

# Inverse Suspension Polymerization of Sodium Acrylate: Synthesis and Characterization

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**ABSTRACT:** Crosslinked Poly(acrylic acid) was synthesized by inverse suspension polymerization. This process was investigated to determine the influence of different parameters like temperature, stirring speed, solution pH, and crosslinker concentration and to obtain the best control of the kinetics. An aqueous phase containing partially neutralized acrylic acid, crosslinking agent, and initiator agent was dispersed in an organic phase and stabilized by a surfactant. The inverse suspension was carried out in heptane as the organic phase with a different ratio of neutralization of the monomer, different crosslinker concentrations, and several stirring speeds. The polymerization was initiated by potassium persulfate ( $K_2S_2O_8$ ) with *N-N'*-methylenebisacrylamide ( $MBA_C$ ) as the crosslinker and sorbitan monooleate as the surfactant. The influence of several parameters on the bead size and the swelling capacity was investigated. Particle diameters ranged from 10 to 130  $\mu\text{m}$ . The kinetic results obtained by differential scanning calorimetry showed that conversion and polymerization rates are a function of the solution pH, and they fell when the concentration of the crosslinking agent was higher than 7.5% in the mass of  $MBA_C$ . © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2621–2630, 2000

**Key words:** inverse suspension polymerization; sodium acrylate; crosslinked poly(acrylic acid)

## INTRODUCTION

Crosslinked Poly(acrylic acid) (PAA) is produced in abundance because this polymer can absorb a large quantity of water; this remarkable property has found applications in different domains such as medicine, agriculture, the construction industry, optical fibers for communication cables,<sup>1</sup> humidity control, and fire fighting agents.<sup>2</sup> In 1938 Kern<sup>3</sup> was the first to study this polymer. Also, Khun et al.<sup>4</sup> investigated the physical and the

chemical properties of PAA and poly(methacrylic acid). It was only in the early 1980s that this polymer with superabsorbent properties was introduced into the Japanese market and used in the manufacturing of baby diapers.

The final form of the polymer and its field of application determine the method used for its production. Presently, PAA is manufactured solution crosslinking copolymerization, graft copolymerization, crosslinking after polymerization, and suspension crosslinking copolymerization. In the latter process polymerization is conducted in an inverse suspension, so the aqueous phase containing the monomer and the crosslinking agent is dispersed in oil to produce spherical particles;

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this form is particularly attractive for industrial applications. Polymer synthesis was recently reported as having the best control of the reaction kinetics to determine the influence of different parameters such as temperature, crosslinking ratio, stirring speed, or pH.<sup>5</sup> Their choice is indeed crucial to reach the conditions for which the inverse suspension is kept stable.

However, the literature does not describe a general reaction; each author presents a personal recipe<sup>6–8</sup> with different concentrations of parameters for a specific polymerization temperature. Thus, in this article we describe the synthesis of crosslinked PAA and the chosen method is justified. Then we show the influence of particular parameters such as the neutralization ratio, crosslinker concentration, and stirring speed on particle sizes and swelling capacity. Powders were characterized by laser diffraction and microscopies [light microscopy and scanning electron microscopy (SEM)] to determine the particle size and polymer morphology. The results concerning the kinetics of the reaction are presented. Data were obtained by differential scanning calorimetry (DSC). The conversion and reaction rate were followed at different pH values and at different crosslinker ratios.

## EXPERIMENTAL

### Polymerization Procedure

#### *Aqueous Phase*

The AA (Aldrich Chemical Co.) was partially neutralized drop by drop by a caustic solution (20% w/w), kept cool to prevent an exothermic reaction, and from AA precipitation. Ateruperiore elevation could perturb the AA solubility. The partial neutralization degree is defined as

$$\alpha = \frac{n_B}{n_A}$$

where  $n_A$  and  $n_B$  are the number of moles of AA and of NaOH, respectively. A defined amount of  $K_2S_2O_8$  (1%/mass of the aqueous phase, Aldrich) and  $MBA_C$  (1–10% mass of the aqueous phase, Aldrich) was dissolved in the solution and the clear mixture obtained was degassed by nitrogen bubbling for about 30 min.

#### *Organic Phase*

The surfactant SPAN 80 (Aldrich) was dissolved in heptane (Prolabo). After 15 min of nitrogen bubbling, this phase was heated to 60°C and the reactor stirred at 600 rpm. The aqueous phase was added dropwise and the agitation of the mixture was kept constant. At the end of this stage (20–30 min) the temperature was increased to 70°C and maintained for 2–3 h to consume all the monomer. During the reaction the viscosity of the medium increased and the color changed from opaque to milky. As observed in the inverse suspension polymerization of acrylamide,<sup>9</sup> a phase inversion probably occurs and the aqueous phase becomes the continuous phase. At the end of the reaction stirring was stopped and two phases were observed: the liquid constituted of heptane was at the top of the reactor and the aqueous suspension of PAA particles was at the bottom.

