

Optimization of the Preparation of a Poly(aspartic acid) Superabsorbent Resin with Response Surface Methodology

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ABSTRACT: A poly(aspartic acid) superabsorbent resin was synthesized with polysuccinimide through chemical crosslinking with a crosslinking agent (diamine). The optimization of its preparation was investigated with response surface methodology. According to the Plackett–Burman design, the crosslinking temperature, drying temperature, and dissolving time of polysuccinimide had significant influences on the swelling ratio of the poly(aspartic acid) resin, which was the criterion for describing the water

absorption capacity. Central composite design and response surface analysis were employed subsequently to further optimize the three aforementioned factors. A maximum swelling ratio greater than 500 g/g was attained; this was more than a 60% increase in comparison with previous results. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2616–2622, 2006

Key words: crosslinking; resins; swelling

INTRODUCTION

Biodegradable polymers have attracted interest as globe-compatible materials in recent years.^{1,2} Poly(aspartic acid) (PAsp), with many free carboxylic acid groups or amino groups, comes from a natural amino acid. As a modification of it, the PAsp superabsorbent resin also has good biodegradability. In addition, it is able to become its monomer (aspartic acid) in water or soil. Therefore, it is commonly used in soil conservation and in the manufacturing of diapers, sanitary napkins, medicals, cosmetics, fabrics, metal absorbent materials, and so on.^{3–5} The material's biodegradability is an important focus of the research in this field because of the renewed attention toward environmental protection issues,⁶ so the PAsp superabsorbent resin has been studied actively in recent years.

The properties of the PAsp resin depend on various experimental conditions. The general single-variable optimization is carried out through the variation of one parameter while the others are kept constant. The disadvantage of this optimization is that it does not reflect the interaction effects among all variables and does not describe the net effect of the various conditions on the swelling ratio, which is the criterion for describing the water absorption capacity and is the most important property of a superabsorbent. To overcome these problems, our optimization studies have been carried out with response surface methodology (RSM), which is a mathematical and statistical technique widely employed to reflect the effects of several variables and to optimize different biotechnological processes.^{7–14} In particular, it has been commonly used to study the optimization of physiochemical parameters and factors of many fermentation culture media and processes with various microorganisms.^{14–17} However, this method has not been used to optimize the preparation of a novel PAsp resin.

In an earlier magnifying study, when small-scale experiments were magnified 20-fold, the maximum swelling ratio could reach as high as 300 g/g. The aim of this optimization was enhancing the swelling ratio of the magnifying experiment. In this work, RSM included the Plackett–Burman (P–B) design, the path of steepest ascent, and central composite design (CCD), which was employed for optimizing the preparation of the PAsp superabsorbent resin.

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EXPERIMENTAL

Materials

Polysuccinimide (PSI) with a high molecular weight was prepared in our laboratory.¹⁸ *N,N*-Dimethylformamide (DMF), the crosslinking agents (diamine), sodium hydroxide, and methanol (all from Beijing Chemical Co., Beijing, China) were analytical-grade.

Preparation of the PAsp superabsorbent resin

The PAsp resin was prepared from PSI with a molecular weight of 199,500, which was synthesized by the thermal polycondensation of L-aspartic acid.^{18,19} As the raw material, 1.0 g of PSI was dissolved in 32 mL of an organic, aprotic, polar solvent, such as *N,N*-dimethylformamide (DMF), in a beaker with a magnetic stirring bar. Deionized water (8 mL) as a dispersant was added to the beaker. A mixture containing PSI, DMF, and deionized water was stirred for half an hour. Then, the crosslinking agent (diamine) was added to the beaker, and the crosslinking reaction was carried out for 2 h at 36.6°C so that the crosslinked polymer would be formed. Next, the imide ring of the crosslinked polymer was hydrolyzed with a NaOH solution until the emulsion's pH was 9. Then, about 200 mL of methanol was poured into the solution, and the precipitate was recovered by filtration and dried at 100°C under a vacuum condition. In this way, a crosslinked PAsp resin as a superabsorbent polymer was obtained. These optimum parameters were determined by this optimization experiment.

