

Theoretical Energy Consideration of the Gas-Phase Polymerization of Sodium Acrylate

Ronald D. Sanderson, E. Rotimi Sadiku*

Division of Polymer Science, Department of Chemistry, University of Stellenbosch, Private Bag X1, Matieland 7602, Republic of South Africa

Received 5 June 2001; accepted 31 May 2002

ABSTRACT: The kinetics of the spray polymerization of sodium acrylate were investigated. The technique in which the heat of polymerization was used for solvent removal showed better energy efficiency than the solution or emulsion polymerization methods for preparing sodium polyacrylate. The monomer solution was injected into the nozzle of the spray machine via a venturi effect to siphon up the solution. Two siphon tubes feeding through two control valves into a mixing chamber before the spray operation resulted in separate feeds of a sodium hydroxide solution

and a mixture of acrylic acid, water, and a catalyst. These two feeds generated the heat of neutralization of sodium acrylate. This heat raised the temperature of the monomer solution to the reaction temperature, thereby initiating the exothermic polymerization reaction. Theoretical calculations of these energy sources were compared with the energy required to give a dry product. The results revealed that the energy cost for spray polymerization was $4783.5 \text{ kJ kg}^{-1}$, whereas the energy cost was $7830.4 \text{ kJ kg}^{-1}$ for the conventional system. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 928–935, 2003

INTRODUCTION

Many reports are available in the literature on the spray polymerization of several polymers,^{1–16} particularly sodium polyacrylate,^{17–20} the equipment for spray polymerization, and the properties of the polymers produced. There exist, however very few discussions (if any) on the energy consideration of the spray-polymerization technique and how this consideration compares with the conventional techniques of producing dried polymer microparticulates. Before the energy crisis of the 1970s, there were very few problems in preparing sodium polyacrylate by conventional free-radical solution polymerization and transporting the product as a 10–40% concentration (depending on the molar mass).^{21–26} However, the advent of higher transport costs and limits on storage space has resulted in increasing demands for dry products that can be solubilized. If sodium polyacrylate is prepared by a solution or emulsion process, it can be subsequently dried. The latter processing step requires further time and energy. Energy is also wasted because the polymerization stage is exothermic, requiring cooling for product control, and the drying stage is endothermic, requiring heat.

It is theoretically possible to prepare poly(acrylic acid) by a bulk-phase polymerization to yield a 100% product, but control over such a process is extremely

difficult and not very practical.²² Similarly, conversion to the sodium salt also presents problems. Even if sodium polyacrylate is prepared by suspension polymerization, there is still the requirement for a solvent removal stage when polymerization is complete, even if only by filtration or centrifugation.

Renard and McKenna²⁷ investigated the inverse suspension of partially neutralized acrylic acid and reported that the variations of the initiator and surfactant concentrations had little effect on the rate of reaction. They found, however, that the apparent activation energy was very high.

The combined thermokinetic method for measuring exothermic chemical processes in drops surrounded by a gaseous phase with spray technology was reported by Michael et al.²⁸ According to Michael et al., this thermodynamically open system can be evaluated only if the drop in volume as a function of time is detected and the mass and heat exchange coefficients are known. They employed a photographic method for this detection during the radical bulk polymerization of droplets of acrylonitrile. Zhang et al.²⁹ reviewed the development, the technological process, and the characteristics of spray polymerization and its application in synthesizing polystyrene and poly(sodium acrylate) powder.

The entraining of metal powders in an air flow, which was accelerated by a de Laval-type nozzle, allowed the investigation of the kinetics of spray coatings.³⁰ According to Vanueteenkiste et al.,³⁰ the effect of the choice of the substrate metal on the kinetics of spray polymerization was relatively weak. The coat-

*Present address: Sastech R & D (Polymer Division), PO Box 1, 1 Klasie Havenga Ave., Sasolburg 1947, South Africa.
Correspondence to: R. D. Sanderson (rds@maties.sun.ac.za).