The particles were recovered by methanol precipitation. After drying under a primary vacuum at 40°C, a powder was obtained from which the swelling ratio and the bead size were measured.

### Characterization

#### *Swelling Ratio*

A weight fraction of powder was introduced in a test tube filled with a sufficient amount of water to obtain a saturated mixture.<sup>10</sup> When the polymer network looked relaxed, the swelling ratio ( $G$ ) was calculated according to the following relationship:

$$G = \frac{M_f}{M}$$

where  $M_f$  is the weight of the relaxed polymer network and  $M$  is the weight of the dried fraction.

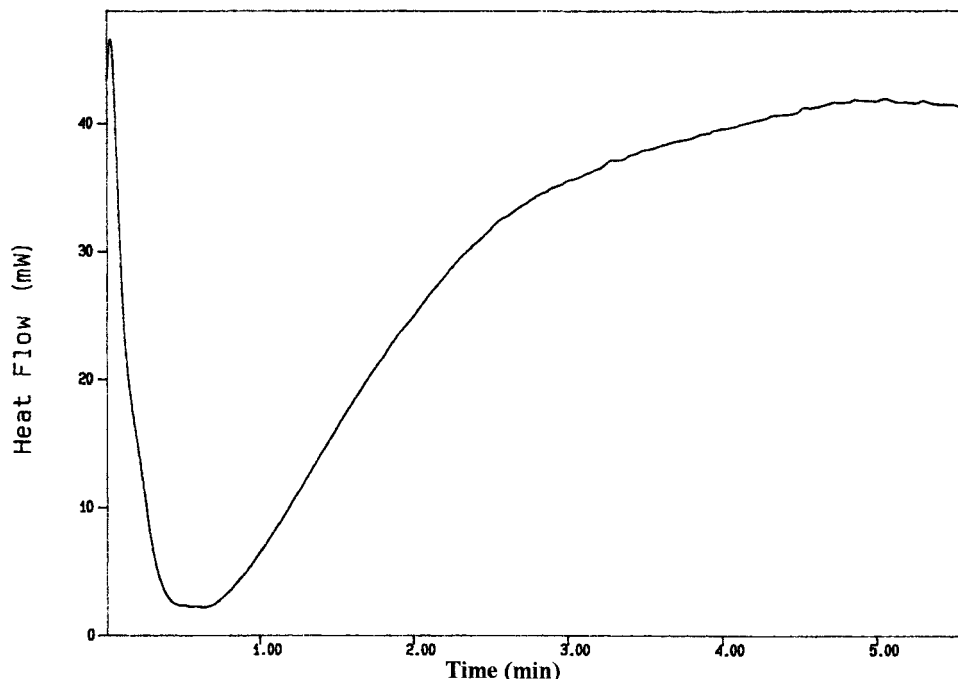
#### *Particle Size and Morphology*

*Laser Diffraction.* The measurements were performed with a Malvern instrument (Malvern Instruments SB.OD). In the cell, heptane was chosen as a solvent because we noticed that it had no influence on either the shape or the particle size.

*Microscopy.* A light microscope and a scanning electron microscope were used to determine the particle size.

#### *Kinetics*

The use of DSC is well suited for recording the heat production of chemical and physical pro-



**Figure 1** An example of a DSC trace of the isothermal polymerization. The pH is 6 and the crosslinking ratio is 4.5%.

cesses and for procuring data with time to follow the kinetics of the reaction. Modern software makes it possible to determine the kinetic parameters, even for complex chemical reactions.<sup>11</sup>

### Products

The AA was distilled at 27°C/2.5 mmHg (0.33 kPa) to remove the inhibitor. Solutions were prepared by mixing AA with different amounts of NaOH to give the desired neutralization ratio ( $\alpha$ ), the MBA<sub>C</sub> in variable concentrations, and the K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> to initiate the reaction. The neutralization was realized under the same conditions described in the polymerization procedure (i.e., under cooling).

The neutralization degree ( $\alpha$ ) ranged from 0.4 to 0.8 and the crosslinking ratio was from 1 to 10% of the MBA<sub>C</sub> in mass to the AA.

### Process

The reaction was performed in a power-compensated DSC calorimeter (Perkin-Elmer Corp.). Sample masses of 10–20 mg in sealed aluminum crucibles were scanned at the polymerization temperature (i.e., 66°C). In these experiments the temperature of the polymerization (66°C) was

chosen so that the reaction was achieved after a short time but was adequate to detect the signal because of the complete reaction. This temperature had to be reached rapidly at the beginning of the measurement. Reaction rate profiles were obtained using an empty reference pan. The isothermal polymerization was finished when the signal returned to the linear baseline (Fig. 1).