Swelling measurements

The swelling ratio is the criterion for describing the water absorption capacity. The measurement of the swelling ratio of the PAsp resin was conducted at 22°C by the tea-bag method, with deionized water as the liquid to be absorbed. The tea bags used in this method were made of a 300-mesh nylon net and

were 40 cm in diameter. The weight of the wet nylon net was measured and marked as W_n . The weight of the dry PAsp resin was marked as W_0 . The dry resin was placed in the tea bag, and then the tea bag with the sample was hung on a rail and fully immersed in deionized water at 22°C. After 24 h, the tea bag was taken out and hung in the air for 15 min, and then the weight of the tea bag, including the swollen resin, was measured and marked as W_t . The swelling ratio of the PAsp resin was calculated as follows:

$$\text{Swelling ratio (g/g)} = (W_t - W_0 - W_n)/W_0 \quad (1)$$

P-B design

In previous experiments,¹⁹ to obtain a high swelling ratio of the PAsp superabsorbent, various parameters were studied. Earlier results indicated that the major parameters with some effect on the swelling ratio of the product were the solvent volume, dissolving time of PSI, crosslinking temperature, stirring speed, dispersant volume, mass of the crosslinking agent, crosslinking time, terminal pH, precipitation time, and drying temperature. Moreover, other factors had almost no influence. Therefore, these 10 factors were chosen for optimizing the production process to increase the swelling ratio.

Drying is the last step of this production process and is a physical process that is applied to the product. On the basis of our previous experiments, vacuum drying is best for increasing the swelling ratio. In addition, its temperature has a significant effect on the swelling ratio. It was combined with other parameters in one optimization section, which resulted from the aim of this work (improving the swelling ratio of the PAsp superabsorbent resin).

As a two-level experimental design, the P-B design requires fewer runs than the comparable fractional design. It can be employed to determine more important independent variables from many candidate factors to carry out a complete factorial design.

The influences of the aforementioned 10 variables on the swelling ratio were investigated with the

TABLE I
Ten Independent Variables and Their Values at the Different Coded Levels

Independent variable	Symbol	Coded level		
		-1	0	+1
Solvent volume (mL)	X_1	32	36	40
Dissolving time of PSI (h)	X_2	16	24	32
Crosslinking temperature (°C)	X_3	40	45	50
Stirring speed (rpm)	X_4	600	675	750
Dispersant volume (mL)	X_5	8	9	10
Mass of the crosslinking agent (g)	X_6	0.076	0.0855	0.095
Crosslinking time (h)	X_7	2	2.25	2.5
Terminal pH	X_8	9	10	11
Precipitation time (h)	X_9	48	54	60
Drying temperature (°C)	X_{10}	85	110	135

TABLE II
Matrix of the P-B Design Experiments and Experimental Data

Run	X ₁	X ₂	X ₃	X ₄	X ₅	X ₆	X ₇	X ₈	X ₉	X ₁₀	Dummy variable	Swelling ratio (g/g)
1	40	16	50	600	8	0.076	2.5	11	60	85	1	220.30
2	40	32	40	750	8	0.076	2	11	60	135	-1	438.57
3	32	32	50	600	10	0.076	2	9	60	135	1	203.80
4	40	16	50	750	8	0.095	2	9	48	135	1	200.27
5	40	32	40	750	10	0.076	2.5	9	48	85	1	451.25
6	40	32	50	600	10	0.095	2	11	48	85	-1	251.74
7	32	32	50	750	8	0.095	2.5	9	60	85	-1	277.61
8	32	16	50	750	10	0.076	2.5	11	48	135	-1	199.52
9	32	16	40	750	10	0.095	2	11	60	85	1	395.19
10	40	16	40	600	10	0.095	2.5	9	60	135	-1	331.96
11	32	32	40	600	8	0.095	2.5	11	48	135	1	391.96
12	32	16	40	600	8	0.076	2	9	48	85	-1	413.90

methodology of P-B. Each independent variable was tested at two coded levels: a high level (+1) and a low level (-1). For this design with 10 factors at two levels, 12 experimental runs were carried out. One dummy variable was used to evaluate the experimental error and check the adequacy of the first-order model. The 10 independent variables and their values at different coded levels of the P-B design experiments are shown in Table I.

