

# Processing of Polymer Latex Emulsion: Batch Coagulation

ANUP K. GHOSH and J. THOMAS LINDT,\* *Department of  
Material Science and Engineering, University of Pittsburgh,  
Pittsburgh, Pennsylvania 15261*

## Synopsis

A small-scale batch experiment has been developed to establish processing conditions for latex coagulation in an extruder environment—characterized by the prevailing flow field, temperature, and pressure. Our experiments have shown that the most effective processing means to control the particle size distribution and also the particle morphology is the coagulation temperature. The changes in hydrodynamics, introduced by variations in the channel depth and rotor speed, affect the average particle size to a lesser degree. The morphology of the coagulated particles and their size distribution have been found to play an important role in the latex dewatering process. By coagulating well above the glass transition temperature(s) of the polymer, an order of magnitude drop in the specific surface area of the coagulated particles has been observed.

## SCOPE OF THE WORK

The isolation of polymers from latex, produced by emulsion polymerization, is typically a semicontinuous process involving latex coagulation, removal of water, washing, and drying. However, latexes can be processed on a continuous basis in a multistage screw extruder. A continuous process for the coagulation of the polymer latexes in a counterrotating twin screw extruder environment has been described by Nichols and Kheradi.<sup>1</sup> They combined the coagulation process with the dewatering and drying steps. In contrast to the conventional latex technology, the processing of the latex in an extruder replaces a latex plant by a single machine.

It is believed that the prevailing flow field, processing temperature, and pressure in the extruder have a significant effect on the particle size distribution of the coagulated latex. In this work, the coagulation of latex is extracted from the overall process and studied separately with the objective to interpret the effect of the externally imposed extruder operating conditions on the particle size distribution of the coagulated latex and their consequences concerning the initial water content in the coagulated latex, and the water removal.

The energy requirements of the direct dewatering extrusion coagulation process are strongly affected by the morphology of the coagulated latex. A macroscopic energy balance of the extrusion dewatering process suggests that the removal of water as vapor presents the single most significant contribution to the thermal energy requirements. For each part of water percent to be removed from the coagulated latex in the vapor form, some 5% of the overall energy consumption required for direct dewatering extrusion process may be expended. Since the amount of water retained in the coagulated latex slurry is

\* To whom correspondence should be sent.

a function of the structure of the wet latex cake, it can be expected that the coagulation kinetics also affects the energy consumption of the process. Nichols and Kheradi's work<sup>1</sup> on the extrusion latex dewatering process indicates that, after the liquid water removal through the on-line mechanical filters, approximately 15 vol % of water remains in the latex cake. For a close packing of monodisperse rigid spheres one can expect about 32% of the volume of the coagulated latex slurry to be filled with water. The lower residual water content reported in Nichols and Kheradi's work can be attributed to the combination of probable compressibility effects affecting the shape of the coagulated particles exposed to temperatures well in excess of their respective glass transition temperatures.

In the present study we will investigate the influence of temperature and shear rate on the coagulation kinetics to control particle size distribution during the coagulation of polymer latex emulsion. The morphology of the coagulated latex particles will also be characterized by determining the density and the specific surface with reference to the coagulation kinetics.

## INTRODUCTION

Coagulation is the process of encounters between two or more particles by transport mechanisms, such as Brownian motion, fluid shear, etc., and coalescence of these particles due to short range interfacial forces. The coagulation process thus modifies the size distribution of the suspended particles in dispersive systems and controls the behavior of suspensions. The particle-particle interaction leading to any such coagulation is one of the major factors determining the design parameters in latex processing operation. Rapid and controlled coagulation of latex, induced by chemical coagulant, mechanical shear, and heat, has been found to be the most effective process for the recovery of polymer from the latex.

Early works on coagulation of suspensions in shear fields have received a good deal of recent interest in this field and became the starting point for the current trends in the coagulation modeling. A detailed survey of the recent developments in the theory of coagulation is given by Valioulis.<sup>2</sup> He reviewed different models, available so far, to model the particle-particle interactions in colloidal systems and identified a few practical problems yet to be solved. Tadros<sup>3</sup> reviewed the different factors which govern the stability of polymer lattices. He described the state of latex dispersion in terms of the interaction forces between the particles and examined the destabilization criteria of a latex dispersion in the presence of absorbed polymer. The kinetics of the coagulation process occurring in colloidal dispersions have also been studied extensively.<sup>4,5</sup> Although shear coagulation of colloidal suspension has been studied in detail both theoretically and experimentally,<sup>6-10</sup> the coagulation of synthetic polymer latex especially at elevated temperature has not received much attention so far. Utracki<sup>11</sup> investigated the mechanical stability of polymer latex and indicated a change in interfacial tension and zeta potential for such systems at temperatures above the glass transition temperature of the polymer. He also developed a relation between the coagulation time, the applied shear, and the particle volume fraction based on the viscosity measurements of the latex. But this study does not reveal any functional depen-