Two parameters were calculated to analyze the data:

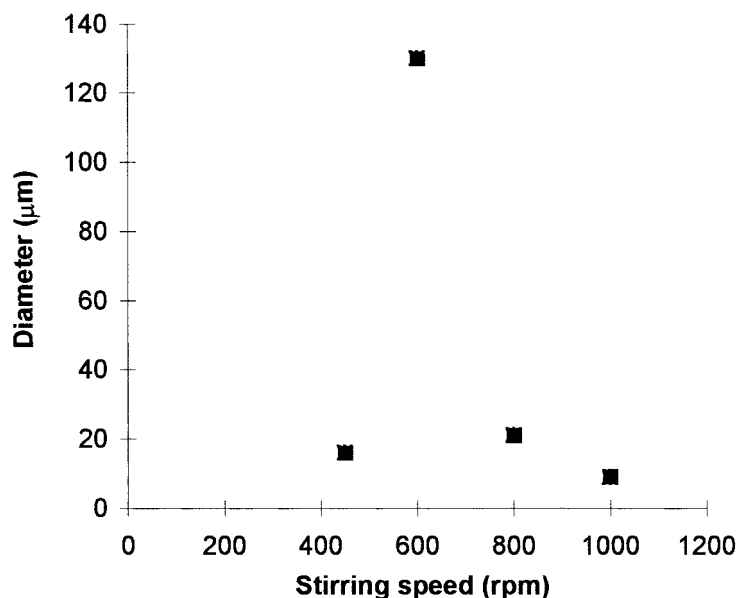
$$X = \frac{a}{A}$$

where  $X$  is the conversion rate,  $a$  is the heat provided at time  $t$ , and  $A$  is the heat provided at the instant of total conversion.

$$R_p = \frac{dX}{dt} \times [M]_0$$

where  $R_p$  is the polymerization rate and  $[M]_0$  is the initial monomer concentration.

The dependence of the polymerization rate on various reaction parameters was analyzed and is presented in the following section.



**Figure 2** The bead sizes vs. stirring speed. Each value obtained by the granulometry technique represents 90% of the particle population.

## RESULTS AND DISCUSSION

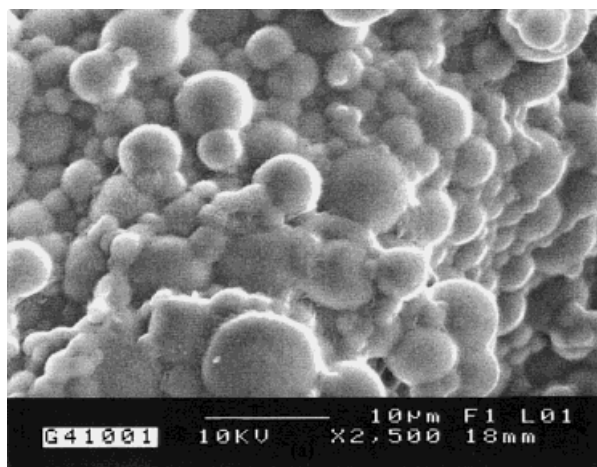
### Emulsion Stability

The radical polymerization of AA was conducted in an inverse suspension to obtain microspheric particles. This process requires an aqueous phase containing the neutralized monomer, the initiator, and the crosslinking agent and an organic phase in which a surfactant is dissolved. We established that a balance between these two phases must be kept and also in the aqueous phase where there is an equilibrium between the ionized and the nonionized form of AA. Contrary to the study reported by Zhao et al.,<sup>6</sup> the influence of the operating conditions on the reaction was limited to some parameters in order to maintain the inverse suspension in conditions where it was stable. So we tested the nature and concentration of the components of the suspension: the surfactants, initiators, neutralization ratio of AA, and hydrocarbon solvent.

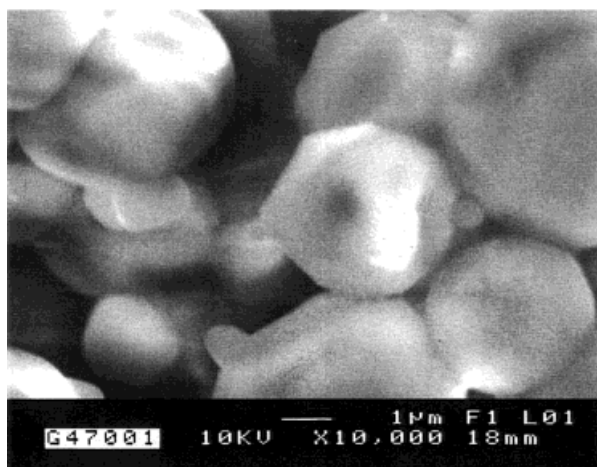
In the present study the ratio  $\varphi_{\text{org}}/\varphi_{\text{aq}}$  between the organic and the aqueous phase, the type of the surfactant, and its concentration were kept constant while the temperature was controlled during the reaction. However, the influence of the stirring speed, crosslinking, and neutralization ratio was studied in the variation range where these parameters did not perturb the stability of the system.