Table I lists the 0 level. However, this was not contradictory to the P-B design theory because it was not shown in the matrix of the P-B design, and it was only the base point for the following path of steepest ascent (descent). All experimental data were treated with Statistical Analysis System (SAS) 8.0 from the SAS Institute, Inc. (Cary, NC). The quality of fit of the first-order model equation was expressed by the coefficient of determination (R^2), and its statistical significance was determined with an F test. The significance of the regression coefficients was evaluated with a t test.¹³

Path of steepest ascent (descent)

This is a procedure for moving sequentially along the path of steepest ascent (descent), that is, in the direction of the maximum increase (decrease) in the response. According to the results obtained from the P-B design, the fitted first-order model is

$$Y = \beta_0 + \sum_{i=1}^k \beta_i x_i \quad (2)$$

where Y is the predicted response, β_0 and β_i are constant coefficients, and x_i is the coded independent variable or factor k is number of variables. The direction of steepest ascent (descent) is the direction in which Y increases (decreases) most rapidly. This direction is parallel to the normal to the fitted response surface. As the path of steepest ascent

(descent), one usually takes the line through the center of the region of interest and normal to the fitted surface. Thus, the steps along the path are proportional to β_i . The path of steepest ascent (descent) starts from the zero level in the P-B design.¹³

To move away from the zero level along the path of steepest ascent (descent), we move -4°C , -5°C , and 2 h in the crosslinking temperature, drying temperature, and dissolving time of PSI directions, respectively. These three factors, which, to a great extent, influence the swelling ratio of the PAsp resin, were obtained through the P-B design. These step units were determined by the value range of the unity level from the first design and the regression coefficients from the first-order model equation.

CCD and response surface analysis

A CCD with five coded levels was used for investigating the region of the response surface in the neighborhood of the optimum. For the three aforementioned factors (crosslinking temperature, drying temperature, and dissolving time of PSI), this design should be a full 2^3 factorial design with six axial

TABLE III
Significance of the Regression Coefficients of the First-Order Model

Factor	t	Pr > t	Significance level (%)
Solvent volume	0.24	0.8503	14.97
Dissolving time of PSI	5.02	0.1251	87.49
Crosslinking temperature	-21.17	0.0301	96.99
Stirring speed	2.94	0.2085	79.15
Dispersant volume	-2.16	0.2760	72.4
Mass of the crosslinking agent	-1.56	0.3637	63.63
Crosslinking time	-0.61	0.6509	34.91
Terminal pH	0.37	0.7767	22.33
Precipitation time	-0.82	0.5645	43.55
Drying temperature	-4.83	0.1300	87

TABLE IV
Experimental Results for the Path of Steepest Ascent (Descent)

	Crosslinking temperature (°C)	Drying temperature (°C)	Dissolving time of PSI (h)	Swelling ratio (g/g)
1. Base point (zero level in the P-B design of Table I)	45	110	24	
2. Origin step unit (concentration range of the unity level)	5	25	8	
3. Slope (estimated coefficient ratio from the equation)	-91.6325	-21.15917	21.9825	
4. Corresponding concentration (origin step unit × slope)	-458.1625	-528.97925	175.86	
5. New step unit (corresponding concentration × 0.01) ^a	-4.581625	-5.2897925	1.7586	
6. Practical step unit (elimination of decimal digits of the new step unit)	-4	-5	2	
Experiment 1	45	110	24	289.01
Experiment 2	41	105	26	411.77
Experiment 3	37	100	28	482.12
Experiment 4	33	95	30	404.34
Experiment 5	29	90	32	310.09
Experiment 6	25	85	34	196.40