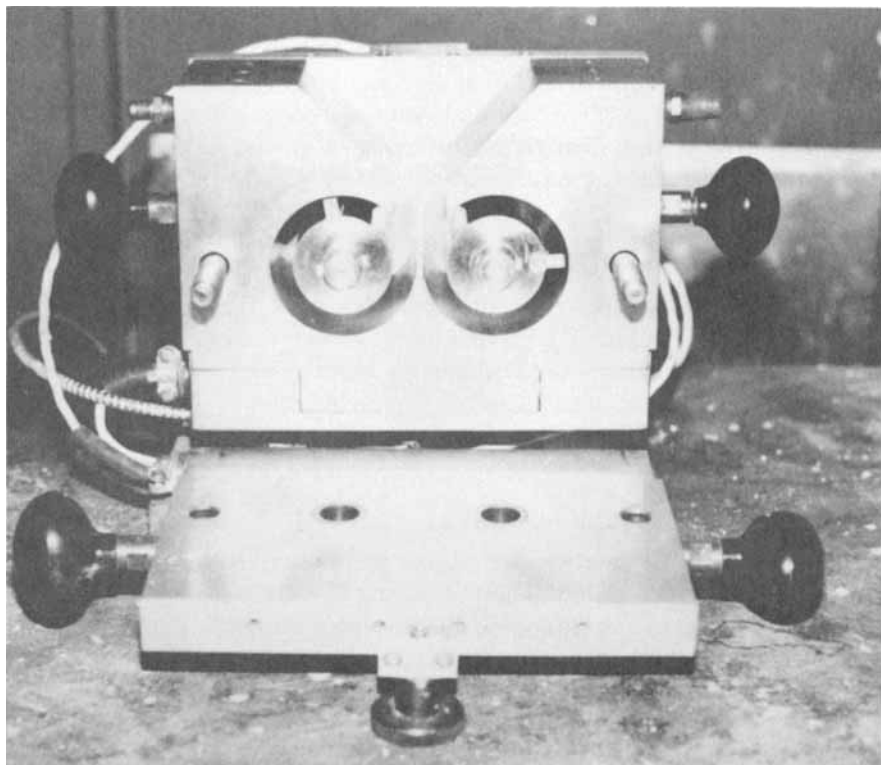


Fig. 1(a). Rheomix 3000 shear cell.

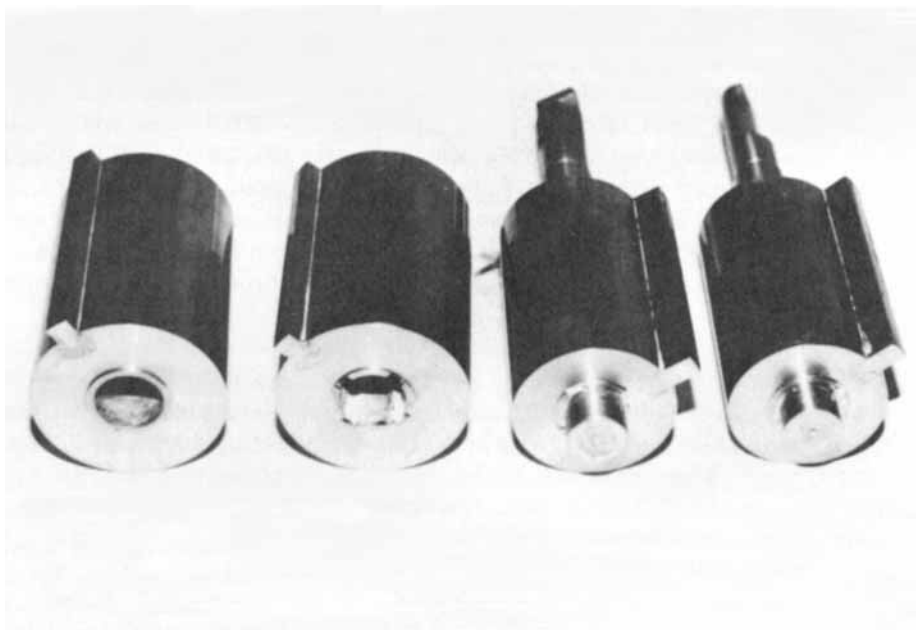


Fig. 1(b). Rotors used in shear cell.

dence of coagulation on the particle size distribution of the coagulated latex. Kinetic studies of mechanical coagulation in the case of high solid content latexes were also attempted by Lin et al.<sup>12</sup> and Lowry et al.<sup>13</sup> But their studies were mostly limited to the interpretation of the coagulation kinetics in terms of particle-particle interactions in thickened latex and did not consider any effect of temperature on the coagulation efficiency.

## EXPERIMENTAL

For this study, acrylonitrile-butadiene-styrene (ABS) latex having 29.8 vol % of polymer is used. The latex is made of two kinds of particles: (i) 64.5 wt % styrene-acrylonitrile (SAN) having a number average particle diameter of 95 nm and (ii) a mixture of 25 wt % of polybutadiene (PB) and 7.5 wt % of graft SAN with a number average particle diameter of 315 nm. About 3% soap solution is used as an emulsifier and the resulting latex has a bimodal size distribution. The pH of the latex is adjusted to 10.2 and the higher glass transition temperature of the polymeric system is 102°C. ABS resin is isolated from the latex by coagulation with dilute salt or acid solution such as NaCl, MgSO<sub>4</sub>, CaCl<sub>2</sub>, Al<sub>2</sub>(SO<sub>4</sub>), and H<sub>2</sub>SO<sub>4</sub>. Among these, CaCl<sub>2</sub> solution 1.25 wt % by weight of polymer is found to be the most effective coagulant for our system.

To study the effect of flow field on coagulation, experiments were carried out in a sealed shear cell (Rheomix 3000), shown in Figure 1. The rotor pairs used had identical cylindrical roots with axial flight of heights of 5 and 9 mm and are termed batch screw model I (BSMI) and batch screw model II (BSMII), respectively. The cross section of the mixer chamber was similar to that of a latex processing extruder, a nonintermeshing counterrotating twin-screw extruder. Depending on the rotors used, the liquid volume of the mixing chamber was  $160 \times 10^{-6}$  or  $220 \times 10^{-6}$  m<sup>3</sup> corresponding to the flight depths of 5 and 9 mm, respectively. The Rheomix had a temperature control up to 400°C and the maximum attainable rotational speed was 200 rpm.

