

# Effect of the Polymerization Conditions on the Swelling of a Copolymer of AA/AMPS/BA via Experimental Design

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**ABSTRACT:** To study the effect of the polymerization conditions on swelling, a copolymer was synthesized from the monomers acrylamide (AA), 2-acrylamido-2-methylpropanosulfonic acid (AMPS) and *N,N*-methylenebisacrylamide (BA) as crosslinker by an inverse emulsion technique. The conditions were: concentration of organic solvent, *s* (an isoparaffinic hydrocarbon, commercially Isopar M), concentration of emulsifier, *e* (sorbitan trioleate, commercially Tween 85), and reaction temperature, *T*. These three variables (factors) were explored to achieve highest water absorbency, a 2<sup>3</sup> factorial experimental design having been applied to find the main and two-factor interaction effects of those variables on the swelling

capacity. A predictive model including the factors for the swelling is proposed, allowing for the estimation of absorbency capacity in this type of copolymers. The results show that the optimum values of the variables given by the experimental design were *s* = 8.1, *e* = 1.0, and *T* = 49°C, with predicted swelling capacity of 1041 and experimental of 1014. The variables are relevant, with a preponderance of *s*, and the effect of the square of temperature is also significant. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 520–525, 2010

**Key words:** swelling; copolymer AA/AMPS/BA; experimental design

## INTRODUCTION

Polymers with a high water absorption capacity, usually designated as superabsorbents, have attracted attention<sup>1</sup> due to their applications in many domains, such as biomedical, pharmaceutical, agricultural, or civil construction. Some of these applications are, respectively, optical lens materials; encapsulated cells and carriers for controlled drug delivery; improvement of the water capacity of sandy soils; sealing or caulking materials.<sup>2–4</sup> In many of these applications, water absorbency is an essential aspect, and research done to enhance the property of superabsorbency has shown the importance of various parameters of the polymerization reaction as having an influence on the absorption capacity of the polymer.<sup>5–8</sup>

In this study, to obtain copolymers with a high degree of swelling, the radical inverse emulsion polymerization technique was adopted, as it leads to larger swelling than, namely, the solution technique. For the synthesis, the selected monomers were acrylamide (henceforth, AA), 2-acrylamido-2-methylpropanosulfonic acid (AMPS), and *N,N*-methylenebisacrylamide (BA) as a crosslinker. The monomers were selected because AA is cheap and commonly

used for polymerization; AMPS minimizes chain transfer reactions and permits comparatively high molecular weight generation; and BA promotes the swelling capacity of the copolymer due to its bifunctionality.<sup>9</sup> In the technique chosen for the synthesis, the organic phase emulsifier was prepared with an organic solvent, Isopar M (the commercial designation of an isoparaffinic hydrocarbon) and an emulsifier, Tween 85 (the commercial designation of sorbitan trioleate).

The experimental design methodology was used to determine which values of the reaction parameters lead to the maximum swelling. When the response, in this case swelling, depends on several variables and their interactions, a tool used to optimize the process is the response surface methodology (RSM), the “surface” being the multidimensional representation of the function, whose maximum is sought.<sup>10,11</sup> Various reaction parameters have an influence on the swelling ability of the polymers, namely the following, with convenient choices from previous studies: the molar ratio of the monomers, 70 : 30 (AA:AMPS), amounting to 99.5% (molar) and 0.5% (molar) of BA; pH of the medium, kept at 10; initiator, potassium persulfate. The three parameters chosen to find their influence on the swelling were: content of organic solvent, which permits droplet formation; content of emulsifier, which preserves the droplets where the monomers react; and reaction temperature, affecting the effectiveness of the initiator.