TABLE I
Sources of Raw Materials (and Their Purity or Concentration)
Used in the Experiments

Raw material	Purity (%)	Concentration (%)	Source
Acrylic acid	98.5	43-50	Japan Catalytic Chemical Co.
NaOH			AECI Ltd.
(NH ₄) ₂ S ₂ O ₈	98.0		Protea Industrial Chemical Pty Ltd.
K ₂ S ₂ O ₈	98.0		Protea Industrial Chemical Pty Ltd.
Na ₂ S ₂ O ₈	98.0		Protea Industrial Chemical Pty Ltd.
ZnAc dihydride	99.5		Merck SA Ltd.
Acrylamide	98.0		South Africa Cyanamid (Pty), Ltd.

ing process depended primarily on the kinetic energy of the incident powders.

The spray polymerization of a sodium acrylate solution in a system in which the heat of polymerization contributed to the removal of the reaction solvent, in this instance water, to yield a dry product was carried out. This was done in a one-stage process, with minimal energy input. The purpose of this was to produce some energy savings and compare the energy input required in spray polymerization with that of the conventional method of producing dry products after polymerization.

EXPERIMENTAL

The energy input in the spray polymerization of sodium acrylate was evaluated (theoretically) by the consideration of the heats of polymerization, evaporation, vaporization, and neutralization, which were used in the spray drying of the polymer.

Monomer solution preparation

Raw materials {acrylic acid (CH₂=CH—COOH), sodium hydroxide (NaOH) solution, ammonium peroxydisulfate [(NH₄)₂S₂O₈], potassium peroxydisulfate (K₂S₂O₈), sodium peroxydisulfate (Na₂S₂O₈), zinc acetate (ZnAc) dihydrate, and acrylamide} were used as received without any further purification (as would be the case in an industrial situation). The sources of these materials and their purities and concentration are shown in Table I. The sodium acrylate monomer was prepared by the slow addition of a 45% NaOH solution to a previously prepared acrylic acid/water (1.42:1) mix. During the neutralization, the mix tem-

perature was maintained below 50°C. This was done to eliminate any chance of premature polymerization (unlikely in the absence of an initiator, however). The degree of neutralization was varied for different experiments. In experiments in which a coiniciator was used, it could be added at any stage before spray drying. However, in all experiments, the initiator was added before spray drying to eliminate any prepolymerization or aging effects. The formulations of the acrylic acid monomer, used in the experiments to prepare dried sodium polyacrylate, are shown in Table II.

Degree of conversion

The residual unsaturation in the final product was a measure of the unconverted sodium acrylate monomer remaining in the product. This was determined by a bromination titration technique to give the percentage of free monomer after spray drying. The difference in unsaturation between the sample before spray drying and the percentage of free monomer was a measure of the conversion percentage. This test method was evaluated by the addition of sodium acrylate monomer to a commercial sodium acrylate solution.

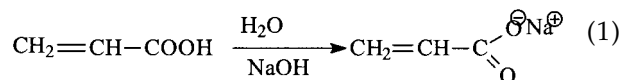
Degree of neutralization

A 1% solution (in distilled water) of the product was obtained from the spray dryer. A known volume of the solution was taken and titrated with a 1M NaOH solution. A plot of the pH of the solution versus the volume of the NaOH solution added was obtained. An inflection point (an indication of the number of moles of the unneutralized product) was reached on

TABLE II
Formulations of the Acrylic Acid Monomer Solution

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 titration curve. The pH of an identical volume of a solution of the product was reduced by the addition of concentrated hydrochloric acid. This was again titrated with a 1M NaOH solution to the same inflection point. Another inflection point was reached before the initial point of inflection. The difference between the two inflexion points was a measure of the total number of moles of acid in the product. From the two titration values, the degree of neutralization was calculated. Equation (1) shows the reaction scheme illustrating the steps involved in the neutralization:

