

Influence of Polymerization Conditions on the Viscosity of Polyacrylamide via Experimental Design

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ABSTRACT: Polyacrylamide was synthesized by a free-radical inverse emulsion technique and optimized via statistical experimental design, with the objective of developing a polymer with a high viscosity within this synthesis technique. The factors considered to affect the response variable, the viscosity of the polymer, were initiator ($K_2S_2O_8$) concentration (c), reaction temperature (T), stirring rate (r), and initiator addition method (s , batch or dropwise). An experimental design of the four factors at two levels (2^4) was carried out to study the effect of these process variables on the vis-

cosity of the polymer. The results show that the main factor having an effect on the viscosity was T , with smaller contributions from r and c . The optimum combination of values for the factors yielding maximum viscosity was $T = 65^\circ\text{C}$, $c = 1 \text{ mM}$, $r = 230 \text{ rpm}$, and $s = \text{dropwise addition}$. A close fit was obtained between the experimental and predicted values of the viscosity of the polymer solution. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5719–5724, 2006

Key words: emulsion polymerization; viscosity

INTRODUCTION

The viscosity of a polymer is important in its use as a rheology modifier, which is a frequent application of polyacrylamide (PAA), a water-soluble homopolymer of the monomer acrylamide (AA). It is well known that polymers of AA have attracted much interest because of their practical applications.^{1–3} In most cases, the AA polymers act as flocculants, coagulants, or encapsulating agents. The use of these polymers is expected to alter the thickening properties of substances that find applications in industry, such as oil recovery,⁴ paper fabrics, and water purification.⁵ Namely, in the case of oil recovery, the main role of the polymer is to increase the viscosity of the aqueous phase.

The purpose of this study was to synthesize an AA polymer with the highest viscosity by the examination of the best reaction conditions in the parameter ranges adopted, with the experimental design technique being the adequate approach. The free-radical inverse emulsion polymerization technique was chosen, as it is known to produce polymers with a higher viscosity than the solution technique.⁶ The chosen initiator, among others that might have led to other results, was potassium persulfate, which decomposes at relatively low temperatures. An ex-

perimental design was applied to the processing conditions to study the influence, with possible interactions, of the polymerization conditions on viscosity, the conditions being polymerization initiator concentration (c), reaction temperature (T), stirring rate (r), and initiator addition method (s).

Through experimental design, information may be obtained on each of the processing conditions and the interactions between them with fewer experiments.^{7–9} The number of experimental runs in a full factorial design, 2^N , is a function of the number of variables or treatments studied (N). As known, in each experiment all of the variables' settings are changed in a systematic manner, and each variable takes on one of usually two settings, high and low (a designation used later even for a qualitative variable). The analysis produces an empirical mathematical model, which may then be used to obtain the best performance.

Under the assumption of a significant dependence of the viscosity of the AA polymer on its synthesis parameters, the experimental work was conducted and is described in the following sections on statistical experimental design, polymer synthesis, characterization by Fourier transform infrared (FTIR) spectroscopy, and viscosity measurements. Finally, the optimization via experimental design is addressed, with conclusions drawn.

EXPERIMENTAL

The polymers were prepared by a free-radical inverse emulsion polymerization technique, with AA as the

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monomer [itself a 50% (w/w) aqueous solution] and potassium persulfate as the initiator.

To study the influence of the parameters, two values were considered for each of the variables mentioned, and the viscosity behavior in deionized water was then observed.

Statistical experimental design

T , c , r , and s (dropwise or batch) were chosen as the independent variables of the experimental design. Two levels, low and high, were defined for each independent variable, with the following pairs of values: for T , 65 and 70°C; for c , 1.0 and 1.8 mM; for r , 230 and 280 rpm; and for s , which is a qualitative variable, batch and dropwise procedures. These four variables lead to a 2^4 factorial design to study the viscosity of PAA as the response (dependent) variable.

The experimental design, shown later, resulted in a total of 16 experiments, that is, 2^4 different combinations of production treatments. Three additional replicates were performed to provide information on the reproducibility of the synthetic process.

Polymer synthesis

Polymerization of AA was carried out in a 1000-cm³ glass reactor equipped with a stirrer, a reflux condenser, a thermometer, a dropping funnel, and a gas inlet tube.