### Stirring Speed

It was essential to keep the solution in turbulent conditions, so the particle sizes were governed by the stirring speed as shown in Figure 2. The data reported correspond to the mean value of three experiments. It could be observed that a 600 rpm speed led to a maximum particle size. Away from this maximum, the particle diameter could be 10 times smaller. It seems that when the stirring speed was in the domain of 600 rpm there was an agglomeration of particles. Figure 3(a,b) shows the particles observed through SEM. Larger beads sizes may be obtained by increasing the surfactant concentration, but this point is discussed by Wang et al.<sup>12</sup> who showed that this parameter had no influence on the particle size. A recent patent described a process where the reaction is performed with two monomer additions.<sup>13</sup> At first, the polymerization was carried out to obtain particles in an inverse suspension. The stirring speed was kept constant and a second quantity of monomer was added to the reactor. The second stage must take place in the presence of a surfactant with a low hydrophilic balance, contrary to the surfactant used in the first stage, which had a high hydrophilic balance. However, this is a specific process with conditions differing from the one presented in this study.



(a)



(b)

**Figure 3** (a) Scanning electron microscopy of PAA beads obtained at (a) 1000 or (b) 400 rpm. (a,b)  $[AA] = 1.8 \text{ mol/L}$ ,  $\alpha = 0.6$ ,  $[K_2S_2O_8] = 4.8 \times 10^{-3} \text{ mol/L}$ , and  $[MBA_C] = 8.5 \times 10^{-3} \text{ mol/L}$ : Scale bar = (a) 2 cm  $\rightarrow$  10  $\mu\text{m}$  and (b) 0.8 mm  $\rightarrow$  1  $\mu\text{m}$ .

### Crosslinking Ratio

The variation of the crosslinking concentration does not perturb the inverse suspension stability, even if its concentration is over the solubility threshold. As a consequence, in a range from 1 to 10% of  $MBA_C$  in the mass, a polymer with a specific swelling capacity was obtained in relation to the network crosslinking density. Table I shows that the water absorption is increased when the crosslinking ratio is decreased, and this trend was already reported by Askari et al.<sup>8</sup> In fact, the polymer is a 3-dimensional network whose mesh size depends on the crosslinking con-

centration. If the latter is low, the number of water molecules confined to each mesh is higher than for an important crosslinking concentration for which the mesh has a reduced size.

An example of particles observed through an optical microscope is shown in Figure 4(a,b).

The particle sizes presented in Table I show that, when 2.5% of the  $MBA_C$  in the mass is added to the reacting mixture, the particle diameter falls. The mechanism of the reaction could explain this behavior. However, the size of the polymer formed in the aqueous phase depends on the crosslinking density. After gelification, the reaction rates decrease because the diffusion of the macroradicals and the monomers in the gel is limited by the viscosity increase. When the crosslinking ratio is increased, the reaction is stopped earlier in comparison to a 1%  $MBA_C$  concentration.

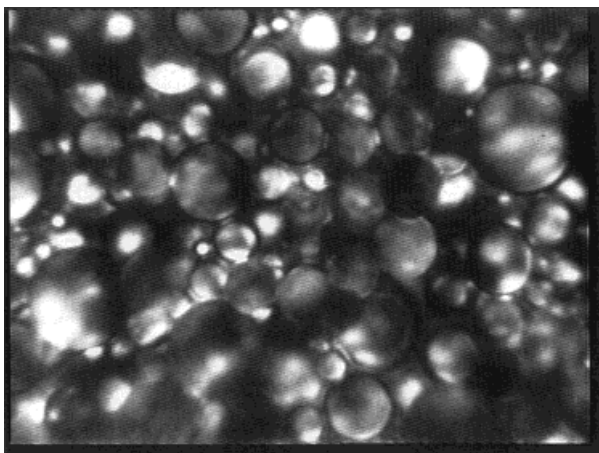
### Neutralization Ratio

Three neutralization ratios were used. If the NaOH amount used to neutralized AA is out of the 0.4–0.8 range, the polymerization fails. The swelling capacity and the size of the dry particles are presented in Table II for different neutralization ratios. Figure 5(a,b) gives an illustration of the morphology of the beads.

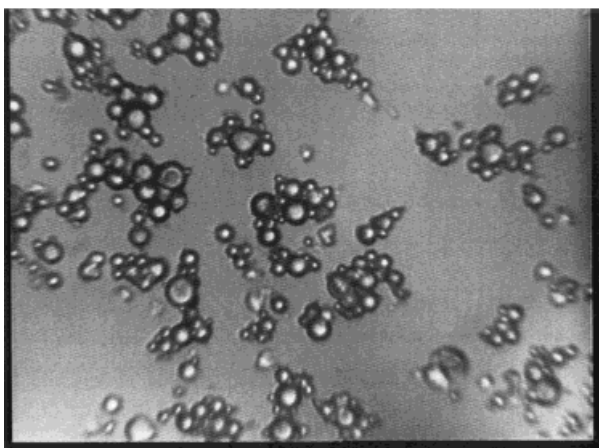
A polymer synthesized with an  $\alpha$  value of 0.8 leads to better swelling capacity that is due to a smaller bead diameter. As pointed out in previous studies,<sup>14,15</sup> the water absorbed by the superabsorbent polymer is composed of bound water and a large amount of free water in a tridimensional network. A polymer with small particle sizes presents an important degree of absorption because more bound water could be absorbed because of a high surface to volume ratio. This bound water can be observed by FTIR measurements at approximately  $3400 \text{ cm}^{-1}$  [Fig. 6(a,b)]. This band was confidently assigned to hydrogen-bonded wa-