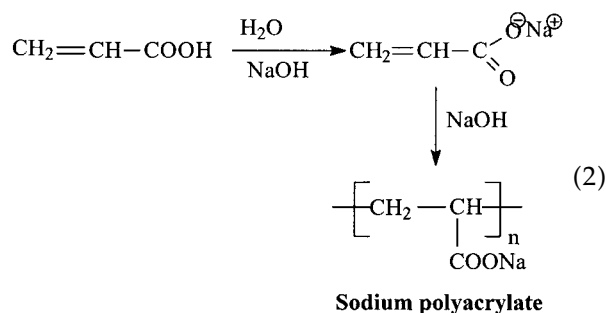


Acrylic acid

Sodium acrylate monomer

Polymerization of partially neutralized sodium acrylate monomer

The feasibility of polymerizing partially neutralized sodium acrylate monomer in a spray drier to give a product in the form of a dried powder was studied. A partially neutralized sodium acrylate monomer was chosen for evaluation (as opposed to a fully neutralized sodium acrylate) to match a product commercially available from Bevaloid SA (Pty), Ltd. (Durban, South Africa), albeit as a 25% solution. A formulation (21.7 kg of acrylic acid, 13.0 kg sodium hydroxide and 15.3 kg of water), which yielded a 49.6% neutralized solution of acrylic acid monomer with a concentration of 50%, was prepared. The initiator was prepared from 1 kg of water and 91 g of $(\text{NH}_4)_2\text{S}_2\text{O}_8$. Mixing this monomer and the initiator solution resulted in 0.182% initiator on the monomer. The mixture was sprayed into the drier through a brass Jet T-type SX 1 nozzle from Spray Systems, Inc. (Durban, South Africa), at a pressure of 1.5–3.0 MPa and at a feed rate of 10–12 $\text{dm}^3 \text{h}^{-1}$. The feed rate was governed by the viscosity of the solution that was being sprayed and by the pressure required to achieve a good spray pattern. The reaction equation for the polymerization of the partially neutralized sodium acrylate is shown in eq. (2):



Spray-drying equipment

A siphon-spray system using a compressor and a venturi was used. The compressor delivered air pressure

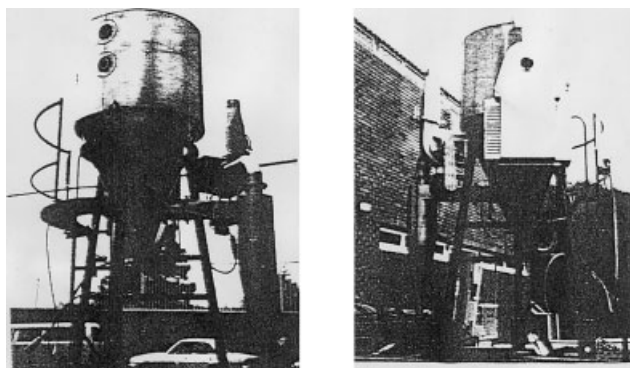


Figure 1 Photographs (taken at different angles) of the spray drier used for the experiments.

at 14.5 kPa. The nozzles were supplied by Spray Systems Inc. The fluid and air caps were varied to give different monomer solution feed rates and droplet sizes. This system, being a direct feed, avoided the problem associated with the pumping system. With the siphon-spray system, when we desired to increase the feed rate, the feed tank containing the monomer solution was raised to reduce the siphon height.

Air was drawn through the inlet fan, passed over electrical heating elements, and entered the drying chamber. The aqueous monomer solution was fed into the spray-dryer counter-current to the incoming air. The monomer reacted to give the polymer, and the water was driven off. The air, water vapor, and dry particles passed into the cyclone, in which the particles were removed and the air and water vapor were drawn out by the exhaust fan. The inlet and outlet air flows could be adjusted separately to vary the particle residence time in the drying chamber. Figures 1 and 2 show photographs (taken at different angles) and a diagrammatic sketch of the spray drier, respectively. The heating elements were adjusted to allow variations in the inlet air and the drying-chamber temperatures. The outlet air temperature correlated closely with the drying-chamber temperature. Therefore, in all experiments, the reaction temperature (T_r) quoted was the outlet air temperature.

Kinetics of the spray polymerization of sodium polyacrylate

In the computation of the energy costs associated with the spray polymerization of sodium polyacrylate, the parameters considered were (1) the residence time of the microparticles of sodium polyacrylate in the spray drier, (2) the microparticle size, (3) the monomer solution feed rate, and (4) the rate of polymerization of sodium polyacrylate.