Coagulation of ABS latex at temperatures above 100°C was conducted under pressure to reduce any disturbances due to additional agitation and water loss associated with boiling. A Teflon block was used to seal the opening of the mixer bowl at the top where the coagulant injection port was also located. The pressure inside the Rheomix was that of water vapor pressure at the operating temperature and remained constant throughout the time of mixing.

In each run, the mixing unit was set to the desired temperature. The latex and the diluent were then promptly placed in the annulus between the rotor and the inner wall of the mixer bowl. The rotors were turned on to the selected speed while the sample was heated to the operating temperature. The coagulant was preheated to the mixing temperature separately and injected into the latex under pressure by a syringe. After the coagulation was completed, the Rheomix was halted and the coagulated latex was taken out by removing the front plate of the mixer. Any further coagulation is minimized by redispersing the coagulate in ice-cold water.

The available range of shear rates in the Rheomix with two different rotors lies between 2 and 160 s<sup>-1</sup>. The process temperature of mixing is varied from 85 to 112°C.

For any given set of operating conditions, the particle size distribution is determined by using the wet sieving technique for the larger particle sizes, and the Microtrac particle size analyzer for the smaller sizes. Conventional wire sieves of 20, 40, 60, 80, and 100 mesh are used for the sieve analysis. After the coagulated latex slurry sample has been passed through the sieve stack, the size fractions are collected from the different sieves and dried in a vacuum oven before weighting to determine the weight percentages. Samples containing particles of subsieve size ( $< 100$  mesh) were collected from the bottom of the sieve stack and analyzed in the Microtrac size analyzer to determine the particle size distribution in the range between 150 and 1.5  $\mu\text{m}$ .

The amount of water retained in the wet coagulated latex was determined gravimetrically. The rate of loss of water from the freely drained coagulated latex slurry sample during drying was followed by weighing the sample at regular time intervals. The drying was conducted at atmospheric pressure and the drying temperature was maintained at 70°C. The surface area of the dish holding the latex sample was  $32.2 \times 10^{-4} \text{ m}^2$ .

The measurement of both the inner and outer porosity in terms of density and specific surface area of the dried coagulated latex samples were helpful in determining the nature of aggregation of the coagulated particles, including the type of packing or compactness of the particles. The mercury intrusion method was used to determine the density of the coagulated latex particles.

## RESULTS AND DISCUSSION

To evaluate the coagulation efficiency as a function of processing conditions, a series of particles size analyses were carried out. The particle size analysis data are often represented by the moments of the distribution curve. Generally, the measure of the central tendency of the distribution is described by the mean, the mode, and the median, whereas, the variance gives a measure of the dispersion. If in a distribution  $x_1, x_2, \dots, x_n$  occur with frequencies of  $f_1, f_2, \dots, f_n$ , respectively, then the  $k$ th moment is defined as

$$\mu_k = \left( f_1 x_1^k + f_2 x_2^k + \dots + f_n x_n^k \right) / \sum_i f_i \quad (1)$$

The first moment  $\mu_1$  represents the mean value of  $x$  and the variance is related to the moments as follows:

$$\sigma^2 = \mu_2 - \mu_1^2 \quad (2)$$

The third moment  $\mu_3$  characterizes the skewness. If  $\mu_3$  is positive, the long tail of the distribution is on the right side of the mean; if it is negative, the distribution is skewed left, which implies suppression of small particles. The degree of asymmetry of the size distribution can also be expressed in terms of the coefficient of skewness,  $\beta$ , as follows:

$$\beta = \mu_3^2 / \mu_2^3 \quad (3)$$

Results of our coagulation studies are expressed in terms of the apparent kinetics of the rate of the disappearance of the primary latex particles associated with the rate of growth of the secondary particles. The progress of

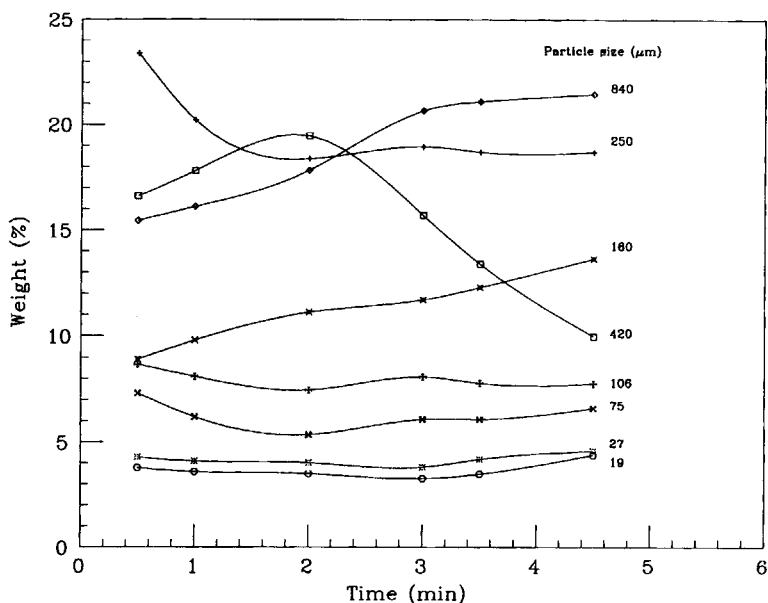


Fig. 2. Coagulation kinetics of ABS latex (coagulation temp, 90°C; rotor speed, 200 rpm).

the coagulation process is monitored by drawing off samples at regular time intervals. The kinetic data for the coagulation of latex processed at 90°C and with rotors having 9 mm gap width running at 200 rpm are given in Figure 2. Initially the amount of large particles increase by buildup from the small particles. As the mixing proceeds, the amount of smaller size particles decreases as they further agglomerate to form larger particles. The particles grow until they approach the upper size limit depending on the applied shear and aggregate strength. At this stage a dynamic equilibrium for the particular particle size is attained. The approach to this dynamic equilibrium is also shown in Figure 3, where the change of mean diameter of coagulated particles, calculated as the first moment of the distribution, is plotted against the time of mixing. On the other hand, the variance of the particle distribution is found to increase linearly throughout the mixing period as was also shown in Figure 3. The corresponding size distributions of latex coagulated for different mixing time are given in Figure 4. Hence, under the present conditions, efficient coagulation with the narrowest size distribution possible can only be obtained by limiting the mixing time to 2 min.