To synthesize the polymer of the AA monomer by an inverse emulsion technique, a 50% aqueous monomer solution was dispersed in the organic phase. We prepared the organic phase by weighing (1) white spirit (a mixture of C₇–C₁₂ hydrocarbons), 5 times the monomer amount, and (2) Tween 85 (polyoxyethylene sorbitan trioleate), 0.57% (w/w) of the white spirit. Both products were supplied by Petrogal (Lisbon, Portugal). The mixture of white spirit and Tween was introduced in the glass reactor with continuously stirring. The agitator used was a stainless steel turbine designed to promote in the vessel a degree 9 in a conventional scale of agitation,¹⁰ when rotated above 200 rpm. The monomer solution was then added to the organic phase. Nitrogen was bubbled into this mixture at a slow rate for 3 h to remove oxygen, with permanent stirring, and heated (according to the experimental design). Dissolved oxygen has a large influence on the induction time and also an inhibitory effect, and therefore, the long N₂ purging swept out the residual levels of O₂, which led to a much more reproducible start of the reaction. Afterwards, the initiator solution of potassium persulfate (Merck, Lisbon, Portugal) in distilled water was added to the top of the reactor. After 4 h of reaction in nitrogen flow, the polymer was isolated by precipitation with acetone. The polymer was finally dried in an oven at 60°C.

Characterization by FTIR spectroscopy

The AA monomer and the polymer synthesized were characterized by FTIR spectroscopy. This characterization gave semiquantitative information on the degree of conversion of the polymerization through observation of the reduction of the size of the peak ascribed to the double bond. FTIR spectra were made and recorded in a PerkinElmer 1600 FTIR spectrophotometer (Q-Labo, Lisbon, Portugal) from sample wafers of each compound. The spectra of the monomer and the polymer after scale adjustment are shown in Figure 1; this allows for comparison of the two spectra. The spectra present, in terms of percentage transmission, the absorption peaks that were characteristic of the expected functional groups. The C=C peak of the vinyl monomer (upper curve) around 980 cm⁻¹ was expectedly absent in the spectrum of the polymer (lower curve) according to effective conversion, as this bond is key to the propagation step of the polymerization reaction.

Typical peaks of the amides were observed, namely, C=O, in the range 1650–1680 cm⁻¹, in agreement with the reported range 1630–1700 cm⁻¹,^{11,12} NH₂ deformation at 1610 cm⁻¹, in the reported range 1500–1690 cm⁻¹,¹¹ primary amides at 1426 cm⁻¹, generally not well resolved but in the reported range 1420–1400,¹³ and C–N stretching at 1280 cm⁻¹.¹⁴ The position of the peaks in the range 1280–1200 cm⁻¹ assigned to N–H in the polymer was slightly affected by molecular association, that is, hydrogen bonding to heteroatoms.¹⁵

Viscosity measurements

In this study, the response of interest was the intrinsic viscosity (η') of the polymer synthesized. The value of η' was obtained by extrapolation of the so-called reduced viscosity (η_{sp}/c) to infinite dilution, according to its definition. In this expression, the specific viscosity (η_{sp}) is given by $\eta' = (t - t_0)/t_0$, where t is the flow time for the solution and t_0 is

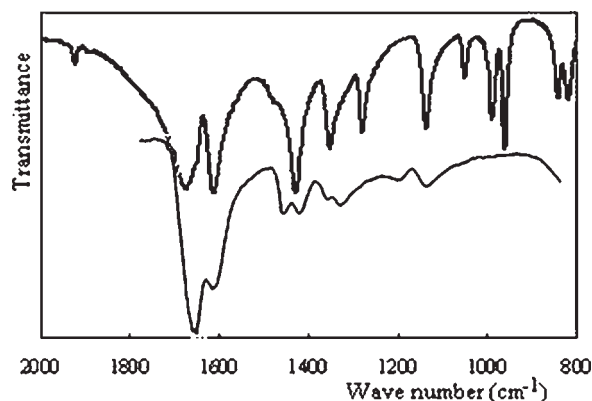


Figure 1 FTIR spectra of the AA monomer (upper curve) and its polymer (lower curve).