^a 0.01 is a factor determined by the experimenter on the basis of process knowledge or other practical considerations.

points (so-called star points) and six replications of center points, leading to a total number of 20 experiments. The experimental results of the CCD were fitted with a second-order polynomial equation by a multiple regression technique:

$$Y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i x_i + \sum_{i < j} \beta_{ij} x_i x_j \quad (3)$$

where Y is the predicted response; β_0 , β_i , β_{ii} , and β_{ij} are constant coefficients; and x_i and x_j are the coded independent variables or factor k is number of variables. The quality of fit of the second-order model equation was expressed by R^2 , and its statistical significance was determined with an F test. The significance of the regression coefficients was evaluated with a t test.¹³

The design matrix, shown later in Table VI, was obtained with the SAS 8.0 software. A second-order polynomial model was obtained by multiple regression analysis of the experimental data with the same software.

RESULTS AND DISCUSSION

P-B design

The experimental results with the P-B design are shown in Table II. Analyzed by the SAS 8.0 software,

a first-order model was fitted to the data obtained from the experiment. The effects of the 10 factors were calculated. We obtained the following model in the coded variables (first-order model equation):

$$Y_1(\text{g/g}) = 314.7058 + 2.015833X_1 + 42.28257X_2 - 178.3325X_3 + 24.76025X_4 - 18.19167X_5 - 13.05083X_6 - 5.105833X_7 + 3.125833X_8 - 6.900833X_9 - 40.73917X_{10} \quad (4)$$

where X_1 is the solvent volume, X_2 is the dissolving time of PSI, X_3 is the crosslinking temperature, X_4 is the stirring speed, X_5 is the dispersant volume, X_6 is the mass of crosslinking agent, X_7 is the crosslinking time, X_8 is the terminal pH, X_9 is the precipitation time, and X_{10} is the drying temperature. This fit of the model was checked with R^2 , which was calculated to be 0.9585, indicating that 95.85% of the variability in the response could be explained by the model. The statistical significance of the first-order model equation was evaluated with the F -test analysis of variance (ANOVA), which revealed that this regression was statistically significant ($P = 0.042323$) at the 95.77% confidence level.

The t test was used to identify the significance of the regression coefficients, Pr is Probability and the results are shown in Table III. The dissolving time of PSI, crosslinking temperature, and drying temperature were the three most important factors.

TABLE V
Three Variables and Their Values at Different Coded Levels

Factor	Symbol	Range or level				
		-1.6818	-1	0	+1	+1.6818
Crosslinking temperature (°C)	U_1	33.6364	35	37	39	40.3636
Drying temperature (°C)	U_2	83.182	90	100	110	116.818
Dissolving time of PSI (h)	U_3	24.6364	26	28	30	31.3636

TABLE VI
Matrix of the CCD Experiment and Corresponding Experimental Data

Run	U_1 (°C)	U_2 (°C)	U_3 (h)	Swelling ratio (g/g)
1	35	90	26	409.925
2	35	90	30	409.12
3	35	110	26	404.95
4	35	110	30	407.61
5	39	90	26	401.72
6	39	90	30	398.29
7	39	110	26	401.24
8	39	110	30	403.84
9	33.6364 \approx 33.6	100	28	409.27
10	40.3636 \approx 40.4	100	28	413.17
11	37	83.182 \approx 83.2	28	436.33
12	37	116.818 \approx 116.8	28	436.80
13	37	100	24.6364 \approx 24.6	436.32
14	37	100	31.3636 \approx 31.4	475.62
15	37	100	28	501.04
16	37	100	28	499.23
17	37	100	28	505.86
18	37	100	28	507.96
19	37	100	28	505.23
20	37	100	28	502.66

Path of steepest ascent (descent)

The aforementioned first-order model equation and three important factors were used to find a proper direction for changing the variables. The path of steepest ascent started from the zero level in the P-B design and moved along the path on which the dissolving time of PSI increased, whereas the crosslinking temperature and drying temperature decreased. The design and experimental results are shown in Table IV. The highest swelling ratio was 482.12 g/g when the parameters were a dissolving time of PSI of 28 h, a crosslinking temperature of 37°C, and a drying temperature of 100°C. This suggests that the point was near the region of the maximum swelling ratio response.

