

Solution Properties of Gas-Phase-Polymerized Sodium Acrylate Microparticles. I. Influence of Coinitiators

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ABSTRACT: A partially neutralized sodium acrylate (NaAc) monomer was polymerized in the gas phase in the presence of ammonium peroxydisulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ as the primary initiator and zinc acetate (ZnAc) as the coinitorator. The effect of the coinitorator on the solution properties of the spray-polymerized product was investigated for the conversion percentage as a function of (1) the primary initiator $(\text{NH}_4)_2\text{S}_2\text{O}_8$ concentration, with the concentration (14.8% with respect to the monomer) of the coinitorator kept constant; (2) the coinitorator (ZnAc) concentration, with the primary initiator concentration (4% with respect to the monomer) kept constant; and (3) the reaction temperature. The viscosity of the product as a function of the coinitorator concentration was also investigated. The conversion percentage of gas-phase-polymerized NaAc increased by approximately 8% (i.e., from 91.6 to 99.3%) with an increasing $(\text{NH}_4)_2\text{S}_2\text{O}_8$ concentration (0.5–5% with respect to the mono-

mer). The conversion percentage as a function of the coinitorator concentration (0–15% with respect to the monomer) increased by 25% (from 75 to 100%). When the concentrations of the initiators $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and ZnAc were kept constant at 4 and 14.8% (with respect to the monomer), respectively, the conversion increased from 48 to 83% when the reaction temperature was increased from 100 to 140°C. The viscosity (at 20°C) of sodium polyacrylate decreased with an increasing coinitorator concentration. The relative rate of polymerization, as a function of the pH of the polymer, showed a minimum at $\text{pH} \approx 6$ and subsequently increased steeply, reaching a plateau at $\text{pH} \approx 11$; it then decreased again very sharply. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1034–1043, 2003

Key words: initiators; sodium polyacrylate; gas-phase polymerization

INTRODUCTION

There is little mention of the influence of coinitiators on the properties of gas-phase-polymerized products in the literature. There are, however, a few references to the synthesis and properties of emulsion, bulk, suspension, and (especially) photoinitiated polymerized products with coinitiators.^{1–16} Costela et al.¹ investigated the photophysics, photochemistry, and polymerization activity of *p*-nitronaphthylaniline (NNA) as an initiator in the presence of *N,N*-dimethylaniline (DMA) as a coinitorator for the preparation of poly(lauryl acrylate). They established the relationships between the excitation energy transfer of NNA and the influence of the initiator on the photosensitized generation of free radicals derived from the coinitorator, DMA, which induced the photoreduction of NNA in a very low quantum yield. Penczek et al.² found that Sn^{2+} dicarboxylate (dioctotate) required a coinitorator to initiate polymerization, and both kinetic and spec-

troscopic evidence indicated that the propagation proceeded on the Sn—OR bonds. Bu_2SnO , dissolved in Bu_4Sn with the addition of benzyl alcohol as a coinitorator, was used as the main initiator in the polymerization of poly(ϵ -caprolactone) to yield benzyl ester chain ends.³

Amphiphilic star polymers possessing a hyperbranched core and hydrophilic graft arms were prepared with Ph_2 -(chloromethyl) benzoate as a model initiator to study the effect of different coinitiators on the initiator efficiency.⁶ When potassium iodide (KI) was used, a conversion of 56–86% was achieved,⁶ whereas only a 30–37% conversion was achieved with KCF_3SO_3 or AgCF_3SO_3 as a coinitorator. Hoffman and Farrington⁷ reported on the curing of radiation-curable coating compounds such as acrylate epoxides, urethanes, and polyesters with photoinitiators such as benzophenone. The use of 2-dimethylamino-1-butanol as a coinitorator resulted in improved curing speed, depth of cure, or both.

Andrzejewska et al.¹⁰ used 1,3,5-trithiane derivatives, including α - and β -isomers of the methyl and phenyl derivatives, as coinitiators in benzophenone-induced photopolymerization. To study the mechanism of the photoinitiated production of initiating radicals, they used nanosecond laser-flash photolysis. The polymerization efficiency of the coinitiators did not

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follow the efficiency of the photoinduced formation of the initiating radicals. This was discussed in terms of how the hydrogen-donating ability of the coinitiators and the reactivity of the radicals formed affected the various stages of the polymerization.

Saito and Amano¹⁶ described a method for the manufacture of vinyl chloride polymers by emulsion polymerization in an aqueous medium with oil-soluble polymerization initiators. Perester compounds and/or percarbonate compounds were used as the oil-soluble initiators. The supply of water-soluble peroxide and/or oil-soluble hydroperoxide initiators and water-soluble reducing agents to the polymerization from the commencement of the reaction to a 20% conversion accelerated the rate of polymerization and reduced the formation of colored compounds.

This article reports on the influence of a zinc acetate coinitiator on the degree of polymerization (conversion percentage) of sodium acrylate polymerized in the gas phase. This research was carried out to compare the effectiveness, in terms of the extent of the conversion of sodium acrylate, of this method of polymerization with that of the conventional method of synthesizing sodium polyacrylate. The effect of the coinitiator on the solution properties of the gas-phase-polymerized product was investigated for the conversion percentage as a function of (1) the concentration of the primary initiator, ammonium peroxydisulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$, with the concentration of the coinitiator (14.8% with respect to the monomer) kept constant; (2) the concentration of the coinitiator, with the primary initiator concentration (4% with respect to the monomer) kept constant; and (3) the reaction temperature (T_r). In addition, the viscosity of the product as a function of the coinitiator concentration was investigated.