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The variables' ranges were selected taking into account results from previous experience and the information found in literature, such as the patents by Laskey,<sup>12</sup> Engelhardt et al.,<sup>13</sup> and Clarke.<sup>14</sup> According to these sources: the quantity of organic solvent must be in the range of 2–10 times that of the monomeric solution; the quantity of emulsifier must be in the range of 0.1–10% (weight) of that of the organic solvent; and the temperature must be in the range 50–130°C. An experimental design for these three variables each at two levels, leading to a 2<sup>3</sup> design, was used to determine the effects of the operating conditions and interactions of the effects on the swelling of the copolymer synthesized. A central composite design for the experiments, which accounts for single effects of the variables and their interactions, was adopted. The analysis produces a mathematical model, which may then be used to lead to the best performance.

The aim of this study is to investigate the conditions of polymerization carried out by a radical inverse emulsion technique, to reach an optimum. In the following sections, the experimental work is described, including: the synthesis of the polymer; its characterization regarding the synthesis completion; the swelling of the copolymer in water; and the optimization via RSM.

## EXPERIMENTAL

All the copolymerizations were done by the radical inverse emulsion technique from the monomers AA, AMPS, and BA, as mentioned. The synthesis of the copolymers and a characterization by Fourier transform infrared (FTIR) spectra are now presented, as well as the experimental design for optimization of the syntheses regarding the swelling ability.

### SYNTHESIS OF THE COPOLYMERS

The monomers AMPS (Lubrizol Corporation, USA) and AA 50% w/w solution (Resiquímica, SA, Sintra, Portugal) were dissolved in distilled water in a molar ratio of 30 : 70. As a crosslinker agent, BA (also from Resiquímica, SA) in a molar ratio of 0.5% to the other monomers was added to the monomer solution.

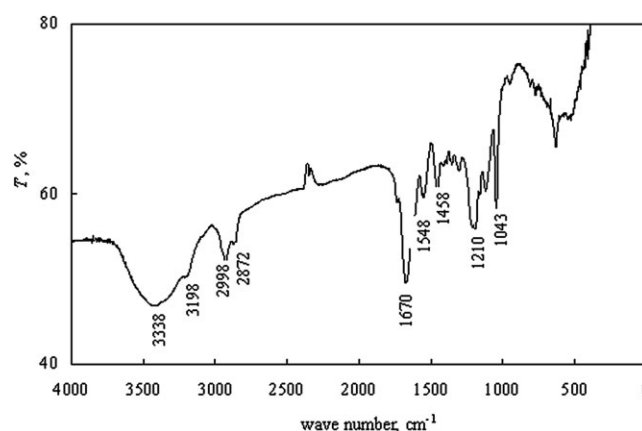
In all the copolymerization runs, using the technique mentioned, the aqueous monomer solution was dispersed in the organic phase. The organic phase was prepared by weighing the appropriate amounts of Isopar M and Tween 85, and the resulting mixture was introduced in the glass reactor with continuous stirring. The reactor was equipped with a stirrer, a reflux condenser, a thermometer, a dropping funnel and a gas inlet tube, and was placed in an oil bath for temperature control.

The monomer mix, which was previously adjusted to pH 10 by the addition of aqueous sodium hydroxide (Fisher Chemicals, USA), was then added to the organic phase emulsifier under continuous stirring. This mix was purged with nitrogen at a slow rate to remove oxygen for 3 h, while permanently stirred and heated up to the working temperature (values of about 40 to 70°C). The initiator, potassium persulfate (Merck, Lisbon, Portugal), was then added drop by drop, by the funnel in the top of the reactor. The reaction, under a permanent nitrogen flow, took place for about 5 h, a time sufficient for polymerization.

The copolymer, after cooling to room temperature, was isolated by precipitation with acetone. The copolymer was finally dried in an oven at 60°C.