CCD and response surface analysis

CCD was conducted in the optimum vicinity to locate the true optimum parameters of the crosslinking temperature, drying temperature, and dissolving time of PSI for PAsp superabsorber preparation. The levels of the variables for the CCD experiments were selected according to the results of the previous experiments. The CCD design and the corresponding experimental data are shown in Tables V and VI. Among these three factors, the crosslinking temperature and drying temperature are more important than the dissolving time of PSI.

The experimental results of the CCD design were fitted with a second-order polynomial equation.

$$\begin{aligned}
 Y_2(\text{g/g}) = & -16589.1 + 698.7801U_1 \\
 & + 54.71199U_2 + 356.1769U_3 - 9.532306U_1^2 \\
 & + 0.072219U_1U_2 - 0.167812U_1U_3 \\
 & - 0.291691U_2^2 + 0.118687U_2U_3 - 22.30768U_3^2 \quad (5)
 \end{aligned}$$

where U_1 is the crosslinking temperature, U_2 is the drying temperature, and U_3 is the dissolving time of PSI. The fit of the model was checked by R^2 , which was calculated to be 0.9278. Its statistical significance was determined with the F -test ANOVA, which revealed that this regression was statistically significant ($P = 0.000135$) at the 99.99% confidence level. The result is shown in Table VII.

Table VIII shows the significance of the regression coefficients of the model. The squares of the crosslinking temperature and the drying temperature had high significance (their P values both were 0.0001) for the swelling ratio; however, the interaction effects of each factor had no significance. On the one hand, in the preparation process, the crosslinking

TABLE VII
ANOVA for the Second-Order Polynomial Equation

Source	DF	SS	MS	F	Pr > F
Model	9	34,582.07	3,842.452	14.28412	0.000135
Error	10	2,690.017	269.0017		
Total	19	37,272.09			

$R^2 = 92.78\%$; DF = degree of freedom; SS = sum of squares; MS = mean square.

TABLE VIII
Significance of the Regression Coefficients of the
Second-Order Model

Term	Estimate	Standard error	<i>t</i>	Pr > <i>t</i>
U_1	-1.4623	4.438153	-0.32948	0.748587
U_2	-0.04631	4.438153	-0.01043	0.99188
U_3	4.913631	4.438153	1.107134	0.294156
U_1^2	-38.1292	4.320426	-8.82534	0.0001
U_1U_2	1.444375	5.798725	0.249085	0.808336
U_1U_3	-0.33563	5.798725	-0.05788	0.954985
U_2^2	-29.1691	4.320426	-6.75144	0.0001
U_2U_3	1.186875	5.798725	0.204679	0.841929
U_3^2	-22.3077	4.320426	-5.16331	0.000423

reaction, during which the network polymer forms, is the most important. Of course, the crosslinking agent is also a main factor. According to previous experiments, however, the crosslinking agent masses in the aforementioned P-B experiments are near the region of the optimal swelling ratio response, so their influence is less distinct.

On the other hand, the drying temperature influences the terminal form of the products. The swelling process is complicated and involves three successive steps: (1) the diffusion of water molecules into a polymer system, (2) the subsequent relaxation of hydrated polymer chains, and (3) the expansion of the polymer network into an aqueous solution.²⁰⁻²⁴ At the lower drying temperature, a dense layer forms on the surface, preventing heat and mass transfer from the aqueous medium to the inner part of this absorber.²⁵ The diffusion of free water into the polymeric network is blocked, so its swelling ratio is less than that of the product obtained at the higher drying temperature.