EXPERIMENTAL

Sodium acrylate was polymerized in a gas-phase process with $(\text{NH}_4)_2\text{S}_2\text{O}_8$, $\text{K}_2\text{S}_2\text{O}_8$, and $\text{Na}_2\text{S}_2\text{O}_8$ as the main initiators and with ZnAc as the coinitiator. Experiments were carried out in which the concentrations of the initiator and coinitiator were alternately kept constant. The resulting polymers were investigated for the conversion percentage. The dilute solution viscosity of each polymer, as a function of the coinitiator used, was determined with an Ubbelohde viscometer.

Monomer solution preparation

All raw materials were used as received, without any further purification (as would be the case in an industrial situation). Acrylic acid (98.5% purity) was supplied by the Catalytic Chemical Corp (Japan). A sodium hydroxide solution (43.0–50.0% concentration)

was supplied by AECI, Ltd. (South Africa). Ammonium peroxydisulfate, potassium peroxydisulfate, and sodium peroxydisulfate, all 98% pure, were supplied by Protea Industrial Chemicals (South Africa). Zinc acetate dihydrate (99.5% purity) was supplied by Merck (SA agent). Acrylamide (98% purity) was supplied by SA Cyanamid, Ltd (South Africa).

The sodium acrylate monomer was prepared by the slow addition of a 45% sodium hydroxide solution to a previously prepared acrylic acid/water (1:10) mix. During the neutralization, the mix temperature was maintained below 50°C to eliminate any chance of premature polymerization (unlikely, however, in the absence of an initiator). The degree of neutralization was varied for different experiments. In all experiments, the initiator was added before gas-phase polymerization to eliminate any prepolymerization or aging effects. The coinitiator was also added at any stage before the gas-phase polymerization.

Determination of the volatile content of the sodium polyacrylate powder

The volatile content of the spray-dried polymer was determined after oven drying at 105°C for 2 h. The loss in mass, expressed as a percentage of the initial mass, gave the volatile content.

Determination of the degree of conversion

The residual unsaturation in the final product of the sodium polyacrylate is a measure of the unconverted sodium acrylate monomer remaining in the polymer. The unsaturation was determined by a bromination titration technique¹⁷ with the following reagents: 0.1M sodium thiosulfate, 0.1M potassium bromate, a 20% H_2SO_4 solution, and a 20% KI solution. If the volume of the blank titer (i.e., no polymer product present) is v_2 (cm^3) and the volume of the sample titer is v_1 (cm^3), the difference between the sample before spray drying and the percentage of free monomer in the dry product is a measure of the conversion percentage.

Therefore, the percentage of free monomer in the dry polymer product is $[(v_2 - v_1)/2] \times$ the molarity of sodium thiosulfate \times (mmfm/ms), where mmfm is the molecular mass of the free monomer and ms is the mass of the sample. Therefore, the conversion percentage is $100 -$ the percentage of the free monomer. This test method was evaluated by the addition of sodium acrylate monomer to a commercial sodium acrylate solution.

Determination of the solution viscosity

Dilute solution viscometry determinations were carried out with an Ubbelohde viscometer maintained at a constant temperature of 20°C. The measurements of

TABLE I
Formulations of Solutions of Acrylic Acid Monomer

Solution	Amount of acrylic acid used (kg)	46% NaOH solution (kg)	Water (kg)	% Theoretical concentration of monomer	% Neutralization of acrylic acid
1	9.8	5.8	9.4	45	49.0
2	8.7	5.2	11.1	40	49.5
3	6.5	3.9	14.6	30	49.7

the solution viscosity of sodium polyacrylate were made by comparisons of the efflux time (t) for a specified volume (exactly 10 mL for the particular viscometer used) of the polymer solution to flow through a capillary tube with the corresponding efflux time (t_o) for the solvent. From times t and t_o and the polymer concentration, several quantities, including the viscosity ratio $\eta_r = \eta/\eta_o \approx t/t_o$, were determined, leading to the limiting viscosity number (or intrinsic viscosity), $[\eta]$ (η and η_o are the viscosities of the dilute polymer solution and solvent, respectively). η_r was obtained by the plotting of the specific viscosity, $\eta_{sp} = \eta_r - 1$, versus the concentration, c . An extrapolation to $c = 0$ yielded $[\eta]$.

The viscosity-average molecular mass was determined from $[\eta]$ with the Mark-Houwink-Sakurada equation,¹⁸ $[\eta] = KM^\alpha$, where K and α are constants for a particular polymer/solvent system at a given temperature. From the literature¹⁹ and for the polymer/solvent system under consideration, K and α were 42.2×10^{-5} and 0.64, respectively.

pH measurement

An aqueous solution of sodium polyacrylate of a known concentration (0.2 g/dL) was prepared, and the pH was measured at 20°C.

Degree of neutralization

A 1% solution of sodium polyacrylate in distilled water was prepared from the spray-dried product. A volume of 20 mL of the solution was taken and titrated with a 1M sodium hydroxide solution. A plot of the pH of the solution versus the volume of the sodium hydroxide solution titrated gave an indication of the number of moles of the unneutralized product. The pH of a similar volume of the solution of the prepared product was reduced by the addition of concentrated hydrochloric acid. This solution was again titrated with a 1M sodium hydroxide solution to the same inflection point. Another inflection point was reached before the initial one. The difference between the two inflection points is a measure of the total number of moles of acid in the product. From the two titrations, the degree of neutralization was calculated.¹⁷

The feasibility of polymerizing partially neutralized sodium acrylate monomer in a spray drier to give a dried powder product was studied. A partially neutralized sodium acrylate monomer was chosen for evaluation (as opposed to a fully neutralized sodium acrylate) because it was similar to a product commercially available from Bevaloid SA, Ltd., (Durban, South Africa) albeit as a 25% solution. A formulation (21.7 kg of acrylic acid and 15.3 kg of water), which yielded a 49.6% solution of acrylic acid, having a concentration of 50%, was prepared. The initiator was prepared from 1 kg of water and 91 g of $(\text{NH}_4)_2\text{S}_2\text{O}_8$. A mixture of the monomer and initiator solutions gave a concentration of 0.182% initiator with respect to the monomer.