**Table I** Variation of Swelling Ratio and Particle Size Versus Crosslinking Concentration

Mass of $MBA_C$ (%)	Swelling Ratio	Diameter of Dry Particles ( $\mu\text{m}$ )
1	52	130
2.5	45	40–50
7.5	16	~ 10
10	12	20–30



(a)



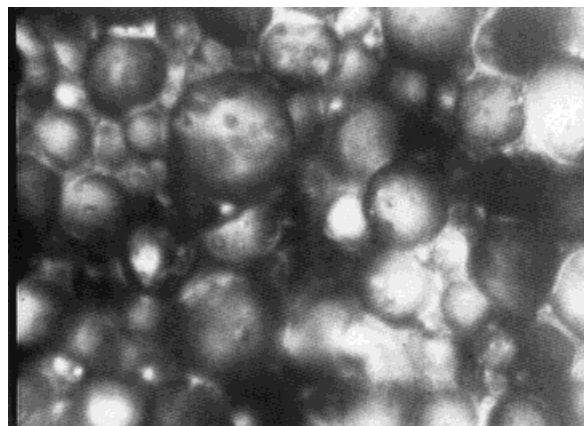
(b)

**Figure 4** Light microscopy of PAA beads at (a,b) [AA] = 1.8 mol/L,  $\alpha = 0.6$ , and  $[K_2S_2O_8] = 4.8 \times 10^{-3}$  mol/L, (a)  $[MBA_C] = 85 \times 10^{-3}$  mol/L (10%), and (b)  $[MBA_C] = 64 \times 10^{-3}$  mol/L (7.5%). Scale bar = 3.2 cm  $\rightarrow$  0.1 mm.

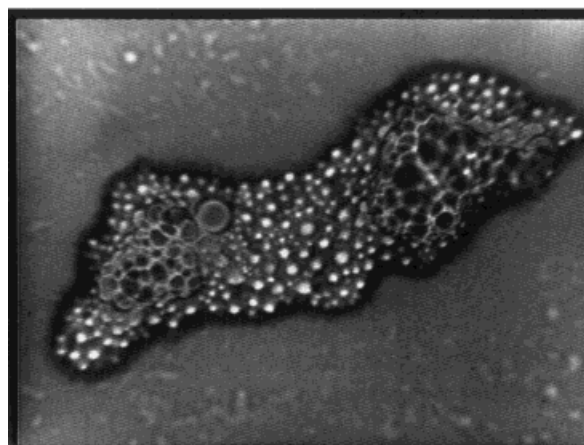
ter in an ethylene-methacrylic acid copolymer.<sup>16</sup> Two spectra of the same sample at different drying ratios are shown in the 3600–2800  $cm^{-1}$  re-

**Table II** Variation of Swelling Capacity and Particle Size versus Neutralization Ratio

$\alpha$	Swelling Ratio	Diameter of Dry Particles ( $\mu m$ )
0.4	52	35
0.6	56	130
0.8	76	< 10



(a)



(b)

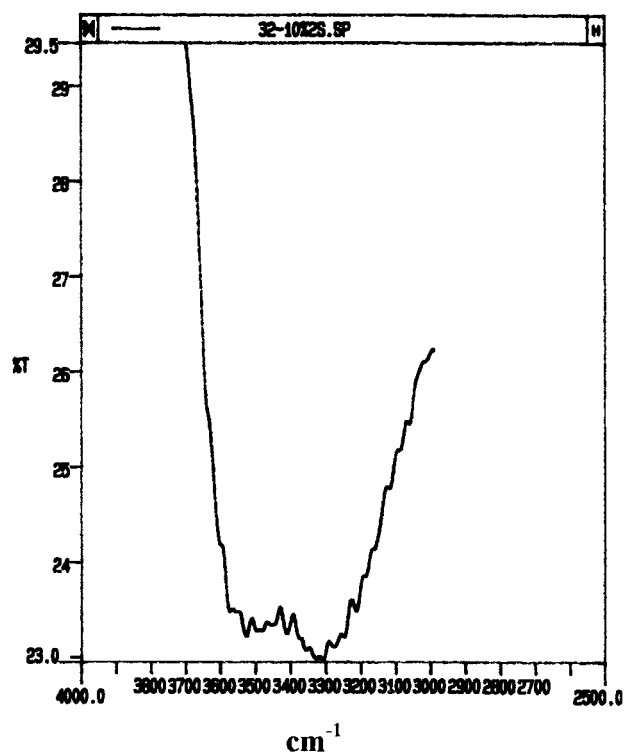
**Figure 5** (a) Light microscopy of PAA beads at [AA] = 1.8 mol/L,  $\alpha = 0.4$ ,  $[K_2S_2O_8] = 4.8 \times 10^{-3}$  mol/L, and  $[MBA_C] = 8.5 \times 10^{-3}$  mol/L. (b) Light microscopy of PAA beads at [AA] = 1.8 mol/L,  $\alpha = 0.8$ ,  $[K_2S_2O_8] = 4.8 \times 10^{-3}$  mol/L, and  $[MBA_C] = 8.5 \times 10^{-3}$  mol/L. Scale bar = 3.2 cm  $\rightarrow$  0.1 mm.