TABLE I
Calculation of η' Leading to $\eta' = 0.227$ L/g

Concentration (g/L)	Flow time (s)	η_{sp}	η_{sp}/c (L/g)
0	32.0	0	η'
1.01	40.2	0.256	0.254
2.50	53.5	0.672	0.268
5.00	79.0	1.469	0.294
10.01	161.0	4.031	0.403

flow time for the solvent, and c is the polymer concentration, with the flow times being considered proportional to the viscosities.

For each of the polymers synthesized, the viscosities of the various solutions at concentrations in a predefined range, 1–10 g of polymer/L of water, were determined in the solvent, distilled water, with an Ubbelohde-type viscometer, which enabled flow time measurements, in a thermostated bath at 25°C.

The polymer solutions were prepared by the dissolution of several quantities of polymer (to obtain concentrations in the range mentioned) with a magnetic stirrer for agitation, which was carried until complete dissolution.

The viscosity experiments were performed at 25°C, the temperature of the viscometric bath, which was maintained to within 0.05°C through the use of a heater–circulator. Shown in Table I, as an example for one of the polymers synthesized, are values that led (by extrapolation to the null concentration) to $\eta' = 0.227$ L/g. (This value was not seen in the factorial design, as it merely contributed to one of the average values used.)

Knowledge of the viscosity values allowed a useful estimation of the molecular weight, according to the Mark–Houwink equation: $\eta = k_m M^\alpha$, with M as the molecular weight, where k_m and α are parameters depending on the solvent–polymer pair. Once it was known that $k_m = 6.31 \times 10^{-3}$ cm³/g and $\alpha = 0.8$ for PAA and water,¹⁶ the values of molecular weight could be calculated from η' . The molecular weights obtained are shown for the smallest and greatest viscosities.

RESULTS AND DISCUSSION

A factorial design was used to organize the experiments of polymerization of AA. The independent variables that were considered in the polymerization process were c , T , r , and s (dropwise or batch). The levels or types of these variables are shown in Table II. The selection of the levels for the different factors was

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

Variable	c (mM)	T (°C)	r (rpm)	s
High level (+1)	1.8	70	280	Dropwise
Low level (–1)	1.0	65	230	Batch

done with consideration of previous experience. Concentration level limits were chosen with consideration of a number of experimental batches previously performed. Values of c below 1.0 mM led to large inhibition, with long induction periods and often no start of the reaction, and concentrations above 1.8 mM produced large amounts of propagating radicals and too low an average molecular weight. Experimental data also indicated that in the temperature range 65–70°C, good polymerization rates were obtained. Values of r below 230 rpm led to inhomogeneity, and with values higher than 280 rpm, a too-large vortex could occur with bubble formation in the liquid phase.

The influence of the four process parameters was studied through 16 experiments of a 2⁴-type factorial design. The matrix of the experimental design and the values obtained for η' are shown in Table III. Each run of AA polymerization was carried out for the set of parameters described in the experimental matrix. In this matrix, values +1 and –1, respectively, correspond to the high and low levels of the independent variables and, relating to s , dropwise and batch addition. The η' values in Table III are each averages of three measurements. For instance, the value for the fifth run listed in Table III, 0.223 L/g, is the average of three viscosity measurements on the same polymer, 0.227, 0.207, and 0.236 (of which the first is the one to which we refer to in Table I).

As to replication, the polymerization corresponding to the same fifth run was performed three times under identical conditions, with η' 's of 0.229, 0.212, and 0.236 L/g, with an average of 0.2257 L/g and a small standard deviation of 0.012 L/g.

Following the design matrix for the experiments, we obtained viscosity values for the AA polymers varying from 0.199 to 0.655 L/g (signaled in Table III).