Table I shows the formulations of the solutions of the acrylic acid monomer. With two different concentrations of the $(\text{NH}_4)_2\text{S}_2\text{O}_8$ initiator for the formulations shown in Table I, six experiments were carried out. The initiator type and level and T_r were investigated for the polymerizations of fully and partially neutralized sodium acrylate. Because sodium acrylate is less water-soluble than acrylic acid, the concentration of the monomer solution was reduced to 30%. The monomer solution consisted of 22.97% acrylic acid, 28.38% sodium hydroxide solution (45% concentration), and 48.65% water. The spray-drier conditions (105°C for 2 h) were kept as close as possible to those mentioned previously for the determination of the volatile content of the powder of sodium polyacrylate, except, of course, for the determination of the effect of T_r variations.

Use of the cointiators in the polymerization of sodium acrylate

Kabanov and Klockhlo¹⁷ determined that the aqueous polymerization of acrylic acid and sodium acrylate is also affected by the addition of salts (e.g., sodium chloride and sodium acetate). Before large-scale experiments were performed in the spray drier, they were done on a laboratory scale. Aqueous solution polymerizations, incorporating salts, were carried out. If their theory is indeed true, we thought that the incorporation of salts into the monomer solution might allow a satisfactory polymerization at an acceptable

TABLE II
Results of the Feasibility Study for Polymerizing Partially Neutralized Sodium Acrylate Monomer in a Spray Dryer to Give a Dry Powdered Product of Sodium Polyacrylate

T_r (°C)	Exhaust air condition	Product				pH of 10% solution
		% Volatile content	% Conversion	% Neutralization	Viscosity at 20°C (mPa.s)	
110	—	1.6	98.32	—	—	—
130	Slight monomer boil-off	1.6	97.80	78	50	5.25
140	Monomer boil-off	4.4	98.82	75	50	5.25

pH. Both sodium acetate and zinc acetate were evaluated. Zinc acetate was chosen because of its superior aqueous solubility in comparison with that of many divalent metal salts. The polymerization was carried out in a 1-L flask fitted with a reflux condenser and immersed in a thermostatically controlled water bath. The formulation was 303 g of water, 32 g of acrylic acid, 47.5 g of methylacrylic acid, 85.7 g of a sodium hydroxide solution (45%), and various amounts of salt.

Experiments were carried out to investigate the following variables: (1) the initiator type [$K_2S_2O_8$ or $(NH_4)_2S_2O_8$], (2) the initiator concentration, (3) the zinc acetate concentration, and (d) T_r (110–140°C). Because of its low aqueous solubility, $K_2S_2O_8$ could only be used to a certain concentration ($\approx 2.0\%$ with respect to the monomer); $(NH_4)_2S_2O_8$ was used for the investigation of higher initiator levels. The monomer solution formulation was 22.97% acrylic acid, 28.38% sodium hydroxide solution (45% concentration), 49.65% water, and various levels of zinc acetate. The monomer solution feed rate into the spray drier was approximately $3 \text{ dm}^3 \text{ h}^{-1}$.

An investigation into the effect of T_r on the aqueous solution viscosity in the spray polymerization of sodium acrylate was carried out with the monomer solution formulation, as detailed previously. The main initiator used was $(NH_4)_2S_2O_8$ at a level of 4% with respect to the monomer.

RESULTS AND DISCUSSION

Table II shows the results of a feasibility study for polymerizing partially neutralized sodium acrylate monomer in the gas phase to give a dry powdered product of sodium polyacrylate. The fact that high degrees ($>70\%$) of neutralization in the partially neutralized sodium acrylate occurred indicated that volatile acrylic acid (sodium acrylate is nonvolatile) was lost in the neutralization process before polymerization. This is supported by the exhaust air condition. Discounting the monomer loss, we found the conversions of monomer to polymer to be very good. This indicates that they are good enough to justify the feasibility of the process.

Monomer-loss consideration during spray polymerization

Attempts to reduce monomer loss during spray polymerization can be approached in three different ways: (1) reducing the concentration of the monomer feed solution so that the polymerization of the volatile monomer is essentially complete before appreciable evaporation with water occurs, (2) increasing the initiator concentration (relative to the monomer) so that the corresponding faster polymerization rate reduces the evaporation of the volatile monomer, and (3) fully neutralizing the acrylic acid with sodium hydroxide and thereby eliminating the volatile monomer. The results of attempts to reduce monomer loss are shown in Table III. Altering the monomer solution concentration from 45 to 30% had no effect on monomer loss [as indicated by the increase in the neutralization percentage from approximately 50% for acrylic acid (Table I) to 75% or more for sodium polyacrylate (Table III)]. However, for each monomer solution, the higher initiator level gave a lower monomer loss, although not eliminating it to a satisfactory degree. Therefore, it was considered necessary to eliminate the volatile monomer completely if polymerization was to be satisfactorily carried out in the spray drier under the selected temperature conditions (110–140°C). The viscosity and physical appearance of 10% sodium poly-

TABLE III
Results of the Experiment Carried Out to Reduce Monomer Loss During Spray Polymerization of Sodium Acrylate by Reducing Monomer Solution Concentration and Changing Percentage of Initiator Concentration

Run	Monomer solution concentration (%)	% Initiator $(NH_4)_2(S_2O_8)$ on dry monomer	% Neutralization of product
1	45	0.36	75
2	45	0.14	80
3	40	0.36	73
4	40	0.14	81
5	30	0.36	79
6	30	0.14	85

A high percentage of neutralization of product is an indication of lower monomer loss.