gion. A broad band is observed when the amount of bound water is large.

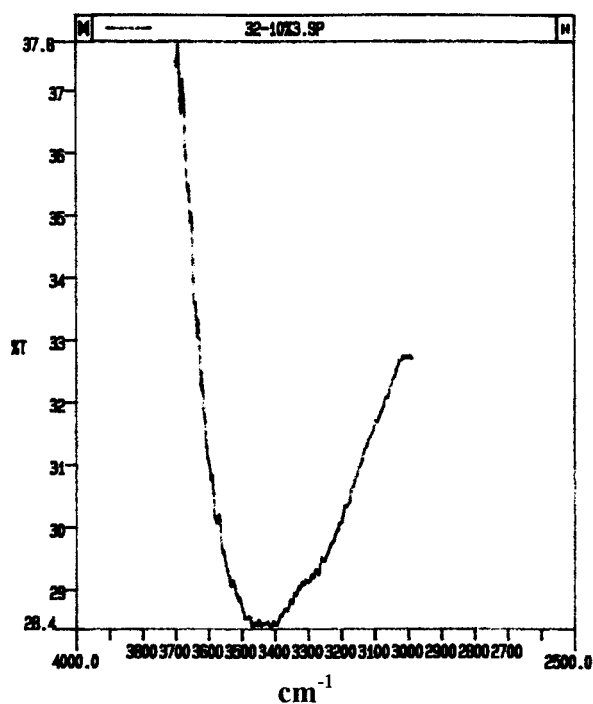
The different particle sizes may be considered as an image of the different conditions of polymerization, showing that the pH must be controlled and chosen according to the desired polymer characteristics.

### Kinetics

The kinetic modeling of inverse suspension polymerization is not easy. Vanderhoff et al.<sup>17</sup> in the 1960s and two other research groups<sup>18,19</sup> afterward showed that a little modification in the recipe could have a significant consequence on the



(a)



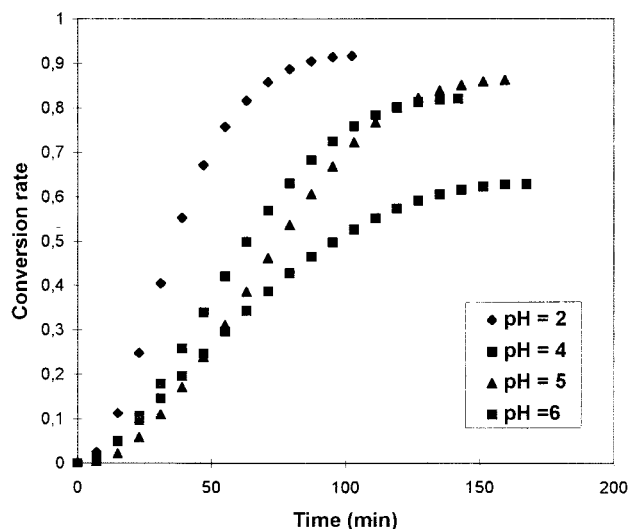
(b)

**Figure 6** FTIR spectra in the 4000–2500  $\text{cm}^{-1}$  range of PAA powder. (b) The spectrum of the result obtained with a dried sample.

structure, as well as on the mechanism. Bartlett and Reichert<sup>20</sup> worked on the influence of the interfacial composition and on the nature of the dispersion media to obtain a good understanding of the micellization phenomena. The polymer formed by the inverse suspension method has a lower molecular weight than the polymer obtained in solution, and Hunkeler et al.<sup>21</sup> explained that this result is due to a transfer reaction to the hydrophilic moiety of the emulsifier. Different mechanisms and kinetics were proposed for the inverse suspension polymerization of acrylamide using sorbitan esters of fatty acids as surfactants and block copolymeric surfactants.<sup>18,22,23</sup> Recently, it seemed interesting to draw attention to emulsifier purity. Concerning an acrylic water-soluble monomer, a *hybrid complex-cage* mechanism was proposed for the persulfate-initiated polymerization.<sup>24</sup> The research methods are numerous and diversified in keeping with the complexity of the process.<sup>30</sup> As explained in a previous paragraph, the synthesis presented in this study must realize a synergy between the different reagents. The aqueous phase containing partially ionized AA is dispersed in the organic phase under vigorous agitation and the droplets can be considered as microbatch reactors. Thus, the kinetics of suspension polymerization of AA is the same as the polymerization of AA carried out in aqueous solution. In this work the influence of the pH and crosslinking ratio were studied through the conversion rate of the monomers ( $X$ ) and the polymerization rate ( $R_p$ ).

