonal test and result analysis

Swelling ratio and solubility are two essential criteria to evaluate the superabsorbent product. Swelling ratio is equal to water absorbency, and solubility reflects the yield of the superabsorbent product. Because of low chain mobility, 100% yields cannot reasonably be obtained. The soluble reaction products are a kind of waste and would have a negative effect on the practical application of superabsorbents. In our experiments, we found that solubility of a superabsorbent might correlate with its own swelling ratio: a high-solubility product often has a high swelling ratio. However, the high solubility of product means a lower yield. Thus, the optimization target of synthesis process is to produce a superabsorbent of high swelling ratio with low solubility.

It has been observed from previous experiments^{15,16} that, when the proportion of sodium acrylate and starch is fixed, the swelling ratio and solubility of a superabsorbent are more related with microwave power, irradiation time, the amount of crosslinker, and initiator. To optimize the process conditions, an orthogonal test of $L_9(3^4)$ was designed to explore how those factors affect the yield of a superabsorbent product. The orthogonal test plan and result analysis is shown in Table I.

In Table I, \bar{Q}_i is the mean of swelling ratio at i level and $\Delta\bar{Q}$ is the extreme deviation. \bar{S}_i is the mean of solubility at i level and $\Delta\bar{S}$ is the extreme deviation. All samples were prepared with 1 g cornstarch, 4 mL acrylic acid, and 4.65 mL (1N) NaOH.

The experimental results in Table I show that sample 5 under the reacting condition of $A_2B_2C_3D_1$ has the lowest solubility (8.1 wt %), but its swelling ratio is lower (389 g/g); sample 2 under the reacting condition of $A_1B_2C_2D_2$ has the largest swelling ratio (614 g/g), but higher solubility (29.9 wt %).

According to the maximum of average swelling ratio of each factor in Table I, the condition for synthesizing the largest swelling ratio superabsorbent should be $A_1B_3C_2D_3$, and the condition for synthesizing the lowest solubility superabsorbent should be $A_2B_2C_3D_1$. Obviously, the two compositions have no identical point at all. It can be observed from the extreme deviation of each factor that the significant sequence of factors affecting swelling ratio of product is $A > B > C > D$ and that of factors affecting solubility of product is $A > D > B > C$.

TABLE I
Orthogonal Test Plan and Result Analysis

Factor	Test plan				Test result	
	Microwave power (W)	Irradiation time (min)	Crosslinker solution volume (mL)	Initiator solution volume (mL)	Swelling ratio (g/g)	Solubility (%)
Symbol No.	A	B	C	D	Q	S
1	1 (85)	1 (12)	1 (0.5)	1 (0.2)	501	26.3
2	1 (85)	2 (10)	2 (1.0)	2 (0.5)	614	29.9
3	1 (85)	3 (8)	3 (1.5)	3 (1.0)	603	32.0
4	2 (100)	1 (12)	2 (1.0)	3 (1.0)	463	16.5
5	2 (100)	2 (10)	3 (1.5)	1 (0.2)	389	8.1
6	2 (100)	3 (8)	1 (0.5)	2 (0.5)	565	28.0
7	3 (115)	1 (12)	3 (1.5)	2 (0.5)	336	30.8
8	3 (115)	2 (10)	1 (0.5)	3 (1.0)	484	30.9
9	3 (115)	3 (8)	2 (1.0)	1 (0.2)	475	25.5
\bar{Q}_1	573	433	516	455		
\bar{Q}_2	472	496	517	505		
\bar{Q}_3	432	548	443	516		
ΔQ	141	115	74	61		
\bar{S}_1	29.4	24.5	28.4	20.0		
\bar{S}_2	17.5	23.0	27.3	29.6		
\bar{S}_3	29.1	28.5	23.6	26.5		
ΔS	11.9	5.5	4.8	9.6		

Figures 1–4 show effects of each factor on swelling ratio and solubility of products that were drawn according to Table I. Microwave power produces the most important effect on swelling ratio and solubility of the superabsorbent product. Figure 1 shows that, with decreasing microwave power, the swelling ratio of product obviously increases, and the solubility reaches the lowest point at 100 W. That means a product of large swelling ratio and low solubility should be obtained at a microwave power that is within 85–100 W.

From Figure 2, it can be seen that the swelling ratio of product would increase when irradiation time is shortened, but the solubility of product reaches its lowest point when the irradiation time lasts for 10 min. Although irradiation time has greater effects on

swelling ratio than on solubility of product, the solubility would increase 24%, and the swelling ratio, 10.5%, when irradiation time varies from 8 to 10 min. Therefore, a 10-min irradiation is more suitable.

In Figure 3, it can be seen that as the amount of crosslinker increases from level 1 to level 2, swelling ratio shows negligible change and solubility has a slight decrease. From level 2 to level 3, the swelling ratio decreases 16.7% and solubility decreases 15.7%. Considering that the crosslinker is not the dominant factor that affects swelling ratio and solubility of product under microwave irradiation, it is more suitable that the amount of crosslinker is fixed at level 2 (1 mL, 0.4 vol %).