### Characterization by FTIR spectroscopy

The identification of the structure of the copolymer synthesized, AA/AMPS/BA, was done by FTIR spectroscopy. In this technique, a small quantity of a thin powder of the sample with a support material is taken. The support material was potassium bromide, KBr (Merck, Lisbon, Portugal), and the spectrometer used was a FTIR "Perkin-Elmer 1600", the spectrum of the copolymer being given in Figure 1, in terms of percent transmission. In the spectrum, absorption peaks characteristic of the expected functional groups are visible, namely those with the following frequencies, in general agreement with published data<sup>15–18</sup>: amide two/stretching, 3338 and 3198 cm<sup>-1</sup>; amide bending, 1548 cm<sup>-1</sup>; C=O stretching, 1670 cm<sup>-1</sup>; asymmetrical and symmetric vibrations of the SO<sub>2</sub> group in the sulfonic acid, 1210 and 1043 cm<sup>-1</sup>; OH (bonded to SO<sub>2</sub>) stretching band, 2998 cm<sup>-1</sup> for the sulfonic acid (usually 3000 cm<sup>-1</sup>). It is to be noted that the C=C peak at 980 cm<sup>-1</sup> of



**Figure 1** FTIR spectrum of the copolymer AA/AMPS/BA synthesized by inverse emulsion polymerization technique.

TABLE I  
Symbols and Values of the Variables Selected in the Polymerization

			Low "axial" (-1.68) <sup>a</sup>	Low value (-1)	Center	High value (+1)	High "axial" (+1.68)
Organic solvent	<i>s</i>	(g) <sup>b</sup>	0.71	1.8	(3.4)	5	6.1
Emulsifier	<i>e</i>	(g) <sup>c</sup>	0.33	0.5	(0.75)	1.0	1.17
Reaction temperature	<i>T</i>	°C	43	50	(60)	70	77

<sup>a</sup> Quantity calculated as a wt % of *s*.

<sup>b</sup> See below ( $\sqrt[3]{2^3} = 1.68$ ).

<sup>c</sup> Quantity calculated from the mass of the monomer solution.

the vinyl monomer is not detectable in the spectrum: this bond is essential to the propagation step of the polymerization reaction, showing high conversion.

### Swelling capacity

The equilibrium swelling capacity measurements were done in distilled water at 20°C using the so-called tea bag method. Following this technique, the sample of copolymer in its initial, dry state was placed in the bag, (the set) weighed, and then transferred into a glass with excess water. The weight of the bag was taken at regular intervals until a constant value was reached, denoting equilibrium. The swelling capacity, *r*, was expressed as mass of water absorbed per unit mass of dry polymer, i.e.,  $r = [m(\text{swollen polymer}) - m(\text{dry polymer})]/m(\text{dry polymer})$ .

The values of *r* obtained for the swelling capacity are given further below (in Table II), each the average from three measurements. They are then designated as  $y_{\text{exp}}$ , the dependent variable in the context of the experimental work to find an underlying empirical model and the optimum conditions leading to the greatest swelling.

### EXPERIMENTAL DESIGN

To investigate the effects of the selected parameters on the swelling capacity, the property that characterizes the copolymer synthesized by the radical inverse emulsion technique, the experiments were planned according to a central composite design. This experimental technique is appropriate to find the optimum of the swelling capacity, in this case, a maximum.

For the experimental design, the selected independent variables, which correspond to the selected parameters, are shown in Table I, as well as the ranges for each variable within which the study was carried out. The variables were: (a) quantity of organic solvent, *s*, taken as a factor of the quantity

of the monomeric solution, with "low" and "high" values of 1.8 and 5 times this amount (values based in the range 2–10 mentioned); (b) quantity of emulsifier, *e*, taken as a factor of the organic solvent, *s*, with low and high values of 0.5% and 1% in weight of this solvent; and (c) temperature of the reaction medium, *T*, with low and high values of 50 and 70°C (values based in the range of 50–130°C mentioned). The center values, also shown in Table I, are the mean of the low and high values for each variable.