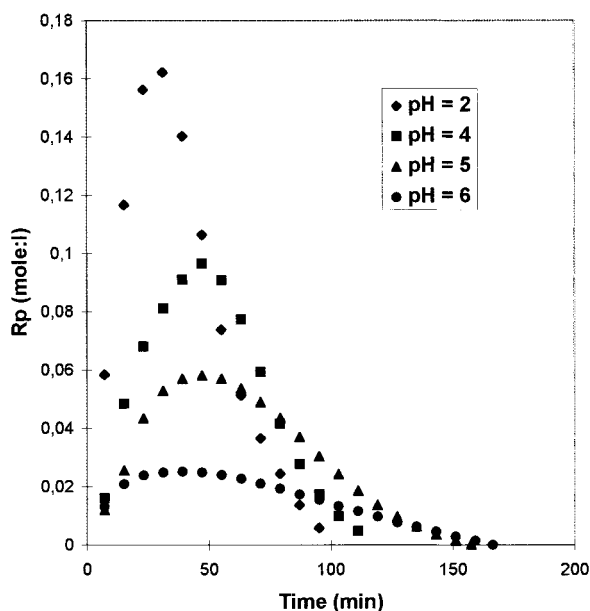
### pH Influence

In an  $\alpha = 0.2$ – $0.8$  range at constant monomer concentration (1.8 mol/L), initiator concentration ( $4.8 \times 10^{-3}$  mol/L), crosslinking concentration ( $8.5 \times 10^{-3}$  mol/L), and reaction temperature, the conversion and the polymerization rate are a decreasing function of the solution pH (Figs. 7, 8). This fact can be explained by the interaction between ionized and unionized species present in the solution. The neutralized monomer exists in two forms:  $\text{CH}_2=\text{CH}-\text{COOH}$  (*acrylic*) and  $\text{CH}_2=\text{CH}-\text{COO}^-\text{Na}^+$  (*acrylate*). When  $\alpha$  is raised, the acrylate concentration is increased. During the polymerization reaction the electrostatic interactions become so strong that the conformation taken by a molecular chain makes the radical center more or less accessible. Moreover, the acrylic form favors the reaction and the electronic delocalization involves a positive charge on

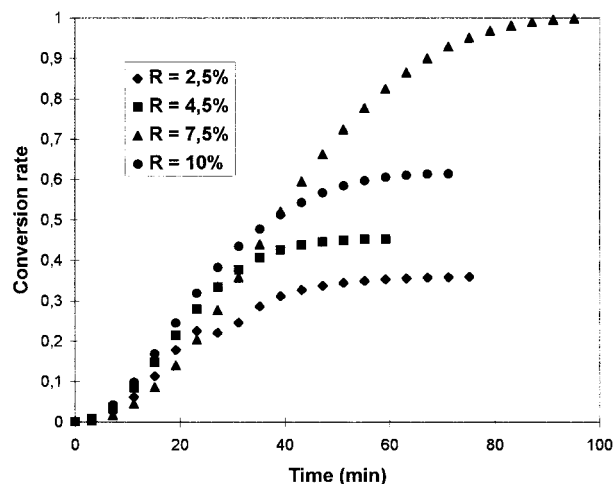


**Figure 7** The conversion rate of AA vs. time at different pH values. Data were obtained from DSC measurements and  $[AA] = 1.8 \text{ mol/L}$ ,  $[K_2S_2O_8] = 4.8 \times 10^{-3} \text{ mol/L}$ ,  $T = 66^\circ\text{C}$ , and  $[MBA_C] = 8.5 \times 10^{-3} \text{ mol/L}$ .

the first methylenic carbon, making it easier for the fixation of the next AA group. As a consequence, the increase in acrylate ion concentration leads to the decrease of the conversion and the



**Figure 8** The polymerization rate of AA vs. time at different pH values. Data were obtained from DSC measurements and  $[AA] = 1.8 \text{ mol/L}$ ,  $[K_2S_2O_8] = 4.8 \times 10^{-3} \text{ mol/L}$ ,  $T = 66^\circ\text{C}$ , and  $[MBA_C] = 8.5 \times 10^{-3} \text{ mol/L}$ .