The particle size analyses have shown a very significant effect of temperature on the coagulation process. The cumulative and distributive plots of the size distributions of the latex coagulated at different temperatures are shown in Figures 5 and 6. The weight percentages of larger size particles ( $> 840 \mu\text{m}$ ) have been found to increase in a progressive manner with the increase of coagulation temperature. The truncated tails of the particle size distributions in Figures 5(b) and 6(b) resulted from the use of 100 mesh as the wire sieve size with the largest opening in the size analysis. The amount of sample retained by this sieve determined the total amount of large particles ( $> 840 \mu\text{m}$ ).

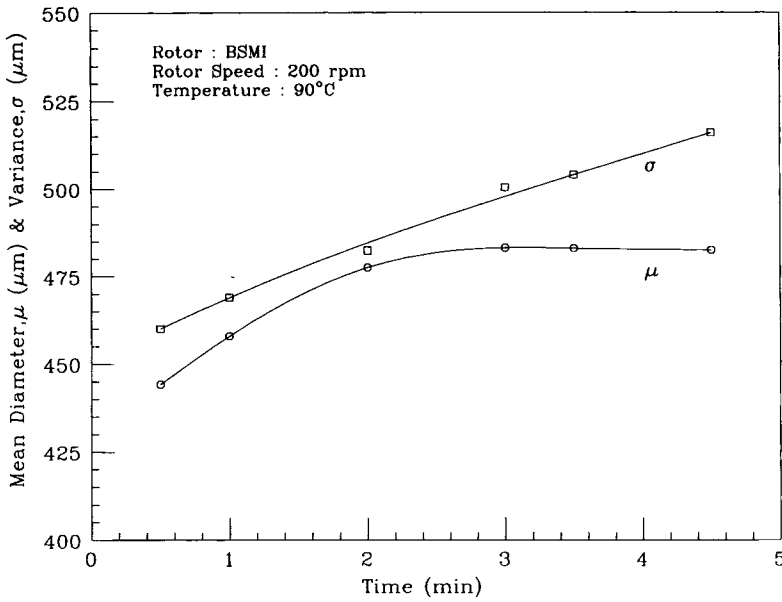


Fig. 3. Rate of change of mean diameter and variance of latex particles due to coagulation.

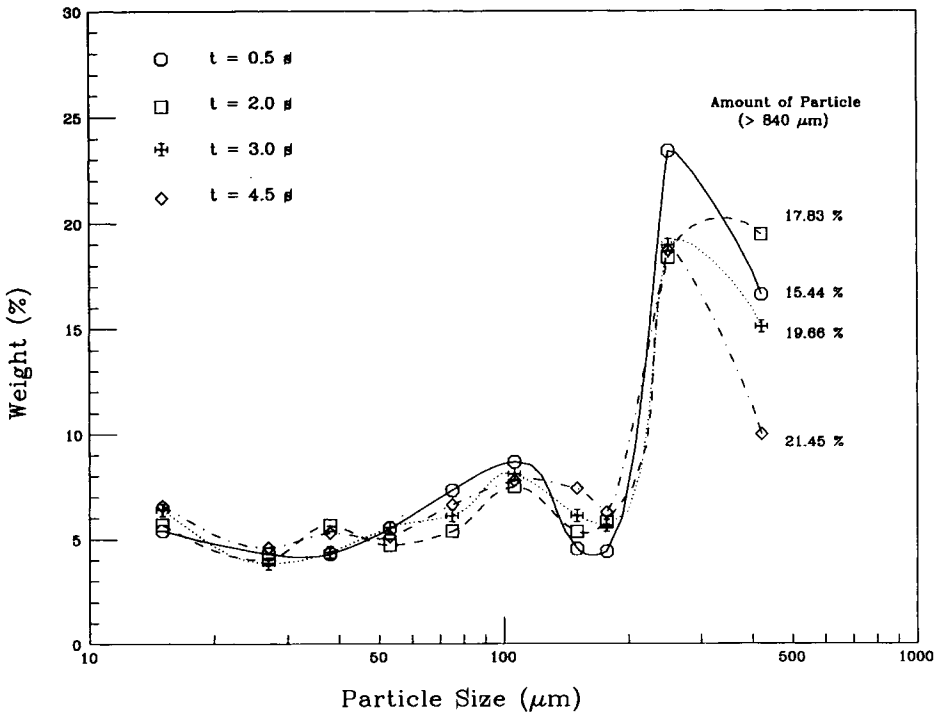


Fig. 4. Size distribution analysis of ABS latex at different coagulation time (coagulation temp, 90°C; rotor speed, 200 rpm).