Those 3 variables, i.e.,  $n = 3$ , lead to a  $2^3$  factorial design to study the swelling capacity of the copolymer, which is the response (or dependent) variable, the experimental design being presented in Table II in the next section. To implement the design, the following experiments were done: eight (i.e.,  $2^n$ ) combinations of the variables, three replicates of the central point, and six axial points. In this design, the central point corresponds to standard process conditions and is replicated (typically in the order of three to five runs) to assess variability, while  $2n$  axial

TABLE II  
Central Composite Design: Variables, *x*, Responses,  $y_{\text{exp}}$ , and Predicted Values,  $y_{\text{pred}}$

	$x_1$	$x_2$	$x_3$	$y_{\text{exp}}$	$y_{\text{pred}}$	$y_{\text{pred}} - y_{\text{exp}}$
1	-1	-1	-1	100	44.04	-55.96
2	+1	-1	-1	851	651.62	-199.38
3	-1	-1	-1	291	155.78	-135.22
4	+1	-1	-1	920	833.87	-86.13
5	-1	-1	-1	50	70.08	20.08
6	+1	-1	-1	121	190.16	69.16
7	-1	-1	-1	150	283.33	133.33
8	+1	-1	-1	484	473.91	-10.09
9	0	0	0	675	664.66	-10.34
10	0	0	0	670	664.66	-5.34
11	0	0	0	665	664.66	-0.34
12	-1.68	0	0	171	161.62	-9.38
13	+1.68	0	0	730	832.80	102.80
14	0	-1.68	0	228	294.92	66.92
15	0	+1.68	0	601	627.49	26.49
16	0	0	-1.68	0	251.60	251.60
17	0	0	+1.68	129	-29.19	-158.19

**TABLE III**  
**Model Coefficients Computed and their Statistical Characteristics**

	Regression coefficient	Standard error	<i>t</i> -value	<i>P</i> -value
Constant	664.6577	96.40709	6.89428	0.000233
$\beta_1$ (organic solvent)	199.5425	45.27358	4.40748	0.003128
$\beta_2$ (emulsifier)	98.87407	45.27358	2.18392	0.065262
$\beta_3$ (temperature)	-83.47814	45.27358	-1.84386	0.107733
$\beta_{11}$	-59.2031	49.83018	-1.18810	0.273538
$\beta_{12}$	17.625	59.15279	0.29796	0.774385
$\beta_{13}$	-121.875	59.15279	-2.06034	0.078325
$\beta_{22}$	-71.93102	49.83018	-1.44352	0.192092
$\beta_{23}$	25.375	59.15279	0.42897	0.680835
$\beta_{33}$	-195.6747	49.83018	-3.92683	0.005699

points are also introduced according to  $x_n = \pm\sqrt[4]{2^n}$ , i.e.,  $x_n = \pm 1.682$  in this case.<sup>10</sup>

The (natural) variables listed in Table I were transformed, as usual, according to  $x_i = (\xi_i - \bar{\xi}_i)/(\Delta\xi_i)$ , where  $x_i$  ( $i = 1, \dots, n$ ) are the coded variables,  $\xi_i$  and  $\bar{\xi}_i$  the natural variables and their central values, and  $\Delta\xi_i$  the variation in each variable (from the "low" to the "high" value). Under the central composite design assumptions, the model proposed for the response, eq. (1), is given by a second order polynomial of  $y$ , the response variable (swelling capacity) versus  $x$ , with coefficients  $\beta$ , to be determined.

$$y = \beta_0 + \beta_1x_1 + \beta_2x_2 + \beta_3x_3 + \beta_{11}x_1^2 + \beta_{12}x_1x_2 + \beta_{13}x_1x_3 + \beta_{22}x_2^2 + \beta_{23}x_2x_3 + \beta_{33}x_3^2 \quad (1)$$

The optimum will be calculated from this model, as seen below.