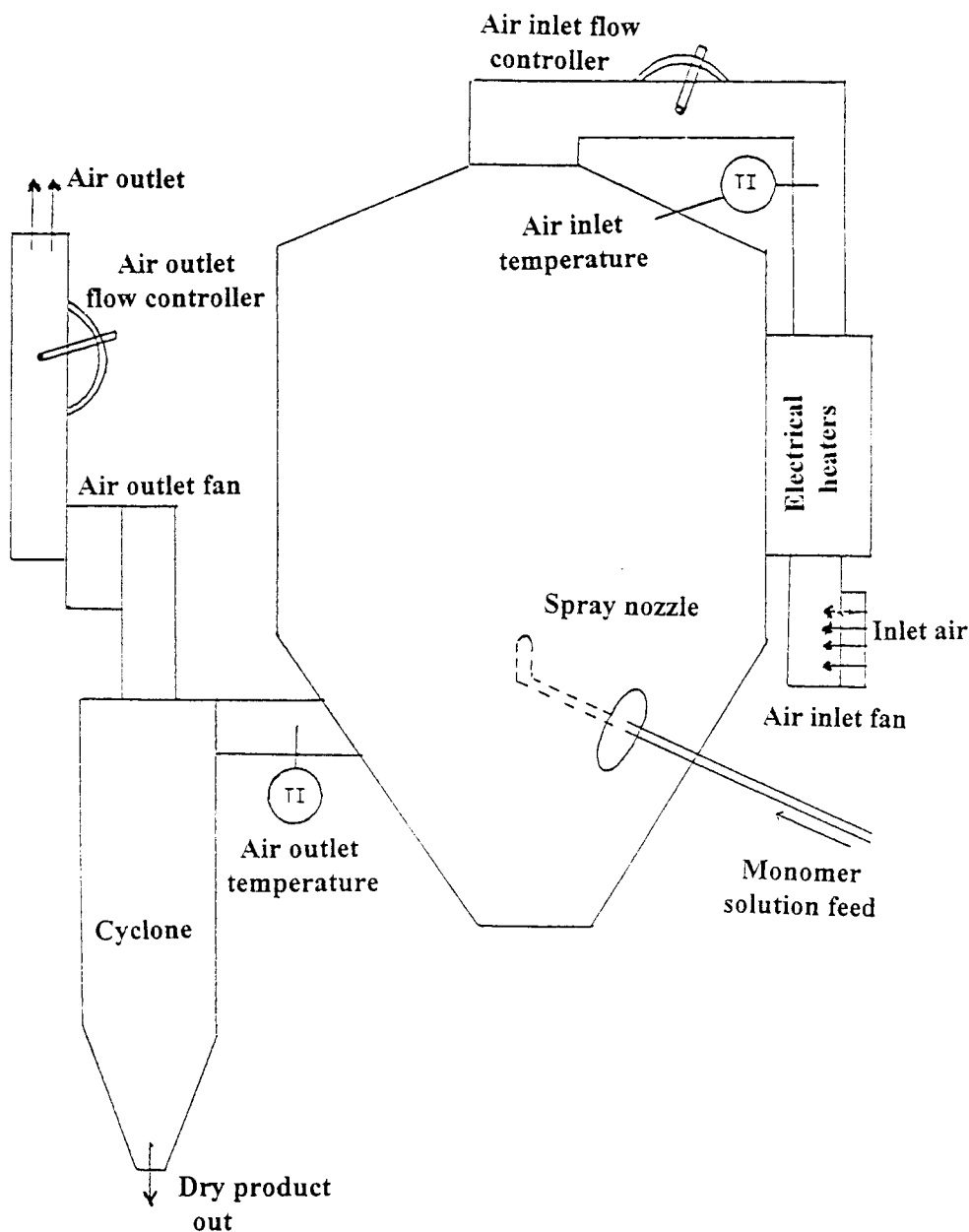


Figure 2 Diagrammatic sketch of the spray drier used.

Residence time of the microparticles in the spray drier

The approximate volume of the spray drier was 8.2 m^3 , and the air-flow rate from the spray drier was $0.134 \text{ m}^3 \text{ s}^{-1}$. Therefore, air changed in the spray drier at approximately 60 s. Consequently, it was reasonable to assume that the residence time of a particular microparticle in the spray drier was approximately 1 min.

Microparticle size

The diameter of the nozzle exit was 2.5 mm, which was assumed to be the particle diameter. This gave a

particle volume of $8.18 \times 10^{-3} \text{ mL}$. The 30% monomer solution had a specific gravity of 1.155, and so the particle mass was $9.45 \times 10^{-3} \text{ g}$, of which $2.836 \times 10^{-3} \text{ g}$ was sodium acrylate and $6.617 \times 10^{-3} \text{ g}$ was water.