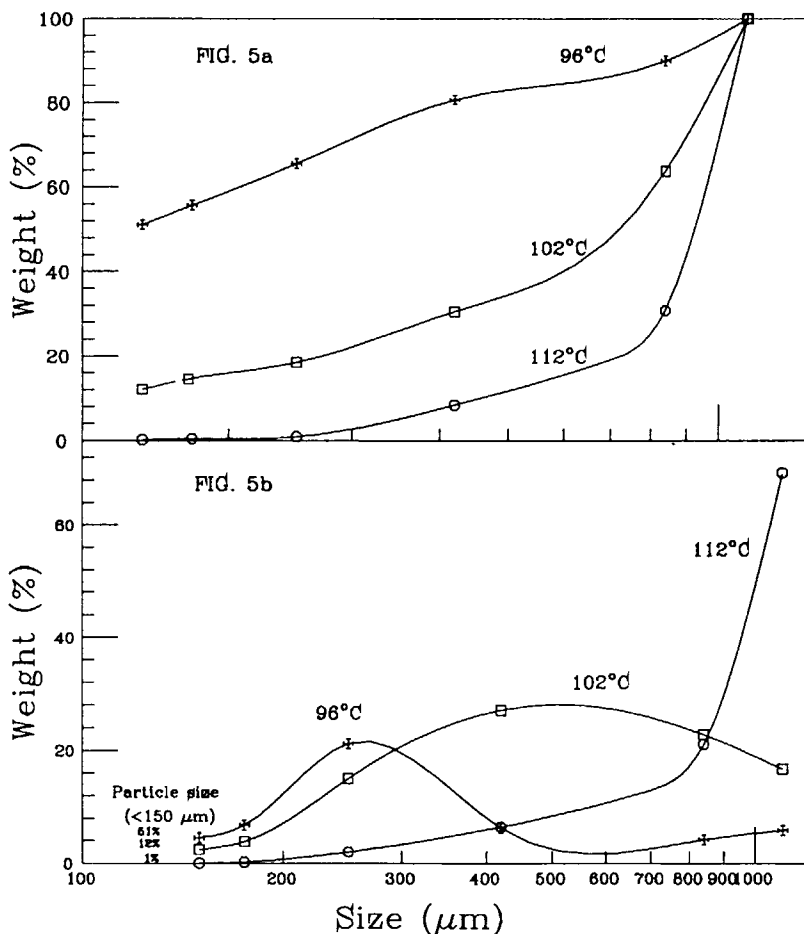


Fig. 5. Size analysis data coagulated at different temp with batch screw model I (rotor speed, 200 rpm): 5(a) cumulative analysis; 5(b) distributive analysis.

Both the median and the mean values of the size distribution increase as the coagulation temperature is increased. This has been found to be true in all experiments. The changes in the mean particle diameter and the variance at the different coagulation temperature has been plotted in Figure 7. The increase in the mean diameter with temperature followed the expected trend, with the maximum rate of increase occurring at or around the glass transition temperature. Though the variance of the distributions, obtained for two batch screw models, BSMI and BSMII, do not strictly correlate with the temperature of the mixing, the distributions are found to be relatively broad near the polymer glass transition temperature for both the rotors. However, at any process temperature the mean particle size from BSMII has been found to be always larger than that obtained with BSMI. Both have shown an apparent maximum variance in the neighborhood of  $T_g$ .

The third moment and the coefficient of the skewness of the particle size distribution are also calculated for samples obtained from coagulation experiments in BSMI and BSMII. The values are reported in Table I. It has been



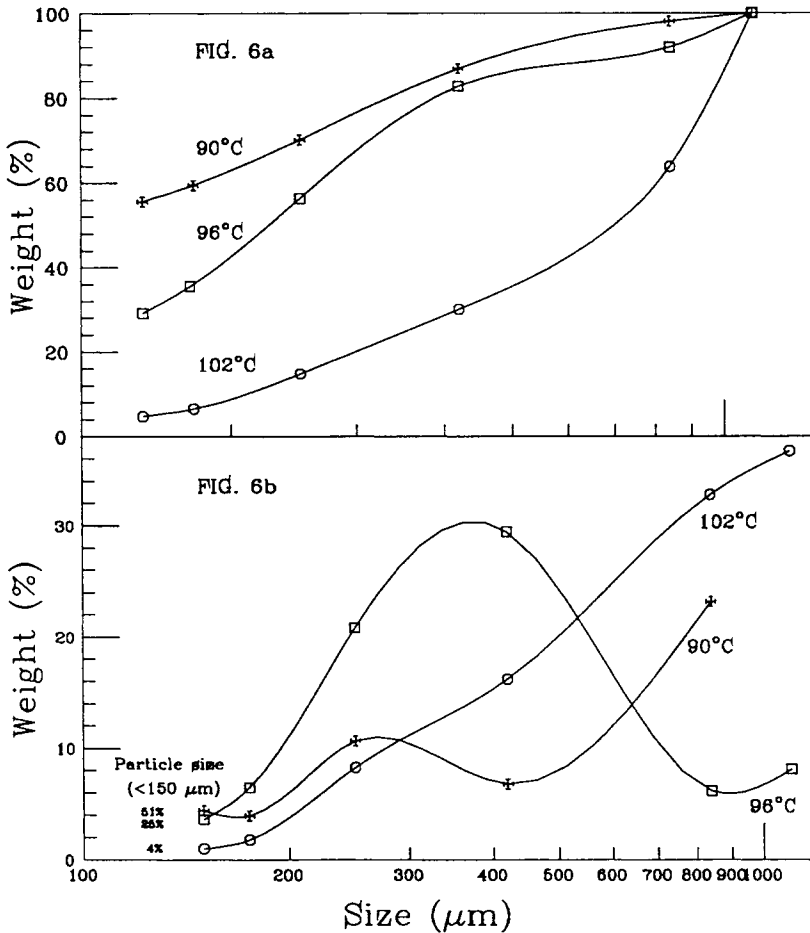


Fig. 6. Size analysis data for latex coagulated at different temp with batch screw model II (rotor speed, 200 rpm): (a) cumulative analysis; (b) distributive analysis.

found that the values of the third moment become negative when the latex is coagulated at or above the polymer glass transition temperature. This has been found to be true for both the rotors used in the coagulation experiments. Interestingly, the coefficient of skewness has also shown its minimum in the neighborhood of the glass transition temperature. Hence, the size distribution is least skewed when coagulation takes place at a temperature near polymer glass temperature. The suppression of small particles thus becomes significant at higher coagulation temperature. In the coagulated latex slurry, the amount of particles smaller than 150 μm has been reduced from 50 wt % at 90°C down to approximately 10 wt % at 102°C, and even lower at 112°C.