TABLE III
Matrix of the Experimental Design and Experimental Results of the η'

Run	Level of variables				η' (L/g)
	c	T	r	s	
1	–1	–1	–1	–1	0.302
2	–1	–1	–1	+1	0.655
3	–1	–1	+1	–1	0.298
4	–1	–1	+1	+1	0.533
5	–1	+1	–1	–1	0.223
6	–1	+1	–1	+1	0.481
7	–1	+1	+1	–1	0.235
8	–1	+1	+1	+1	0.549
9	+1	–1	–1	–1	0.260
10	+1	–1	–1	+1	0.450
11	+1	–1	+1	–1	0.201
12	+1	–1	+1	+1	0.415
13	+1	+1	–1	–1	0.199
14	+1	+1	–1	+1	0.380
15	+1	+1	+1	–1	0.248
16	+1	+1	+1	+1	0.430

TABLE IV
Statistical Analysis of the Experiments

	Regression coefficient	Standard error	$t(5)$	p	-95% confidence limit	+95% confidence limit
Mean/intercept	9.5117	2.1747	4.374	0.007	3.921	15.102
(1) c	-1.1615	0.5326	-2.181	0.081	-2.5307	0.2077
(2) T	-0.1311	0.0320	-4.103	0.009	-0.213	-0.049
(3) r	-0.0275	0.0080	-3.421	0.019	-0.048	-0.007
(4) s	0.3270	0.2146	1.523	0.188	-0.225	0.879
1 by 2	0.0144	0.0074	1.948	0.109	-0.005	0.033
1 by 3	0.0003	0.0007	0.442	0.677	-0.002	0.002
1 by 4	-0.0614	0.0184	-3.327	0.021	-0.109	-0.014
2 by 3	0.0004	0.0001	3.382	0.020	0.000 ^a	0.001
2 by 4	-0.0014	0.0030	-0.489	0.645	-0.009	0.006
3 by 4	-0.0001	0.0003	-0.308	0.770	-0.001	0.001

^a Rounding of 0.00010.

The methodology of the factorial design was expected to allow us to determine the conditions of the polymerization leading to the maximum η' , as this is the objective sought. The experimental data of viscosity obtained were fitted to an empirical second-order model polynomial. This kind of model is widely used in response surface methodology, with the advantages of its flexibility and the ease of estimating its parameters.¹⁷ Thus, the polynomial, with the a 's as the model parameters, was

$$\eta' = a_0 + a_1c + a_2T + a_3r + a_4s + a_{12}cT + a_{13}cr + a_{14}cs + a_{23}Tr + a_{24}Ts + a_{34}rs \quad (1)$$

From the data, the estimation of the significance of the main effects and interactions was done, and a mathematical model summarizing the results and allowing prediction was obtained. This was performed with Statistica,¹⁸ a common program for this purpose. (In this interactive program, the section used was statistics/industrial statistics and six sigma/experimental design.) Table IV shows the results of the statistical analysis for each coefficient of the model:

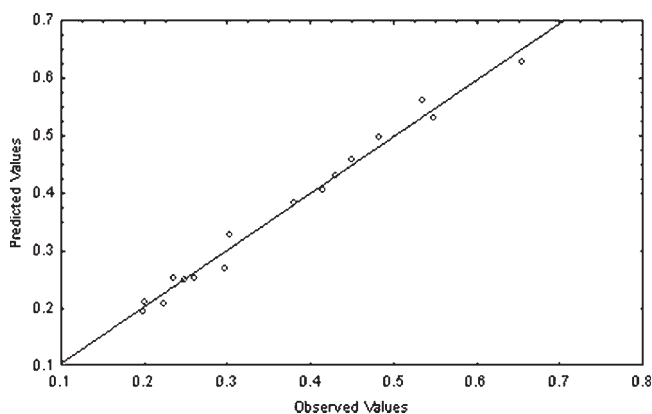


Figure 2 Calculated (predicted) versus experimental (observed) values of η' (L/g), with all of the interactions.

the coefficient obtained by regression, the standard error, the $t(5)$ value [5 degrees of freedom: 16 (points) minus 11 (parameters)], the p value for the response, and the lower and upper 95% confidence limits (within which the true value of the parameter was expected). Thus, in Table IV, the column regression coefficient contains, respectively, the independent term and the coefficients of the various variables and products of these (e.g., 1 by 2 meaning cT). The comparison of the experimental values with the calculated values produced Figure 2.