TABLE IV
Properties of Fully Neutralized Sodium Polyacrylate Prepared Under Different Conditions

Run	Initiator type used	% Initiator on dry monomer	T_r (°C)	10% Solution viscosity at 20°C (mPa.s)	Appearance of 10% solution
1	(NH ₄) ₂ (SO ₄) ₂	0.08	100	—	Gel (soluble, hot)
2	(NH ₄) ₂ (SO ₄) ₂	0.20	100	—	Gel (soluble, hot)
3	(NH ₄) ₂ (SO ₄) ₂	0.24	100	—	Gel (soluble, hot)
4	(NH ₄) ₂ (SO ₄) ₂	0.40	100	40	Clear
5	(NH ₄) ₂ (SO ₄) ₂	0.40	130	8	Clear
6	(NH ₄) ₂ (SO ₄) ₂	2.00	130	25	Clear
7	Na ₂ (SO ₄) ₂	0.20	100	70	Slight gel
8	K ₂ (SO ₄) ₂	0.20	100	210	Clear

acrylate solutions prepared from fully neutralized sodium acrylate monomer are shown in Table IV. The products from trials 1–3 were soluble in hot water, but not in cold water. This was probably due to the high level of unreacted sodium acrylate monomer and its salting-out effect on the sodium polyacrylate. For confirmation, sodium acrylate was added to a sodium polyacrylate solution. The results are shown in Table V. The conversion was less than 55% (i.e., the residual monomer was greater than 45%), and the mixture was insoluble in cold water (at a 10% concentration).

A comparison of the solution viscosities and solution appearances indicated that the polymerization conversion improved as the initiator level and T_r increased. It also showed that Na₂S₂O₈ and especially K₂S₂O₈ gave improved reactions with respect to (NH₄)₂S₂O₈ at an initiator level of 0.2% (with respect to dry monomer) and a T_r value of 100°C.

Kabanov and Klockhlo¹⁷ reported that in aqueous solution polymerizations of acrylic acid salts, the rate of propagation was significantly affected by the pH of the system, as shown in Figure 1. The rate of polymerization and the molecular mass of the polymer decreased rapidly when the pH was increased from 1 to 6, showing a minimum between pH 6 and pH 7. They ascribed this to the increase in the concentration of the acrylate (pK_a for acrylic acid = 4.2) anions because their addition to the growing polymer chain under

these conditions was slower than that of un-ionized monomer. The polyacid formed at pH 1–6 was practically un-ionized [pK_a for poly(acrylic acid) = 6.4]. A further increase in pH (7–11) resulted in a considerable increase in the reaction rate and molecular mass. Kabanov and Klockhlo assumed that this was caused by an increase in the local concentration of Na⁺ in the vicinity of ionized propagating radicals. The polyacid macromolecules were capable of binding the cations present in the aqueous solution. The ends of the growing radicals could then be considered divided ion pairs. The electrostatic repulsion between the charged monomeric anions and radicals approaching one another in the act of propagation would be diminished if ionizable groups at the end of the growing chains were involved in the formation of such ion pairs. This theory was tested in the spray polymerization of sodium polyacrylate, with monomer solutions of various pHs (i.e., 9.0, 10.0, 11.0, and 12.0). T_r was 100°C, and the feed rate and pressure were as stated earlier. The results are shown in Table VI. Again, some of the

TABLE V
Determination of the Salting-Out effect of Sodium Polyacrylate from a 10% Aqueous Solution with Sodium Acrylate

% Sodium acrylate on dry sodium polyacrylate	Viscosity at 20°C (mPas)	% Conversion
15.6	143	86.5
33.8	115	74.8
52.5	90	65.6
72.2	77	58.1
90.0	Slight gel formation ^a	52.6
100.0	Gel formation ^a	50.0

^aSodium acrylate was added to a hot sodium polyacrylate solution, and gel formed on cooling.

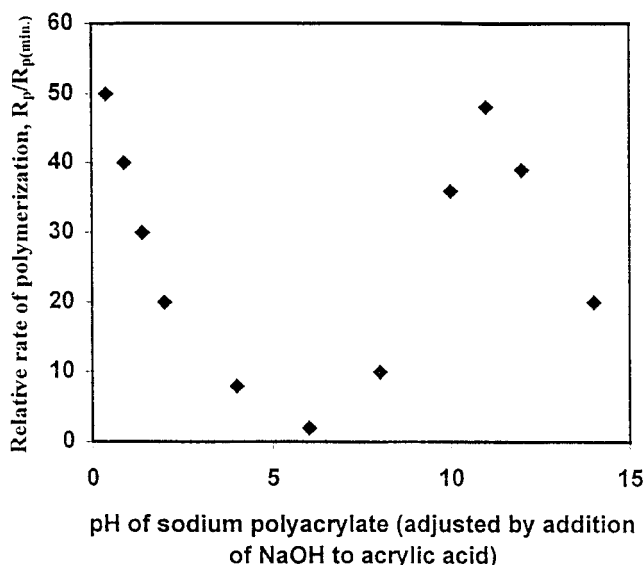


Figure 1 Relative rate of polymerization of sodium acrylate as a function of the pH of the polymer solution (adjusted by the addition of NaOH to acrylic acid).