Besides temperature, the size distribution of the coagulated latex has been found to depend also on the gap width of the rotors used in the mixing cell. A larger amount of bigger size particles are obtained with BSMII (9 mm gap) than that with BSMI (5 mm gap) as shown in Figure 8. In line with this observation, smaller amounts of fine particles result from coagulation in BSMII over the entire temperature range.

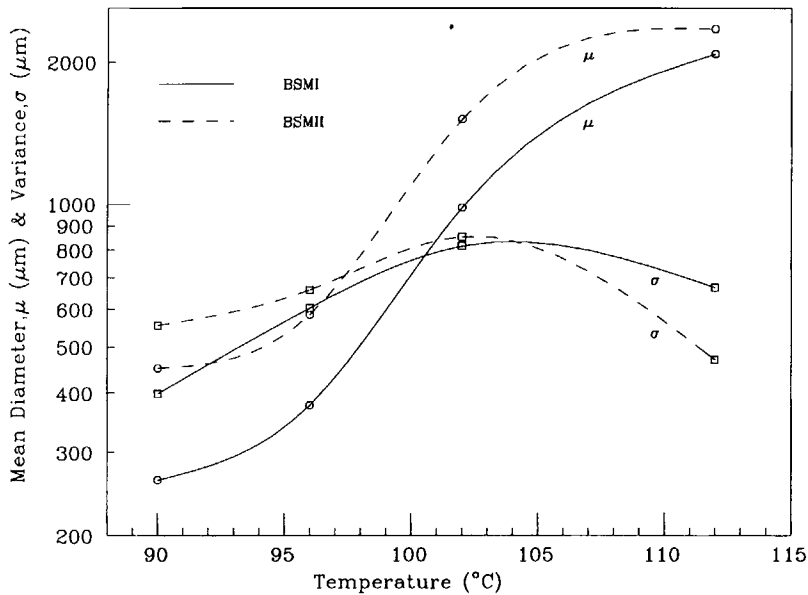


Fig. 7. Effect of temperature on the mean diameter and the variance of the size distribution of the coagulated latex.

Further control of the distribution of the particle size can also be obtained by coagulating the latex at different shear rates as the mean diameter and the mode of the distribution is found to depend mostly on the applied shear. Lesser amount of larger size particles are obtained with increasing rotor speeds at any specified temperature of coagulation as shown in Figure 9.

The particle size distribution of the coagulated latex plays a significant role in the dewatering of latex through its control of the initial water retention volume as well as the subsequent time-dependent capillary flows. The rate of water loss from coagulated latex samples obtained at different operating conditions are plotted in Figure 10. The coagulated latex containing particles of average diameters of approximately 200  $\mu\text{m}$  obtained from the mixing experiment at 90°C have been found to take the longest time for the complete removal of moisture in agreement with the water retention data. A further data analysis is expected to reveal if this is a simple water content effect or a capillary flow effect. Figure 11 shows that the coagulated latex samples having

TABLE I  
Skewness of Particle Size Distribution of the Coagulated Latex

Temp (°C)	BSMI		BMSII	
	Third moment, $\mu_3$	Coefficient of skewness, $\beta$	Third moment, $\mu_3$	Coefficient of skewness, $\beta$
112	$-3.7 \times 10^8$	1.559	$-2.47 \times 10^8$	5.894
102	$4.2 \times 10^8$	0.625	$-7.1 \times 10^7$	0.013
96	$5.9 \times 10^8$	7.302	$5.62 \times 10^8$	3.858
90	$1.3 \times 10^8$	4.307	$1.82 \times 10^8$	1.137

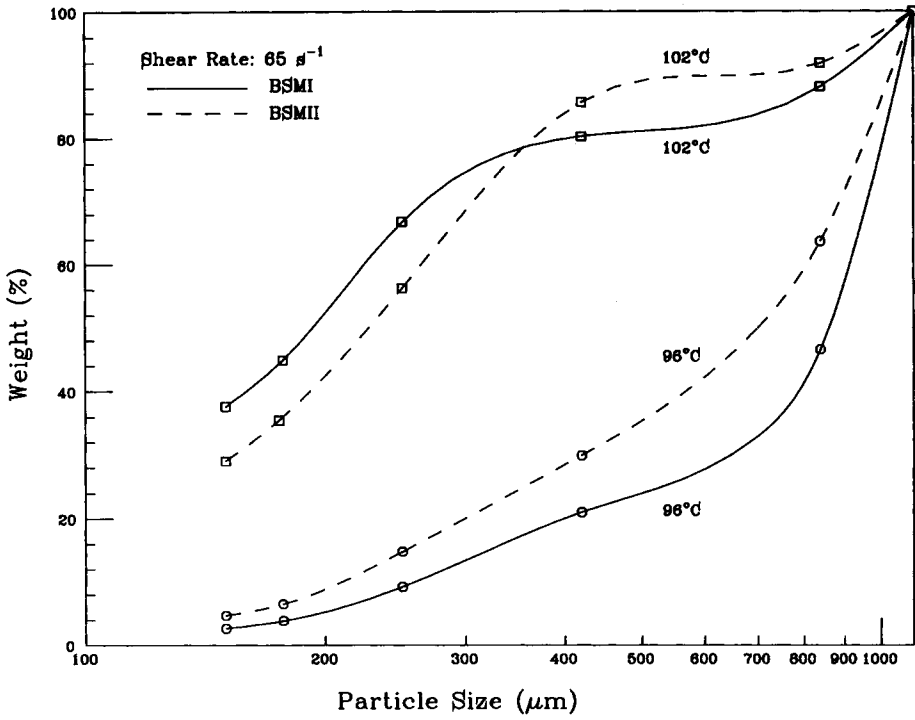


Fig. 8. Comparison of size analysis data of ABS latex coagulated by using two different rotors at different temperatures.