## RESULTS AND DISCUSSION

The experimental design in the form of a central composite design permits obtaining an empirical regression equation, which gives the dependent variable, the swelling capacity, as a function of the three independent variables selected (given in Table I as  $s$ ,  $e$ , and  $T$ ): organic solvent, emulsifier, and temperature. The statistical package used for this purpose was Statistica.<sup>19</sup> The model, an application of the RSM, is typically a second degree polynomial in the variables which permits the optimization of the swelling capacity. The data indicated by the central composite design for the experimental runs were preceded by other experiments leading to a steepest ascent application and to the final design, which is shown in the first columns of Table II.

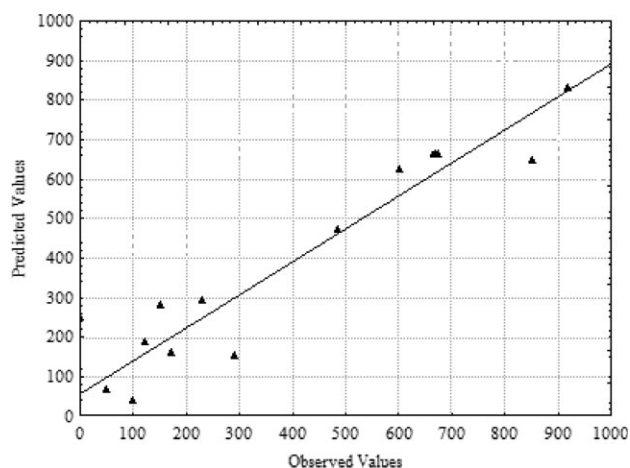
The application of the statistical method of analysis led to the regression coefficients of the polynomial for eq. (1) and, for each of them, the standard error,  $t$ -value and significance level,  $P$ -value, all

shown in Table III (according to the software output). With these coefficients, for which  $R^2 = 0.872$ , the experimental values,  $y_{\text{exp}}$ , the predicted values,  $y_{\text{pred}}$ , and their differences were calculated, and are shown in the last columns of Table II and in Figure 2.

The coefficients in Table III applied to eq. (1) permit now to calculate the optimum through differentiation. [For this simple calculation, the website of one of the authors (M.C.) can be directly used.<sup>20</sup>] The optimum values found were  $x_1 = 2.91$ ,  $x_2 = 0.86$ , and  $x_3 = -1.06$ , yielding a swelling capacity of  $y^* = 1041$ . These results for the coded variables correspond to the natural variables given in eq. (2), with the swelling capacity again noted, as originally, as  $r$ .

$$s = 8.1 \quad e = 1.0 \quad T = 49 \quad r^* = 1041 \quad (2)$$

As a contribution to the validation of the model, this configuration, compatible with the presuppositions referred,<sup>12-14</sup> was experimentally confirmed, yielding a swelling capacity of 1014 (average of



**Figure 2** Predicted versus experimental (observed) values of swelling.



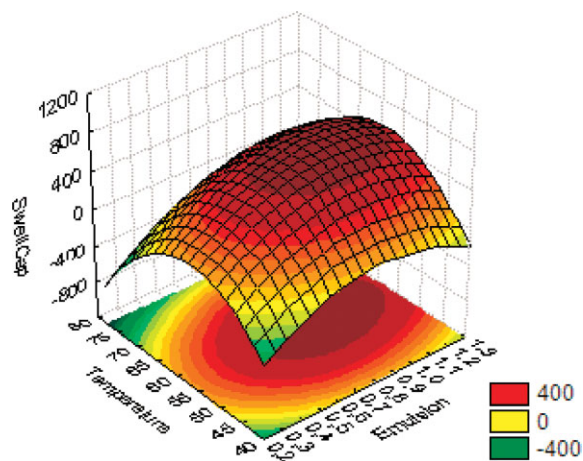
1038, 998, and 1006, with coefficient of variation of 2%).

Besides the variables addressed, concentrations of organic solvent,  $s$ , and of emulsifier,  $e$ , and temperature,  $T$ , which affect the copolymer's structural characteristics, the molar ratio of BA to the other two monomers, which controls the cross-linking density, also has an influence, this ratio having, however, been kept constant in this study at 0.5% of BA to the remaining AA/AMPS (itself in the ratio 70 : 30).