TABLE VI
Properties of Fully Neutralized Sodium Polyacrylate Prepared by the Use
of Various Monomer Solutions of Different pHs

Run	Initiator (at 0.2% dry monomer)	pH of monomer solution (adjusted with NaOH)	10% Solution viscosity at 20°C (mPa.s)	Appearance of 10% polymer solution
1	(NH ₄) ₂ (SO ₄) ₂	9.0	—	Gel
2	(NH ₄) ₂ (SO ₄) ₂	10.0	—	Gel
3	(NH ₄) ₂ (SO ₄) ₂	11.0	—	Gel
4	(NH ₄) ₂ (SO ₄) ₂	12.0	200	Clear
5	Na ₂ (SO ₄) ₂	9.0	70	Slight gel
6	Na ₂ (SO ₄) ₂	12.0	950	Clear
7	K ₂ (SO ₄) ₂	9.0	210	Clear
8	K ₂ (SO ₄) ₂	12.0	800	Clear

polymers were not soluble in cold water, and this indicated a high residual monomer content and poor conversion. The conversion improved for all the initiator types studied, as the pH of the monomer solution increased, as indicated by the solution appearance and viscosity. This effect was most marked in the following order: ammonium > sodium > potassium peroxydisulfate. To confirm that the increased solution viscosity was indicative of increased conversion and not due to increased pH, we measured the viscosity of a standard sodium polyacrylate solution versus pH. The results are shown in Figure 2; the viscosity of a 10% sodium polyacrylate solution varied slightly between pH 7 and pH 12.

Effect of the cointiator on the sodium polyacrylate solution properties

The results of the investigation into the use of cointiators in the polymerization of sodium acrylate are

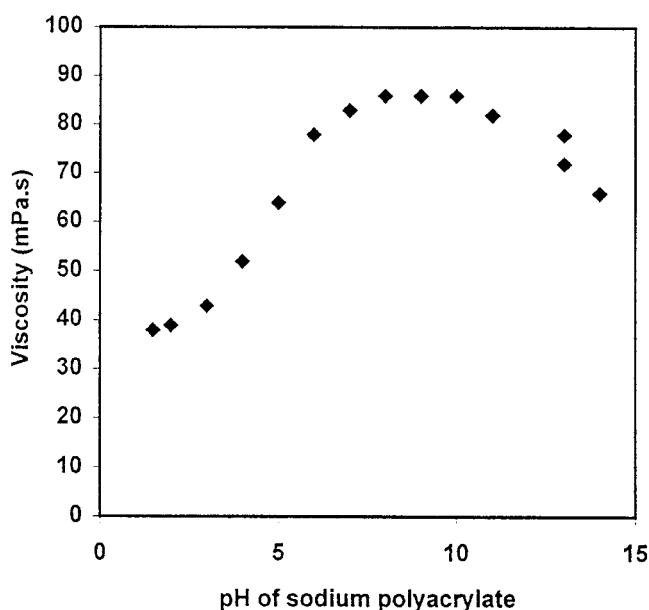


Figure 2 Viscosity of a 10% solution of sodium polyacrylate as a function of the pH.

shown in Table VII. We monitored the conversion during the reactions by taking samples and measuring their residual monomer concentrations. The reaction times indicated were the times taken to achieve 0.1% residual monomer. The solution viscosities were obviously affected by the inclusion of salt, and the rates of polymerization obviously increased. The viscosity of sodium polyacrylate prepared by the gas-phase polymerization technique with the incorporation of zinc acetate as a cointiator was higher than the viscosity of that prepared with the incorporation of sodium acetate as a cointiator. This could possibly be caused by crosslinking of the final polymer.²⁰ To investigate this, we added zinc acetate to a standard sodium polyacrylate solution, and its effect on the viscosity was measured. The results are shown in Figure 3. When zinc acetate was added, the viscosity was reduced. In Figure 3, the conversion percentage and the viscosity of sodium polyacrylate as functions of the cointiator (zinc acetate) percentage are also shown. Ignoring the data for the 11.4% zinc acetate (which appears anomalous) and within the parameters set for this experiment ($T_r = 110^\circ\text{C}$ and initiator concentration = 4%), we deduced that a minimum zinc acetate level of 5% was required for a good conversion (>96%). The viscosity decreased asymptotically with an increasing cointiator percentage.

The experimental variables of the measurements made to investigate the use of zinc acetate as a cointiator and the properties of the products are tabulated in Table VIII. Gel formation correlated with conversions of less than 55%, and solubility curves indicated the conditions needed for conversion, that is, the minimum initiator and zinc acetate levels for a given value of T_r . Figure 4 shows variations in the conversion percentage and viscosity as functions of the initiator [(NH₄)₂S₂O₈] percentage. For the cointiator level considered in this study (14.8%), a minimum initiator level of approximately 2.5% was necessary for a good conversion, that is, a conversion greater than 96%. The viscosity of the polymer decreased with an increasing percentage of the initiator. Figure 5 shows variations

TABLE VII
Some Properties (Results) of the Product Formed by the Aqueous Solution Polymerization of Sodium Acrylate with the Incorporation of Sodium and Zinc Salts

Run	Salt type/% level (g) on monomer	T_r (°C)	Reaction time ^t (h)	Final viscosity at 20°C (mPa.s)	Final pH	% Residual monomer ^a
1	—	70 ^b	4.5	400	8.3	0.1
2	Sodium acetate/4.1	70	2.0	80	7.0	0.1
3	Sodium acetate/8.2	70	2.0	230	7.0	0.1
4	Zinc acetate/4.1	70	2.0	4000	7.0	0.1
5	Zinc acetate/8.2	70	2.0	7000	7.0	0.1
6	Zinc acetate/12.3	70	2.0	46000	7.0	0.1
7	Zinc acetate/8.2	60	2.0	22000	6.7	0.1

^aDetermined by bromination titration.