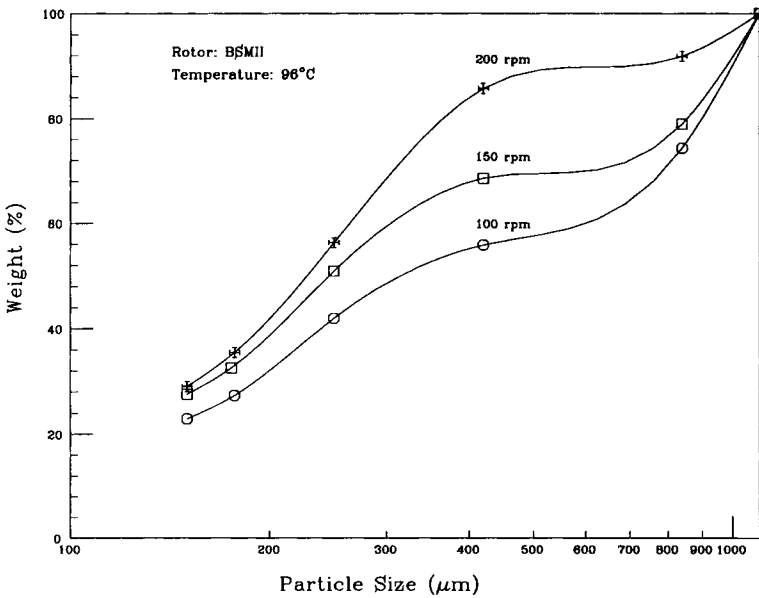


Fig. 9. Comparison of size analysis data of ABS latex coagulated at different rotor speeds.

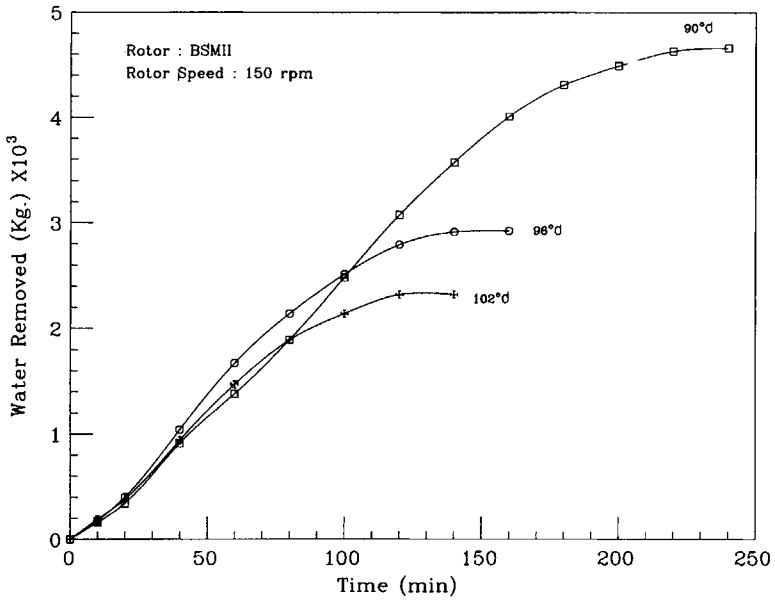


Fig. 10. Drying rate of coagulated latex obtained from different mixing temperature.

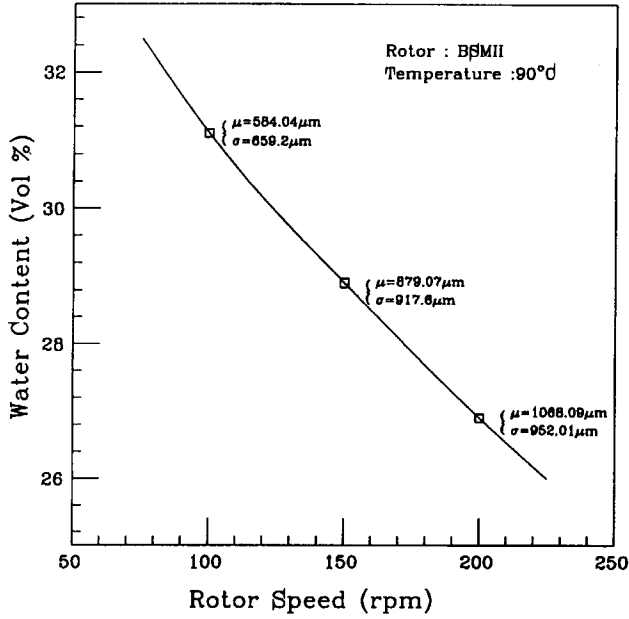


Fig. 11. Water retention capacity of coagulated latex obtained through coagulation at different rotor speeds.