**Figure 9** The conversion rate vs. time for different crosslinking ratios. Data were obtained from DSC measurements and  $[AA] = 1.8 \text{ mol/L}$ ,  $[K_2S_2O_8] = 4.8 \times 10^{-3} \text{ mol/L}$ , and  $T = 66^\circ\text{C}$ .

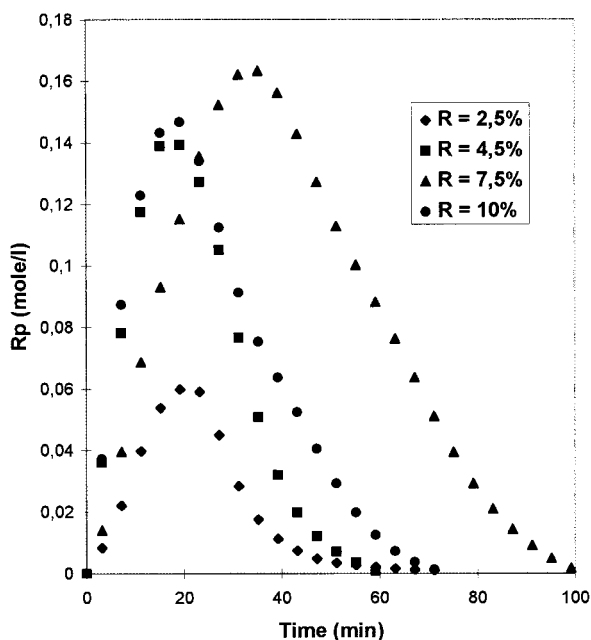
polymerization rates. This pH dependence was pointed out by Ito et al.,<sup>19</sup> Kabanov et al.,<sup>25</sup> and Zhao et al.<sup>6</sup> and was recently confirmed by Scott<sup>26</sup> who completed the study by considering the influence of monomer concentration. Some authors extended the measurements to higher pH values and showed a polymerization increase. A high local concentration of the cation in the vicinity of the ionized monomer and the propagating radical is at the origin of this phenomenon. In particular, Scott demonstrated that above pH 6 the reaction rate showed a weaker dependence on the pH than at lower pH values.<sup>26</sup>

The present work is only concerned with pH values below 6 because we presumed that the kinetic approach must correspond to the same domain as that of the suspension stability (i.e., for a neutralization ratio lower than 0.8). It was shown earlier that this leads to pH values below 6.

### Crosslinking Ratio

Figures 9 and 10 show that the highest conversion rate is obtained for 7.5% mass of the aqueous phase of  $MBA_C$  in weight. If this concentration is higher, the reaction stops earlier with a lower yield. As previously pointed out by Arriola et al.,<sup>27</sup> the temperature had little influence because the activation energy was low for radical propagation reactions. Network formation follows several elementary reactions<sup>27</sup> involving the copolymerization between AA and  $MBA_C$ . The Flory–Stockmayer<sup>28,29</sup> theory is widely used to predict the gel





**Figure 10** The polymerization rate vs. time for different crosslinking ratios. Data were obtained from DSC measurements and  $[AA] = 1.8 \text{ mol/L}$ ,  $[K_2S_2O_8] = 4.8 \times 10^{-3} \text{ mol/L}$ , and  $T = 66^\circ\text{C}$ .

network buildup of a crosslinking polymerization system. Other reactions, such as intrachain cyclization, decrease the efficiency of the crosslinker and lead to a gel point reached for a longer reaction time. The gel time predicted by theories where the number of potential crosslink sites are introduced is not accurate. This deviation from theory could be significant at higher crosslinker levels where pendent groups were found to be less reactive and not fully used to form the network. This reactivity could be modified by a local steric effect, a decrease of the diffusion of the macroradicals, and a lack of chain mobility. Tobita and Hamielec<sup>24</sup> observed very high levels of cyclization in acrylamide/bisacrylamide copolymerization when the total monomer content was very low. When a large excess of monovinyl monomer is present, such as at lower conversion, the intramolecular cyclization rate is very low.

## CONCLUSION

The synthesis of PAA crosslinked in an inverse suspension must be conducted in a stabilized solution. The latter is obtained by adjusting the ratio  $\varphi_{\text{org}}/\varphi_{\text{aq}}$  between the organic and the aqueous phase and the nature and the concentration

of the surfactant and by controlling the temperature during the reaction. The influence of parameters that do not perturb the stability were studied.

A maximum size is obtained in a turbulent condition at 600 rpm. Further away from this stirring speed the diameter is 10 times smaller.

When the crosslinking ratio is decreased, water absorption increases because the number of water molecules confined in the mesh of the 3-dimensional network is governed by its size.

The increase of the neutralization ratio leads to the decrease in the bead size, which presents a larger swelling capacity because of a high surface to volume ratio.

The kinetic study shows that the conversion and the polymerization rates are a decreasing function of the solution pH, and it points out that there is a crosslinker concentration above which the yield decreases significantly.

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