The response surfaces described by eq. (5) are represented in Figure 1. It shows the effects of the interac-

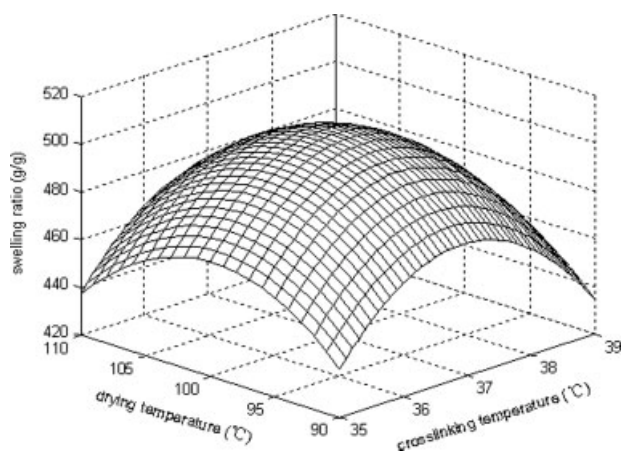


Figure 1 Response surface plot described by model Y_2 , which represents the effect of the crosslinking temperature and drying temperature on the swelling ratio of the PAsp superabsorbent resin. The swelling equilibrium experiments were carried out in deionized water at 22°C.

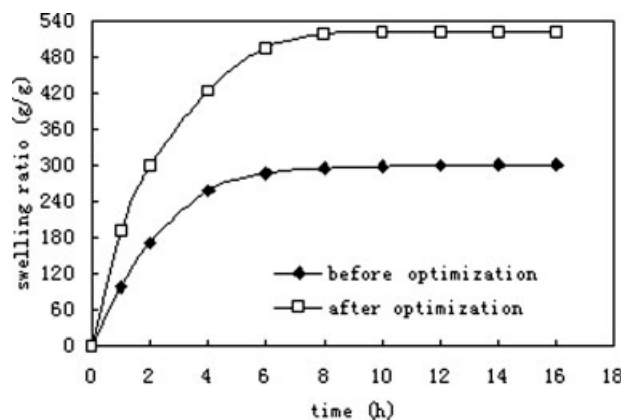


Figure 2 Swelling ratio as a function of time for the PAsp superabsorbent resin in a 20-fold magnifying system (\diamond) before and (\square) after optimized preparation. The swelling equilibrium experiments were carried out in deionized water at 22°C.

tion of the crosslinking temperature and drying temperature on the water absorption capacity of the PAsp resin and indicates that the maximum swelling ratio was approximately 500 g/g. The three optimal parameters (the crosslinking temperature, drying temperature, and dissolving time of PSI) obtained from the maximum point of the model were calculated by the SAS 8.0 software to be 36.6°C, 100°C, and 28 h, respectively. The model predicted a maximum response of a 503.44 g/g swelling ratio for this point.

Verification of the optimum conditions

To confirm these results, the PAsp resin was prepared with the parameters representing the maximum point, with a swelling ratio of 506.84 g/g (the average of three repeats). It improved more than 60% in comparison with previous results. The good correlation between the predicted and measured values of these experiments justified the validity of the response model and the existence of an optimum point.

When small-scale experiments (1.0 g of PSI as the raw material) were magnified 20-fold, PAsp resins were obtained with the unoptimized and optimized parameters. Figure 2 illustrates the dynamic swelling behavior of these two products in deionized water. Initially, the rate of water absorption abruptly rose and then leveled off. Saturated swelling was obtained after 6 h. Under the optimized conditions, the PAsp superabsorbent with a swelling ratio of about 521.73 g/g was obtained. This was more than a 60% increase in comparison with the previous results.

CONCLUSIONS

RSM allowed a rapid screening of the important factors together with a polynomial model to optimize the preparation of the PAsp superabsorbent resin.