Monomer solution feed rate

A feed rate of $3 \text{ dm}^3 \text{ h}^{-1}$ equaled 6190 particles per minute entering the spray drier.

Rate of polymerization of sodium acrylate

Few data are available on aqueous solution polymerization reactions of sodium polyacrylate at tempera-

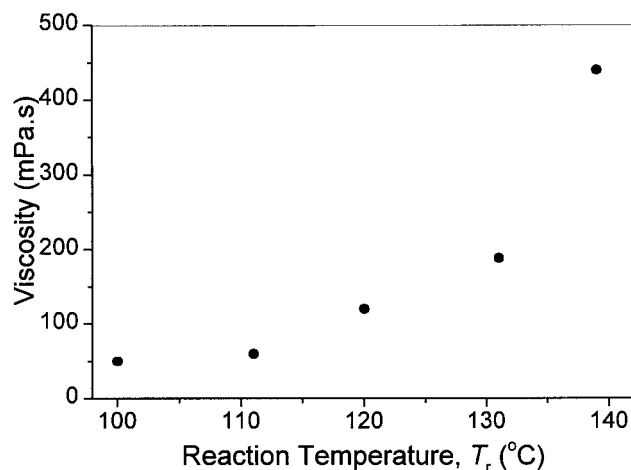


Figure 3 Viscosity of a 10% solution of sodium polyacrylate (measured at 20°C) as a function of T_r .

tures greater than 100°C. Kabanov³¹ and Golubev et al.³² reported the rate of polymerization of sodium acrylate in an aqueous solution at 23°C under UV irradiation with azobisisobutylnitrile as an initiator to be $5.1 \times 10^4 \text{ M s}^{-1}$.

Calculations

Each microparticle contained $2.836 \times 10^{-3} \text{ g}$ of sodium acrylate, that is, $3.01 \times 10^{-5} \text{ mol}$. Therefore, once initiation was begun (at $\approx 65^\circ\text{C}$), the reaction time was 5.9 s. If the air temperature in the spray drier was 110°C, the initiation should have been instantaneous. Because the rate of polymerization used in this computation was based on the reaction of the monomer at 23°C, this reaction time had to be considerably reduced at 110°C. For each microparticle, $6.617 \times 10^{-3} \text{ g}$ of water had to be heated to 100°C and evaporated. Therefore, the heat required was as follows:

From 20 to 100°C: $2.216 \times 10^{-3} \text{ kJ}$.

For evaporation: $14.961 \times 10^{-3} \text{ kJ}$.

Total: $17.177 \times 10^{-3} \text{ kJ}$.

With the specific heat of water ($4.19 \times 10^{-3} \text{ kJ g}^{-1} \text{ }^\circ\text{C}^{-1}$) and the latent heat of vaporization of water (2.261 kJ g^{-1}), the heat of polymerization of each mi-

croparticle was found to be 2.337 kJ g^{-1} , and the heat of polymerization of sodium acrylate was found to be 0.824 kJ g^{-1} . Therefore, for each particle, the heat input required for water evaporation was 14.84 kJ. A feed rate of $3 \text{ dm}^3 \text{ h}^{-1}$ represents 6109 microparticles entering the spray drier every minute. Therefore, the heat required was 90.66 kJ.

For $T_r = 110^\circ\text{C}$, the heater input on the spray drier was 72 MJ (7200 kJ). In light of the air-flow rate through the spray drier, this indicated that more than enough heat was available to dry the microparticles.

RESULTS AND DISCUSSION

The objective of this investigation was to find a more energy-efficient technique for preparing sodium polyacrylate by the use of the heat of polymerization for solvent removal. If this approach is extended further, one can also consider the heat of neutralization of sodium acrylate as a further energy source.

The described monomer solution injection technique (siphon-spray system) used a venturi effect for siphoning up the solution. The incorporation of two siphon tubes, feeding through two control valves (with flow indicators) into a mixing chamber before the spray nozzle, allowed separate feeds of the NaOH solution and a mixture of acrylic acid, water, and a catalyst. The mixing of these two feeds generated the heat of neutralization before the feed nozzle. This heat raised the temperature of the monomer solution to T_r , thereby initiating the exothermic polymerization reaction. The viscosity of a 10% solution of polyacrylate (measured at 20°C) as a function of T_r is shown in Figure 3. The viscosity increased as T_r increased.