^bStandard reaction temperature for this experiment.

of the conversion percentage and viscosity as functions of T_r . T_r values above 110°C had no effect on the degree of conversion; above $T_r = 110^\circ\text{C}$, there was no significant change in the conversion percentage. However, the viscosity increased with increasing T_r .

The results of the determination of the effects of T_r on the product properties of sodium polyacrylate are shown in Table IX. A comparison of runs 1 and 2 in Table X indicates that the conversion of monomer to polymer was reproducible, but there was quite a large variation in the aqueous solution viscosity, from 520 to 1090 mPa s. This may be explained by the fact that two air-inlet temperatures (145°C for run 1 and 130°C for run 2) were employed to achieve the same air-outlet flow rate of $0.134 \text{ m}^2 \text{ s}^{-1}$ at the same T_r value of 110°C. If T_r did not correlate with the air-outlet temperature but was related to the air-inlet temperature, then the viscosity variation could very well correlate with the temperature, as shown in our investigation into the

effect of T_r on the aqueous solution viscosity (Table IX) in the spray polymerization of sodium acrylate. Comparing runs 3 and 4 (Table X), we see that the air-flow rate and particle residence time did not affect the conversion but resulted in an increase in the solution viscosity. The air-inlet temperatures of runs 3 and 4 were 174 and 200°C, respectively. The increase in the solution viscosity would again correlate with T_r .

Increasing the size of the spray nozzle in runs 5 and 6 (Table X) caused very little change in the conversion but did lead to an increase in the solution viscosity. This effect could possibly be due to an oxygen-inhibition mechanism. If oxygen inhibition did occur in the spray polymerization process, it would have been less apparent with a large polymerizing droplet. This is because the larger the reduction in the surface-to-volume ratio (of the droplet) becomes, the greater the particle size is and the more likely oxygen inhibition will be at the droplet surface. In runs 1 and 2, the dry

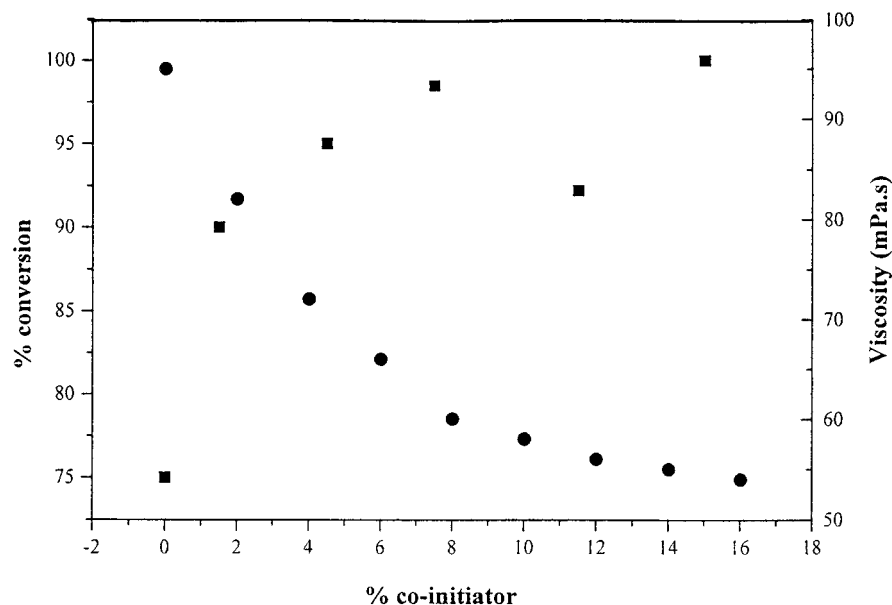


Figure 3 Variations in (■) the conversion percentage and (●) the viscosity of sodium polyacrylate as functions of the percentage of the coinitiator zinc acetate [4% $(\text{NH}_4)_2\text{S}_2\text{O}_8$, $T_r = 110^\circ\text{C}$].

TABLE VIII
Effect of Coinitiator (Zinc Acetate) on the Percentage Conversion, Percentage Volatile Content, Solution Viscosity, and pH of Gas-Phase-Polymerized Sodium Polyacrylate