Of the four factors tested, the amount of initiator plays the lightest role in affecting swelling ratio and ranks the second in affecting solubility of product. It is

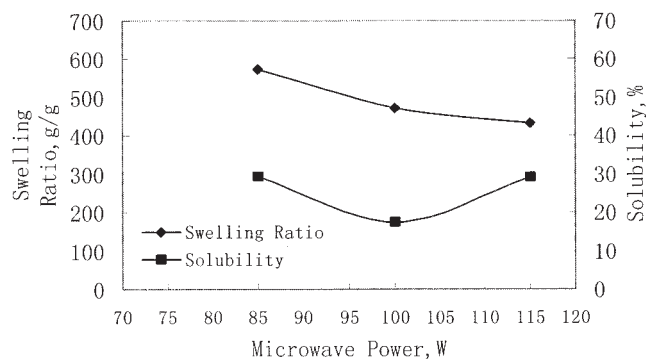


Figure 1 Effect of microwave power on swelling ratio and solubility.

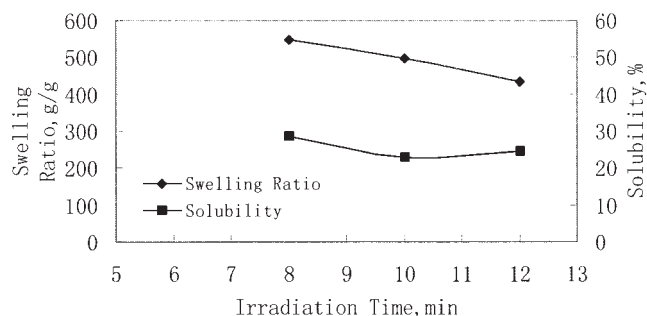


Figure 2 Effect of irradiation time on swelling ratio and solubility.

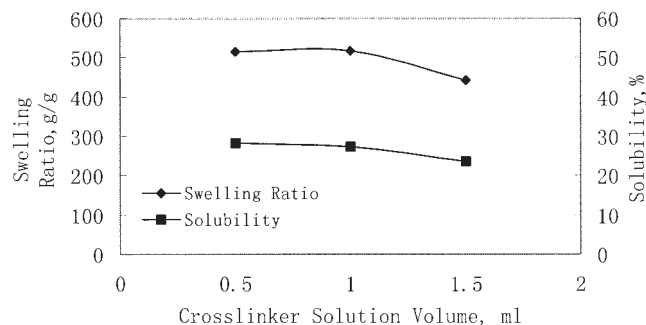


Figure 3 Effect of crosslinker content on swelling ratio and solubility.

shown from Figure 4 that as the amount of initiator increases from level 1 to level 2, swelling ratio and solubility of products both show an increase. From level 2 to level 3, swelling ratio increases and solubility decreases. Thus, the amount of initiator should be increased.

To summarize, a scheme to optimize the experimental conditions for synthesizing superabsorbent with large swelling ratio and low solubility should be as follows: the volume of initiator solution (1.0 mol/L), 1.2 mL; the volume of crosslinker solution (0.4 vol %), 1.0 mL; irradiation time, 10 min; microwave power, 80, 85, 90, 95, and 100 W.

From Table II, it can be seen that within the microwave power from 85 to 90 W, the superabsorbent product with high swelling ratio (527–625 g/g) and low solubility (8.5–9.5 wt %) can be obtained.

Feasibility of eliminating the deaeration process in microwave irradiation copolymerization

In the conventional process of radical polymerization, nitrogen was used to deaerate the reaction mixture to eliminate the inhibiting effect of oxygen on radical polymerization. When the copolymerization of sodium acrylate and starch was carried out under microwave radiation, it was found that there was no obvious influence on the reaction rate and the swelling ratio of products if oxygen-purging process was elim-

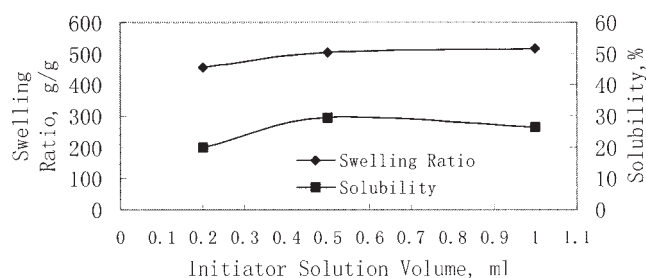


Figure 4 Effect of initiator content on swelling ratio and solubility.

TABLE II
Result of Optimized Experiment

Microwave power (W)	Swelling ratio (g/g)	Solubility (%)
80	670	17
85	625	9.5
90	527	8.5
95	496	9.5
100	488	11

inated. Table III shows the comparison result between the process when oxygen purging is applied and the process when oxygen purging is eliminated. Other reaction conditions were the same as in Table II.

From Table III, it can be seen that the results have no obvious difference whether oxygen is removed or retained. Thus, the process of deaerating with nitrogen can be cancelled when microwave irradiation is applied to prepare a superabsorbent.