The results of polymerizing partially neutralized sodium acrylate monomer in a spray dryer to give a dry powdered product, including the T_r , conversion percentage, neutralization percentage, volatile content percentage, pH of a 10% solution, and product viscosity, are shown in Table III. Tables IV and V show the effects of T_r on the aqueous solution viscosity and the conversion percentage in the spray polymerization of sodium acrylate and the effects of varying the spray-drier operating conditions on product properties, respectively.

TABLE III
Results of the Study for Polymerizing Partially Neutralized Sodium Acrylate Monomer in a spray dryer to Give a Dry Powdered Product

$-T_r$ (°C)	Product				
	Volatile content (%)	Conversion (%)	Neutralization (%)	Viscosity at 20°C (MPa s)	pH of 10% solution
110	1.6	98.32	—	—	—
130	1.6	97.80	78	50	5.25
140	4.4	98.82	75	50	5.25

TABLE IV
Effect of (T_r) on Aqueous Solution Viscosity and the Conversion in the Spray Polymerization of Sodium Acrylate

T_r ($^{\circ}\text{C}$) ± 2	Conversion (%)	Volatile content (%)	Aqueous solution viscosity (%) at 20 $^{\circ}\text{C}$ (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

Theoretical calculations combining all these energy sources were compared with the energy required to obtain a dry product by the conventional method. The results are shown in Tables VI and VII. For the spray-polymerization technique, the energy cost was 4783.53 kJ kg $^{-1}$ of dry product, whereas with the conventional

system, the energy cost was 9459.4 kJ kg $^{-1}$ of dry product.

Obviously, the concentration at which solution polymerization can be carried out in the gas phase depends on the molecular mass and viscosity of the desired final product. This will affect the energy re-

TABLE V
Effect of Varying Spray-Drier Operating Conditions on Product Properties

Run	Variables studied	T_r ($^{\circ}\text{C}$) ± 2	SNFC/AC DIN	Af_r in ($\text{m}^2 \text{s}^{-1}$)	Af_r out ($\text{m}^2 \text{s}^{-1}$)	MSf_r ($\text{dm}^3 \text{h}^{-1}$)	HI (MJ)	Volatile content (%)	10% Aqueous solution viscosity (MPa s)	Conversion (%)	pH of 10% aqueous solution
1	Reproducibility	110 ^a	60,100/120	0.15	0.134	3.5–4.0	72	2.2	1090	99.1	7.20
2		110 ^b	60,100/120	0.15	0.134	3.5–4.0	72	2.2	512	98.1	7.25
3	Af_r	110 ^c	60,100/120	0.15	0.134	3.5–4.0	72	1.8	720	97.4	7.40
4		110 ^d	60,100/120	0.13	0.094	3.5–4.0	72	4.6	1180	97.1	7.25
5	Nozzle	110	60,100/120	0.15	0.134	3.5–4.0	72	1.8	720	97.4	7.40
6	diameter	110	60,100/120	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.

^a Inlet air temperature = 145 $^{\circ}\text{C}$.

^b Inlet air temperature = 130 $^{\circ}\text{C}$.

^c Inlet air temperature = 174 $^{\circ}\text{C}$.

^d Inlet air temperature = 200 $^{\circ}\text{C}$.

TABLE VI
Energy Cost of Spray-Polymerization Product

Process stage	Energy requirement* ^a (kJ)	Energy liberation* ^a (kJ)
1. Neutralization (heat of neutralization) = 0.805 kJ g $^{-1}$ at 25 $^{\circ}\text{C}$.	0	185.15
2. Heat-up to reaction temperature (e.g. 70 $^{\circ}\text{C}$); (specific heat of water = 4.19×10^{-3} kJg $^{-1}$ $^{\circ}\text{C}^{-1}$; hence, specific heat of monomer solution = 3.56×10^{-3} kJ g $^{-1}$ $^{\circ}\text{C}^{-1}$, where similar specific heats for acrylic acid and sodium acrylate are assumed)	178	0
3. Heat of polymerization = 0.824 kJ g $^{-1}$ at 25 $^{\circ}\text{C}$ ⁴	0	247.20
4. Heat-up from 70 $^{\circ}$ to 100 $^{\circ}\text{C}$ (boiling point); where it is assumed that the specific heat of sodium polyacrylate is similar to that of acrylic acid).	106.8	0
5. Evaporation of water (latent heat of vapourization = 2.261 kJ g $^{-1}$)	1582.61	—
Total	1867.41	432.35

The total energy cost for 300 g of dry product is 1435.06 kJ (i.e., 1867.41–432.35 kJ); therefore, the energy cost for 1 kg of dry product is 4783.53 kJ.