Run	Initiator type	% Initiator level	% ZnAc level	T_r (°C) ± 2	% Conversion	% Volatile content	10% Aqueous solution viscosity at 20°C (mPa.s)	Solution Appearance	Solution pH
1	$K_2(SO_4)_2$	0.2	0.0	140	—	0.0	—	Gel	8.30
	$K_2(SO_4)_2$	0.2	3.4	140	—	0.0	—	Gel	6.50
	$K_2(SO_4)_2$	0.2	7.1	140	—	0.0	—	Gel	6.60
	$K_2(SO_4)_2$	0.2	14.8	140	—	0.1	7	Clear	7.00
2	$K_2(SO_4)_2$	0.2	14.8	140	—	0.1	7	Clear	7.00
	$K_2(SO_4)_2$	0.4	14.8	140	—	1.3	18	Clear	7.00
3	$K_2(SO_4)_2$	0.2	7.1	140	—	0.0	—	Gel	6.60
	$K_2(SO_4)_2$	0.8	7.1	140	—	0.0	—	Gel	6.60
	$K_2(SO_4)_2$	1.6	7.1	140	—	0.6	10	Clear	6.60
4	$K_2(SO_4)_2$	0.4	14.8	140	—	1.3	18	Clear	7.00
	$K_2(SO_4)_2$	0.4	14.8	110	—	0.7	—	Gel	7.00
5	$K_2(SO_4)_2$	0.4	14.8	110	—	0.7	—	Gel	7.00
	$K_2(SO_4)_2$	1.0	14.8	110	92.8	0.9	50	Clear	6.40
	$K_2(SO_4)_2$	2.0	14.8	110	97.0	1.5	3700	Clear	6.90
6	$(NH_4)_2(SO_4)_2$	0.4	14.8	110	91.5	0.9	260	Clear	6.70
	$(NH_4)_2(SO_4)_2$	1.0	14.8	110	95.3	0.8	2080	Clear	6.80
	$(NH_4)_2(SO_4)_2$	1.5	14.8	110	93.3	2.2	248	Clear	6.90
	$(NH_4)_2(SO_4)_2$	2.0	14.8	110	96.9	1.6	3900	Clear	6.80
	$(NH_4)_2(SO_4)_2$	2.5	14.8	110	97.5	3.2	942	Clear	7.00
	$(NH_4)_2(SO_4)_2$	3.0	14.8	110	98.3	3.6	1382	Clear	6.90
	$(NH_4)_2(SO_4)_2$	3.5	14.8	110	97.6	3.9	560	Clear	6.85
	$(NH_4)_2(SO_4)_2$	4.0	14.8	110	99.1	3.3	476	Clear	6.95
	$(NH_4)_2(SO_4)_2$	4.5	14.8	110	97.2	3.6	1880	Clear	6.90
	$(NH_4)_2(SO_4)_2$	5.0	14.8	110	98.1	3.6	862	Clear	6.90
7	$(NH_4)_2(SO_4)_2$	4.0	14.8	110	99.1	3.3	476	Clear	6.95
	$(NH_4)_2(SO_4)_2$	4.0	11.4	110	91.7	1.0	300	Clear	7.20
	$(NH_4)_2(SO_4)_2$	4.0	7.6	110	99.2	1.7	262	Clear	7.30
	$(NH_4)_2(SO_4)_2$	4.0	4.5	110	94.4	2.6	113	Clear	7.50
	$(NH_4)_2(SO_4)_2$	4.0	1.5	110	89.7	2.4	365	Clear	7.30
	$(NH_4)_2(SO_4)_2$	4.0	0.0	110	74.9	0.0	25	Clear	7.20

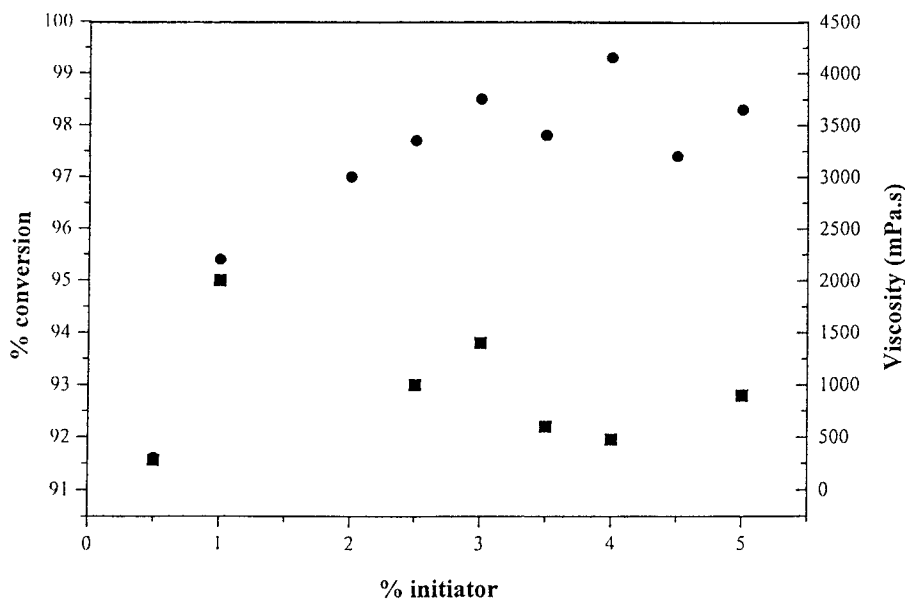


Figure 4 Variations in (●) the conversion percentage and (■) the viscosity of sodium polyacrylate as functions of the percentage of the initiator $(NH_4)_2S_2O_8$.