From the p value for each coefficient, its relevance to the model was ascertained, with the more significant coefficients being those with p values less than 5%, as indicated by a_0 , a_2 , a_3 , a_{14} , and a_{23} in Table IV. The model, from eq. (1), with a correlation coefficient of $R^2 = 0.985$, thus became

$$\eta' = 9.512 - 0.131T - 0.028r - 0.061cs + 4.10^{-4}Tr \quad (2)$$

The model shows that the variables T and r and the c - s interaction had a negative effect on η' , whereas Tr had a small positive effect. Some curvature came from the T - r interaction, with the minimum T and r leading to the best (greatest) viscosity. A stationary point was obtainable from eq. (2), with c and s fixed, at $T = 68.8^\circ\text{C}$ and $r = 328$ rpm, which was a saddle point. The best observable value of the η' was on the region boundary, and the optimum was sought outside of the region explored (as may be graphically seen later), due to the inexistence of maxima in this region.

Several graphical representations of the response variable (η') with selected sets of two independent variables (also from Statistica) are shown in the following figures. Only the graphs corresponding to the variation of the more significant variables are shown.

Figure 3 shows the influence of r (rpm) and T ($^\circ\text{C}$) with a fixed c at 1.4 mM, a test central point between

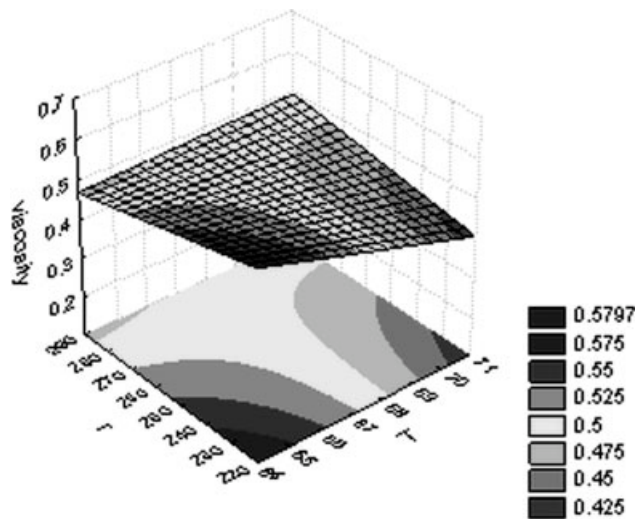


Figure 3 Influence of r (rpm) and T ($^{\circ}\text{C}$) with c fixed at 1.4 mM and $s = +1$ (dropwise addition).

the low and the high, and $s = +1$ (dropwise addition). It was graphically confirmed that to obtain a higher η' , lower temperatures and r values needed to be used in the polymerization of AA. These lower values or their combinations could only be found experimentally, with the initiator becoming ineffective below 40°C ,¹⁹ below which the rate of radical generation was smaller than the rate of destruction, which led to no effective initiation. At lower temperatures, the radical generation rate was most probably lower than the rate of destruction; therefore, no effective initiation took place.

Figure 4 shows the influence of s (batch addition = -1 or dropwise addition = $+1$) and c (mM), with T fixed at 67.5°C and $r = 255$ rpm, test central points,

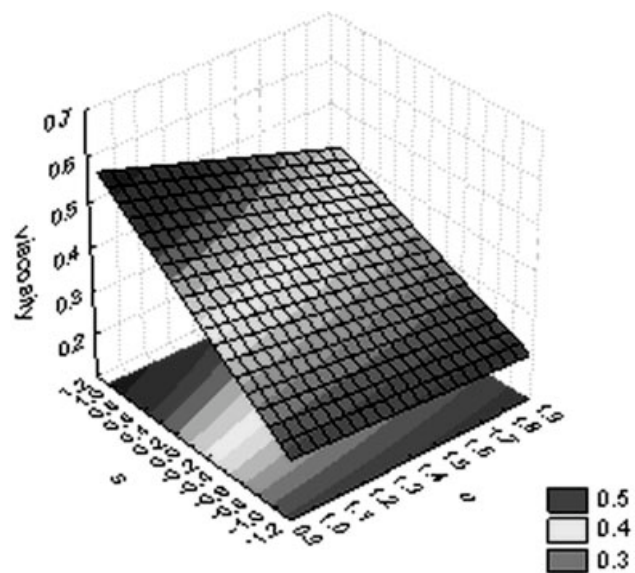


Figure 4 Influence of s (batch addition = -1 or dropwise addition = $+1$, the only possible values in the range) and c (mM) with T fixed at 67.5°C and $r = 255$ rpm.