^a For 1 kg of 30% sodium acrylate monomer.

TABLE VII
Energy Cost of Dry Sodium Polyacrylate Prepared by the Conventional Method

Process stage	Energy requirement ^a (kJ)	Energy liberation ^a (kJ)
1. Heat-up to reaction temperature (80°C).	754.2	0
2. Heat of polymerization.	0	(824)
3. Cooling to remove heat of polymerization to maintain control.	824	0
4. Heat of neutralization.	0	(805)
5. Cooling to remove heat of neutralization to prevent polymer degradation (temperature maintained at 80°C).	805	0
6. Dry heat from 80° to 100°C.	293	0
7. Evaporation of water.	6783	0
Total	9459.4	1629

The process is followed assuming the following steps: (1) charge water to reactor, (2) heat to T_r (80°C), (3) add acrylic acid and catalyst over 2 h, (4) neutralize with NaOH solution at the end of reaction, and (5) dry solution (which is at 25% concentration). Therefore, the energy cost for 1 kg of dry product = 7830.4 kJ (i.e., 9459.4–1629 kJ)

^a Results are expressed as dry kilograms of finished product.

quirements for drying (and cooling during polymerization and neutralization). Using more concentrated monomer solutions for the spray-drier feed could further extend this argument on concentration. When the twin feed system is employed, the monomer solution is always prepared at an elevated temperature, and this increases solubility. From this investigation, it was determined that at 70°C, the maximum solubility of sodium acrylate was 45%. On the basis of this fact, when the energy requirement calculation was performed, the energy cost of the dry product dropped to 1899.2 kJ kg⁻¹. In this investigation, particular attention was paid to sodium acrylate monomer, but it is envisaged that the process should work with other nonvolatile monomers such as sodium methacrylate and sodium acrylamide.

The finding that the viscosity (molecular mass)/ T_r relationship of polymers produced by the spray-polymerization technique is the inverse to that found in a normal solution polymerization corresponds perfectly with the observations of Norrish and Smith³³ and Blair and Schulz.³⁴ These workers postulated a gel or auto-acceleration effect; that is, when certain monomers are polymerized in a concentrated solution, or undiluted, 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 concentration (or type) and is due to a decrease in the rate at which the polymer molecules diffuse through the viscous medium, lowering the ability of two long-chain radicals coming together and terminating. Kabanov³¹ postulated, at a constant concentration, an autoacceleration effect in a concentrated monomer solution. In the spray drier, water was continuously being removed from the polymerizing particles so that the concentration increased all the time, giving an increasing auto-

acceleration effect. The decrease in the termination rate led to an increase in the overall polymerization rate and in the molecular mass because the lifetime of the growing chains increased.

CONCLUSIONS

A more energy-efficient technique for preparing sodium polyacrylate, with respect to the conventional technique, that used the heat of polymerization for solvent removal and a twin-feed process using the heat of neutralization of the acrylate led to an energy cost of 4783.53 kJ kg⁻¹ of dry product. The conventional system led to an energy cost of 7830.40 kJ kg⁻¹ of dry product ($\approx 40\%$ increase over the spray-polymerization technique). This implies that, theoretically, using the spray-polymerization gas-phase technique for preparing sodium polyacrylate could save a lot of energy. Obviously, the use of the twin-feed process utilizing the heat of neutralization is a major priority in the study of the gas-phase spray-polymerization technique.