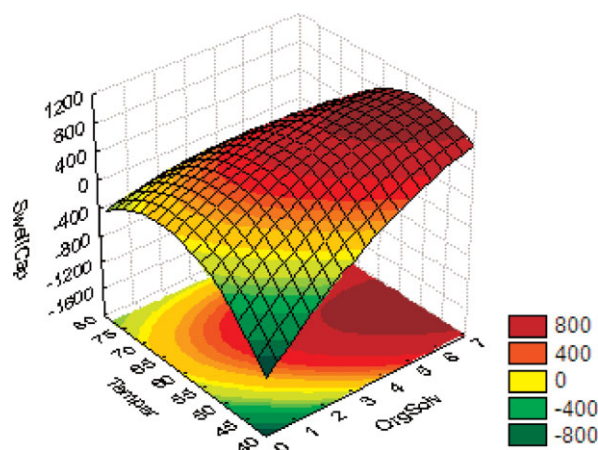
Kinetic studies of the swelling behavior, as in previous work,<sup>9</sup> which have not been conducted at this stage, require a careful assessment of the particle size influence, as well as of the variation in cross-linking density with the equivalent radius of the particle. The particle size distribution, studied earlier,<sup>21</sup> depends chiefly on surface active agent concentration and type.

All the graphical representations of the swelling capacity versus its variables show, of course, a maximum, and some images are shown (only two for brevity): swelling capacity versus emulsifier,  $e$ , and temperature,  $T$ , with fixed organic solvent,  $s = 8.1$  in Figure 3, and versus  $s$  and  $T$ , with fixed  $e = 1$  in Figure 4, with the fixed variables at their optima.

In run no. 16 shown in Table II at  $x_3 = -1.68$ , i.e.,  $T = 43^\circ\text{C}$  (Table I), the polymer obtained in those conditions dissolved in water, instead of swelling (absence of swelling), a fact that calls for attention to the effect of low temperature, the likely reason. The behavior of the initiator used, potassium persulfate, is known to be influenced by temperature, and an adequate range of temperatures should thus be selected.<sup>22,23</sup> Indeed, higher temperature favors the increase of the ratio of free radicals to monomers, and leads to more rapid reactions, which consequently decreases the active life of the radicals, with



**Figure 3** Swelling capacity versus emulsifier and temperature (fixed organic solvent,  $s = 8.1$ ). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 4** Swelling capacity versus organic solvent and temperature (fixed emulsifier,  $e = 1$ ). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

worsening of the subsequent swelling capacity. On the contrary, lower temperature extends the life of the initiator, but is insufficient to promote the cross-linking of the linear chains. This interpretation is compatible with the low values of swelling for the lowest ( $43^\circ\text{C}$ ) and highest ( $70^\circ\text{C}$ ) temperatures tested. The content in surface active agent controls the average droplet size and therefore the particle size distribution at the end of the polymerization reaction.

To reach an operational optimum, other techniques of sequential trials are known, but without supplying a mathematical model. The design of experiments not only reduces the number of experiments but also supplies an equation, useful when the underlying mechanistic model is supposedly complex, as in this case, permitting, namely, the optimization.

## CONCLUSIONS

To obtain copolymers of AA/AMPS/BA with high swelling capacity, and to reach the best synthesis of the copolymers, a design of experiments was used, in central composite design arrangement. The input variables involved in the optimization were organic solvent,  $s$ , emulsifier,  $e$ , and reaction temperature,  $T$ , varying in the direction dictated by the model. The best values of the variables given by the RSM were  $s = 8.1$ ,  $e = 1.0$ , and  $T = 49^\circ\text{C}$  with swelling capacity,  $r$ , of predicted value and experimentally confirmed value of 1041 and 1014, respectively.

The methodology addressed seems therefore to be a useful tool for the planning and optimization of the experiments when performing this type of polymerizations.

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