Feasibility of using unpurified monomer in microwave irradiation copolymerization

Commonly, 0.01–0.1 wt % of inhibitor must be added to monomers to prevent unwanted self-polymerization during transportation or storage; thus, the monomer should usually be purified before used in polymerization. The acrylic acid that we used in our experiment should be purified by vacuum distillation. Moreover, this process would consume a considerable amount of energy. In our experiment, we tried to use unpurified acrylic acid. Table IV shows the comparison results of polymerization that used purified monomer, unpurified monomer, and purified monomer added with a certain amount of inhibitor (quinol). Other reaction conditions were the same as in Table II.

Obviously, the results shown in Table IV demonstrate the feasibility of using unpurified monomer (with 0.01–0.1 wt % of inhibitor) in microwave irradiating polymerization.

Effect of different initiators in microwave irradiation copolymerization

Beside $K_2S_2O_8$, other initiators, such as $(NH_4)_2S_2O_8$, $(NH_4)_2Ce(NO_3)_6$, and $KMnO_4$, were used in reactions

TABLE III
Comparison Between the Results with and Without N_2 Protection of the Reaction

Microwave power (W)	Input nitrogen	Swelling ratio (g/g)	Solubility (%)
85	Yes	607	9.1
85	No	625	9.5

TABLE IV
Comparison Results of Polymerization with and Without Inhibitor

Microwave power (W)	Irradiation time (min)	Inhibitor concentration (wt %)	Swelling ratio (g/g)	Solubility (wt %)
85	10	0	625	9.5
85	10	0.01–0.1 (unpurified)	596	9.1
85	10	0.05	640	9.4

of producing superabsorbents under microwave irradiation. The reaction condition was the same as that used earlier, although the results show that they are not as effective as $K_2S_2O_8$. The products appeared as powders and the swelling ratio was quite low; the results are shown in Table V. Therefore, $K_2S_2O_8$ is more suitable for initiating copolymerization under microwave irradiation.

Comparative experiment of synthesizing superabsorbents by conventional heating

In the experiments of synthesizing superabsorbents by microwave irradiation, it was found that the reactant temperatures measured at the end of reaction ranged from 85 to 95°C. In light of this temperature range, a comparative experiment of synthesizing superabsorbent by conventional heating was conducted at 90°C in a water bath, with the same formula as that of experiments by microwave irradiation, and the result is shown in Figure 5.

From the result of the comparative experiment, it was found that the product's swelling ratio first increased with polymerizing time up to 70 min, and then decreased. The solubility of product showed a trend of slow reduction with prolonged reaction time. Compared with the solubility of product synthesized by microwave irradiation (shown in Table II), it was still high even after the reaction lasted for 130 min, and at the same time the swelling ratio did not continuously increase, but began to decrease after 70 min of reaction. The comparative experiment also showed that, at higher temperature (90°C), the copolymerization could be quickly initiated even when the inhibitor in acrylic acid was not removed and deaeration process was cancelled. That is to say, high reaction temperatures make feasible the copolymerization using unpurified acrylic acid. By comparing the results of

the two experiments, it can be concluded that microwave irradiation has the advantage of quickly synthesizing a superabsorbent with higher swelling ratio and lower solubility.

CONCLUSIONS

In the process of synthesizing superabsorbents by microwave irradiation, the significant sequence of effective factors for swelling ratio is microwave power > irradiation time > crosslinker content > initiator content; and the sequence of factors for solubility is microwave power > initiator content > irradiation time > crosslinker content. To produce a superabsorbent with higher swelling ratio and lower solubility, the most suitable microwave power is within the range of 85–90 W and the irradiation time is 10 min.

Compared with conventional heating, microwave irradiation copolymerization for synthesizing superabsorbents from sodium acrylate and cornstarch can produce products with higher swelling ratio and lower solubility. It can also greatly improve the reaction rate, without the need to purge with nitrogen, and to remove inhibitor. All these advantages would simplify the process of preparing superabsorbents, reduce the consumption of energy and water, and discharge little waste liquid. Microwave irradiation copolymerization, therefore, can serve as a cleaner production technique and can be more suitably used in industrial applications.

TABLE V
Effect of Various Initiators on Swelling Ratio of Products

Initiator	$(NH_4)_2S_2O_8$	$(NH_4)_2Ce(NO_3)_6$	$KMnO_4$
Swelling ratio, $g\ g^{-1}$	115	62	30

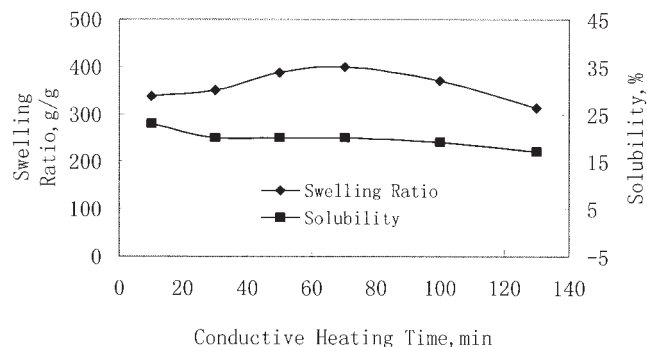


Figure 5 Effect of conductive heating time on swelling ratio and solubility of products.

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