References

1. Flucrand, H.; Doco, T.; Es-Safi, N.-E.; Cheyner, V.; Moutounet, M. *J Chromatogr A* 1996, 752, 85.
2. Ito, H.; Morohashi, M.; Oohara, T. *Jpn. Pat.* 06211904, A2 (1994).
3. Ito, H.; Morohashi, M.; Tsucha, F.; Oohara, T. *Jpn. Pat.* 05132503, A2 (1993).
4. Lynn, T. R.; Williams, C. C. *U.S. Pat.* 6,075,101, A (2000).
5. Williams, C. C.; Goode, M. G.; Ramamurthy, A. V. *U.S. Pat.* 5,962,606, A (1999).
6. Dungworth, H. W. *Austral. Pat.* 9890857, A1 (1999).
7. Ito, H.; Shibuya, H.; Suzuki, Y.; Oohara, T.; Tsuchiya, F. *Jpn. Pat.* 11049805, A2 (1999).
8. Betremieux, I.; Verge, C. *Fr. Pat.* 2759608, B1 (1999).
9. Nakao, M.; Matsuyama, K.; Shimokawa, Y.; Shida, J. *Jpn. Pat.* 09255704 (1997).
10. Lindner, C.; Bamelis, P.; Hinz, J.; Wittmann, D.; Koch, O.; Braun, B. *Ger. Pat.* 3605801, A1 (1997).

11. Pyrlík, M. Ger. Pat. 2849087, A1 (1980).
12. Tsugawa, H.; Miura, S. Jpn. Pat. 48008756, B4 (1997).
13. Frisque, A. J.; Bernot, R. U.S. Pat. 3,644,305, A (1972).
14. Muenster, A.; Rohmann, M. Ger. Pat. 2757329, C2 (1980).
15. Ito, H. Jpn. Pat. 10204105, A2 (1998).
16. Yoshimura, H.; Tokumoto, K.; Tamano, Y. Jpn. Pat. 10219015, A2 (1998).
17. Zhou, Z.; Hong, S.; Zhu, Y.; Long, H. Chin. Pat. 1119653, A3 (1996).
18. Zhang, W.; Cai, Y.; Wang, Z.; Gu, H. *Huaxue Shijie* (in Chinese) 1999, 40, 619.
19. Horkay, F.; Tasaki, I.; Basser, P. J. *Biomacromolecules* 2000, 1, 84.
20. Dairui, T.; Kadokawa, T.; Abe, T.; Ayano, M.; Sano, D.; Moriwaki, M. Jpn. Pat. 53050286, A2 (1978).
21. Parks, R. L. U.S. Pat. 4,295,987, A (1981).
22. *Encyclopedia of Polymer Science and Technology*; Wiley: New York, 1971; Vol. 1, p 203.
23. Glavis, F. J.; et al. U.S. Pat. 2,956,046 (1960).
24. Cohen, L. South Afr. Pat. 79/6373 (1979).
25. Say, T. E. M.Sc. Thesis, University of Stellenbosch, 1983.
26. Say, T. E.; Sanderson, R. D. Presented at the 28th Convention of the South African Chemical Institute, Johannesburg, South Africa, Jan 30–Feb 3, 1984.
27. Renard, B.; McKenna, T. F. *Macromol Symp* 2000, 150, 251.
28. Michael, K.; Pippel, W.; Valdivia, R. *Sekt Chem Tech Univ Dresden Wiss Z Tech Univ* (in German) 1981, 30, 81.
29. Zhang, W.; Cai, Y.; Wang, Z.; Gu, H. *Huaxue Shijie* (in Chinese) 1999, 40, 619.
30. Vanueteenkiste, T. H.; Smith, J. R.; Teets, R. E.; Moleski, J. J.; Gorkiewicz, D. W.; Tison, R. P.; Marantz, D. R.; Kowalsky, K. A.; Riggs, W. L.; Zajchowski, P. H.; Pilsner, B.; McCune, R. C.; Barnett, K. J. *Surf Coat Technol* 1999, 111, 62.
31. Kabanov, V. A. *Macromol Chem* 1973, 8, 121.
32. Golubev, V. B.; Zubov, V. P.; Georgiev, G. S.; Stoyachenko, I. L.; Kabanov, V. A. *J Polym Sci Polym Chem Ed* 1973, 11, 2463.
33. Norrish, R. G. W.; Smith, R. R. *Nature* 1942, 150, 336.
34. Blair, C. M., Jr.; Schulz, D. M. U.S. Pat. 2,423,364 (1947).