The R^2 value of 0.93 showed a good fit of the model to the experimental data. The model predicted accurately the maximum point of the swelling ratio. The optimal parameters were a solvent volume of 32 mL, a dissolving time of PSI of 28 h, a crosslinking temperature of 36.6°C, a stirring speed of 750 rpm, a dispersant volume of 8 mL, a mass of the crosslinking agent of 0.076 g, a crosslinking time of 2 h, a terminal pH of 9, a precipitation time of 48 h, and a drying temperature of 100°C. The water absorption capacity increased to 506.84 and 521.73 g/g in a small-scale system (1 g of PSI as the raw material) and a 20-fold magnifying system, respectively.

References

1. Irizato, Y.; Sukegawa, M.; Katoh, T.; Tamatani, H.; Nagatomo, A.; Wada, M. (to Mitsui Chemicals). Chin. Pat. 1198444 (1998); Chem Abstr 1998, 129, 261357n.
2. Nagatomo, A.; Tamatani, H.; Ajioka, M.; Yamaguchi, A. (to Mitsui Toatsu Chemicals, Inc.). U.S. Pat. 5,525,682 (1996); Chem Abstr 1995, 123, 257943j.
3. Sikes, C. S.; Vickers, T. M., Jr.; Farrington, S. A. (to University of South Alabama). U.S. Pat. 5,908,885 (1999); Chem Abstr 1999, 131, 6031f.
4. Chang, C. J.; Swift, G. (to Rohm and Haas Co.). U.S. Pat. 5,955,549 (1999); Chem Abstr 1999, 130, 52855e.
5. Tomida, M.; Yabe, M.; Arakawa, Y. Polymer 1997, 38, 2791.
6. Lenzi, F.; Sannino, A.; Borriello, A.; Porro, F.; Capitani, D.; Mensitieri, G. Polymer 2003, 44, 1577.
7. Rao, K. J.; Kim, C. H.; Rhee, S. K. Process Biochem 2000, 35, 639.
8. Dasu, V. V.; Panda, T. Bioprocess Eng 2000, 22, 45.
9. Souza, M. C.; De, O.; Roberto, I. C.; Milagres, A. M. F. Appl Microbiol Biotechnol 1999, 52, 668.
10. Hasmann, F. A.; Pessoa, A.; Roberto, I. C. Biotechnol Tech 1999, 13, 239.
11. Kalil, S. J.; Maugeri, F.; Rodrigues, M. I. Process Biochem 2000, 35, 539.
12. Silva, C. J. S. M.; Roberto, I. C. Process Biochem 2001, 36, 1119.
13. Chang, Y. N.; Huang, J. C.; Lee, C. C.; Shih, I. L.; Tzeng, Y. M. Enzyme Microb Technol 2002, 30, 889.
14. Elibol, M.; Ozer, D. Process Biochem 2002, 38, 367.
15. Muralidhar, R. V.; Chirumamila, R. R.; Marchant, R.; Nigam, P. Biochem Eng J 2001, 9, 17.
16. Abdel-Fattah, Y. R. Biotechnol Lett 2002, 24, 1217.
17. Burkert, J. F. M.; Maugeri, F.; Rodrigues, M. I. Bioresour Technol 2004, 91, 77.
18. Tan, T. W.; Fang, L.; Cao, H. (to Beijing University of Chemical Technology). Chin. Pat. 1341676 (2001); Chem Abstr 2003, 138, 338721x.
19. Zhao, Y.; Su, H.; Fang, L.; Tan, T. Polymer 2005, 46, 5368.
20. Mahdavinia, G. R.; Pourjavadi, A.; Hosseinzadeh, H.; Zohuriaan, M. J. Eur Polym J 2004, 40, 1399.
21. Yoshida, R.; Okuyama, Y.; Sakai, K.; Okano, T.; Sakurai, Y. J Membr Sci 1994, 89, 267.
22. Zhang, X. Z.; Zhuo, R. X. J Colloid Interface Sci 2000, 223, 311.
23. Sato, M. E.; Tanaka, T. J Chem Phys 1988, 89, 1695.
24. Zhang, X. Z.; Zhuo, R. X. Langmuir 2001, 17, 12.
25. Ensore, D. J.; Hopfenberg, H. B.; Stannett, V. T. Polymer 1977, 18, 793.