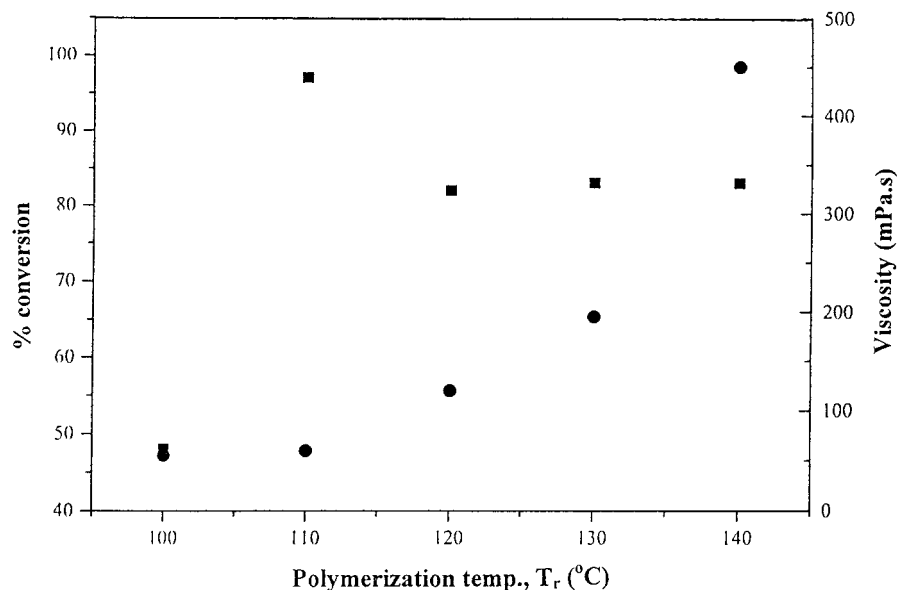


Figure 5 Variations in (■) the conversion percentage and (●) the viscosity of sodium polyacrylate as functions of T_r .

product obtained from the spray drier was weighed and compared with the amount of the monomer solution fed into the equipment. The respective yields from runs 1 and 2 were found to be 73.3 and 83.8%. These yields seem satisfactory if we consider the fact that some fine particles might have been lost with the exhaust air from the cyclone. Products from run 2 were tested for conversion 2 h and 48 h after the completion of the run. These were 97.6 and 98.1%, respectively. This indicates very little, if any, continued reaction after the product's exit from the drier. It may be possible to have a small amount of postreaction occurring while the product cools, but this has very little bearing on the final product's properties.

The solution viscosity and, by implication, the molecular mass of sodium polyacrylate varied with the pH of the initial monomer solution. This correlates with the findings of Kabanov and Klockhlo.¹⁷ With a suitable initiator/coinitiator system, particularly the $(\text{NH}_4)_2\text{S}_2\text{O}_8$ /zinc acetate combination, T_r could be reduced far below what is described in the litera-

ture.²¹⁻²³ The incorporation of the coinitorator also correlated well with the results of previous work,¹⁷ albeit extending the postulate from monovalent salts to divalent salts. The viscosity (and, therefore, the molecular mass)/temperature relationship correlated well with the findings of Norrish and Smith,²⁴ showing an inverse relationship to that found with a solution polymerization technique. Norrish and Smith postulated a gel or autoacceleration effect: when certain monomers are polymerized in a concentrated (or undiluted) solution, there is a marked deviation from first-order kinetics in the direction of an increase in the reaction rate and molecular mass. The effect is particularly pronounced with methyl methacrylate, methyl acrylate, and acrylic acid. It is independent of the initiator and due to a decrease in the rate at which the polymer molecules diffuse through the viscous medium, thereby lowering the ability of two long chain radicals coming close together for a termination process. The decrease in the termination rate leads to an increase in the overall polymerization rate and molecular mass because the lifetime of the growing chains is increased.

TABLE IX
Effect of T_r on the Aqueous Solution Viscosity of Sodium Polyacrylate in the Gas-Phase Polymerization of Sodium Acrylate

T_r (°C) ± 2	% Conversion	% Volatile content	% Aqueous solution viscosity at 20°C (mPa.s)	pH of 10% aqueous solution
100	89.7	2.6	50	7.3
110	91.4	3.1	60	7.1
120	96.2	2.4	120	7.3
130	96.4	2.1	188	7.2
140	96.2	1.7	440	7.1

CONCLUSIONS

The preparation of sodium polyacrylate by the gas-phase polymerization process is very feasible, giving satisfactory conversions (>95%). In the unique environment of the gas-phase polymerization process, there was an accelerating effect or autoacceleration in a concentrated monomer solution. In the spray drier, water was continually being removed from the polymerizing particles, so that the concentration was increasing all the time, and this gave rise to an increas-

TABLE X
Effect of Varying the Spray-Drier Operating Conditions on the Product Properties
of Gas-Phase-Polymerized Sodium Polyacrylate

Run	Variable studied	$T_r \pm 2$ (°C)	SNFC/AC	Af_r in ($m^2 s^{-1}$)	Af_s out ($m^2 s^{-1}$)	MSf_r ($d m^3 h^{-1}$)	HI (mJ)	% Volatile content	10% Aqueous solution viscosity (mPa.s)	% Conversion	pH of 10% aqueous solution
1	Reproducibility	110 ^a	60100/120	0.15	0.134	3.5–4.0	72	2.2	1090	99.1	7.20
2		110 ^b	60100/120	0.15	0.134	3.5–4.0	72	2.2	512	98.1	7.25
3	Af_r	110 ^c	60100/120	0.15	0.134	3.5–4.0	72	1.8	720	97.4	7.40
4		110 ^d	60100/120	0.13	0.094	3.5–4.0	72	4.6	1180	97.1	7.25
5	Nozzle-diameter	110	60100/120	0.15	0.134	3.5–4.0	72	1.8	720	97.4	7.40
6		110	60100/120	0.15	0.134	3.5–4.0	72	4.0	1320	97.9	7.20

Af_r = air flow rate; SNFC/AC = spray nozzle fluid cap/air cap; MSf_r = monomer solution feed rate; HI = heat input.

^aInlet air temperature = 145°C.

^bInlet air temperature = 130°C.

^cInlet air temperature = 174°C.

^dInlet air temperature = 200°C.

ing autoaccelerating effect. The use of a suitable initiator/coinitiator system, particularly the $(NH_4)_2S_2O_8$ /zinc acetate combination, afforded a lowering of T_r (from 140 to 110°C).

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