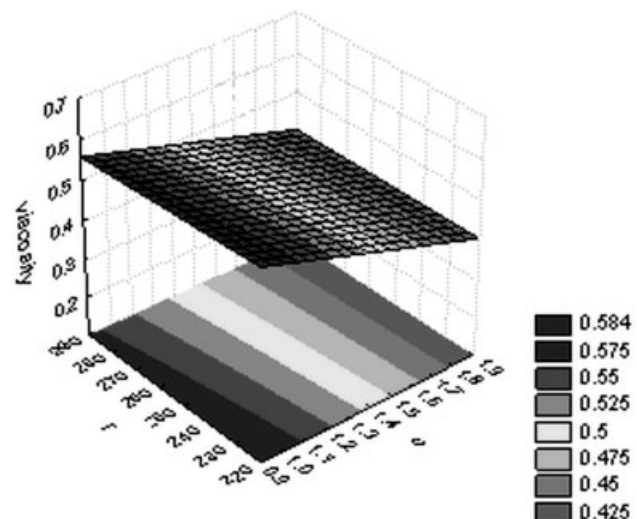


Figure 5 Influence of r (rpm) and c (mM) with T fixed at 67.5°C and $s = +1$ (dropwise addition).

where the only possible values for s were obviously -1 and $+1$ for batch and dropwise initiator addition, respectively. The advantage of the dropwise method ($s = +1$) in the polymerization is clearly illustrated.

Figure 5 shows the influence of r (rpm), and c (mM) with T fixed at 67.5°C , a test central point, and a chosen s at $+1$ (dropwise addition), with a minute effect on viscosity in the range tested (230–280), for all the c values tested.

The analytical search of the maximum η' based on the model [eq. (2)] led to an infeasible stationary point (optimum or saddle point) outside of the experimental range of c , T , and r . The only value used was $s = +1$ (dropwise initiator addition), once this method produced systematically higher viscosities. [The same conclusion of an infeasible stationary point would result from $s = -1$ (batch initiator addition).]

For this model, it was verified that an analytical optimum did not exist, only a saddle point obtained as a stationary point. The best solution was, therefore, chosen on the boundaries of the region explored. Inspection of the graphs led us to the conclusion that lower polymerization temperature and lower r yielded higher η' 's, that is, $T = 65^{\circ}\text{C}$ and $r = 230$ rpm. This was confirmed by previous experiments that had been done at lower values, both of T ($T = 45^{\circ}\text{C}$, above the minimum of 40°C cited) and r ($r = 200$ rpm), which showed smaller values of viscosity. The interaction of c and s was shown to favor low concentrations, that is, $c = 1.0$ mM, the lowest concentration experimented.

The range of molecular weights obtained, in accordance with the smallest (0.199) and greatest (0.655) viscosities, was, via the Mark–Houwink relation mentioned, 0.42×10^6 to 1.86×10^6 Da.

CONCLUSIONS

The objective of this study was to develop high-viscosity water-soluble polymers from AA (PAAAs) by the free-radical inverse emulsion polymerization technique, by examination of the best values of the reaction parameters adopted. A factorial design was used to find a model for the viscosity of the PAA solutions and to determine the most important factors affecting the viscosity. The factors were c , T , r , and s , batch or dropwise.

A 2^4 factorial design was applied, with up to two factor interactions, to study the effects influencing the polymerization. The attainment of polymerization was confirmed by comparison of the FTIR spectra of the monomer and the polymer, with the spectrum of the latter showing the necessary absence of the carbon-carbon double bond.

The study showed that the main operating factor affecting the viscosity was T and that smaller meaningful contributions came from r and the product cs . The best detected optimal conditions were $c = 1.0$ mM, $T = 65^\circ\text{C}$, $r = 230$ rpm, and $s = +1$ for an η' of 0.655 L/g. The corresponding molecular weight was 1.86×10^6 Da.

A close fit, with a correlation coefficient of 98.5%, was obtained between the experimental and predicted values of the viscosity of the polymer solution, which attested to the model adequacy in the prediction of the influence of the polymerization conditions on the viscosity.

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