TABLE II  
Dewatering Characteristics of Coagulated Latex

Coagulation temp (°C)	Bulk density (kg/m <sup>3</sup> )	Water retained in coagulated latex before drying (vol %)	Water retained in coagulated latex before drying (wt %)	$k_L a$ (m <sup>3</sup> /s)
90	410.0	37.2	52.3	$4.30 \times 10^{-10}$
96	403.0	26.9	48.8	$5.38 \times 10^{-10}$
102	398.0	24.5	38.9	$6.75 \times 10^{-10}$

the largest mean particle diameter retained the least amount of water before drying the coagulated latex. Some of our results, as given in Table II, show however considerably less amount of water to be present compared to 32 vol %. For a close packing of monodisperse rigid spheres, 32% of the volume of the coagulated latex slurry is expected to be filled with water. This effect becomes more and more pronounced with increasing temperature. Figure 11 indicates a similar trend in the water content in the coagulated latex samples obtained at higher applied shear in accord with the above arguments. In addition, in these samples the variance of the size distributions have been found to be smaller than the values of the variance calculated for the samples coagulated below the glass transition temperature. Hence both the mean diameter and the variance of the distribution affect the amount of water to be retained in the coagulated latex.

The rate at which water evaporates from the coagulated latex slurry can be described in terms of the product of the mass transfer coefficient  $k_L$  and the interfacial area  $a$  as follows:

$$\dot{m} = k_L a (c - c^*) \quad (4)$$

where  $c$  is the apparent concentration of water in the bulk and  $c^*$  is the equilibrium concentration of water at the temperature and pressure of the measurements. The amount of water retained in the latex cake before drying, specific surface area, bulk density of the dried coagulated latex, and mass transfer factors are given in Table II. Although the specific surface area and the variance of the size distribution of coagulated latex samples at different temperatures correlate well with the total time of drying (Fig. 12), almost no difference in bulk density has been found to exist among the powdered latex samples obtained from dewatering and drying of the coagulated latex slurry. Therefore, the difference in the mass transfer rates in these samples can be attributed to the additional resistance of small pores on the surface of the coagulated particles. Due to the complex nature of the drying process, involving flow phenomena in the porous media, a detailed analysis has not been attempted here, however.

The measured particle size–density relationship of the dried coagulated latex samples for different coagulation conditions are plotted in Figure 13. As shown, the density of particles coagulated below the glass transition temperature of the polymer decreases as the particle size increases. On the other hand, almost no change in the density of the particles has been observed for the

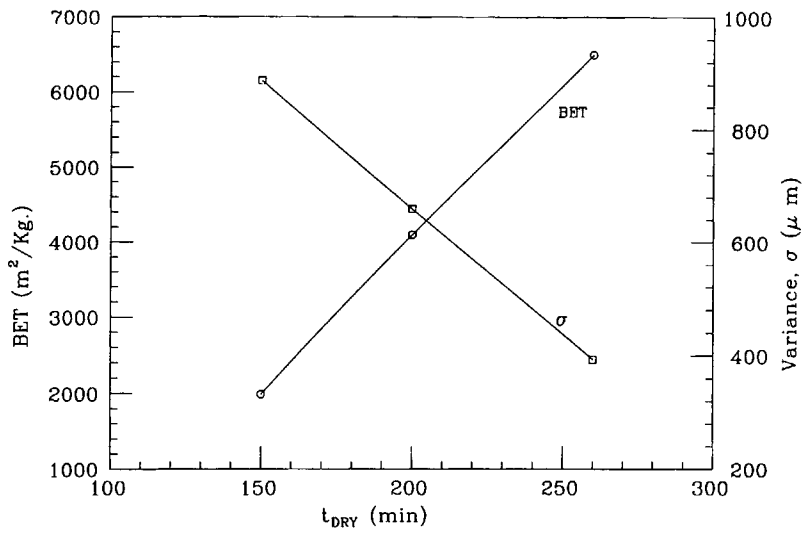


Fig. 12. Correlation of variance and BET data with the drying time of the coagulated latex.

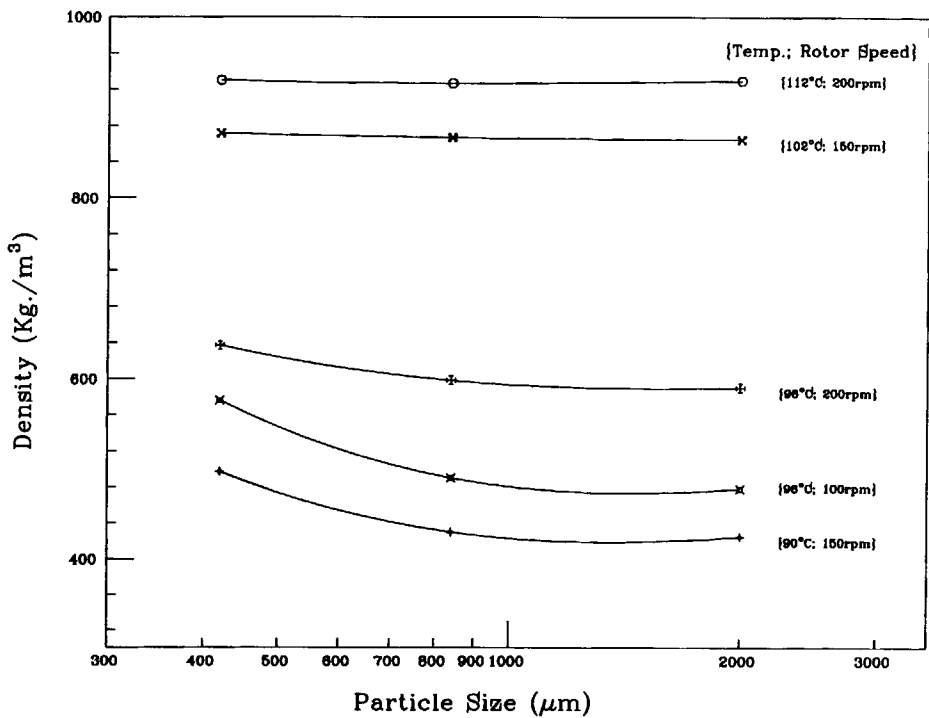


Fig. 13. Particle size-density relationship of latex particles coagulated at different process conditions.

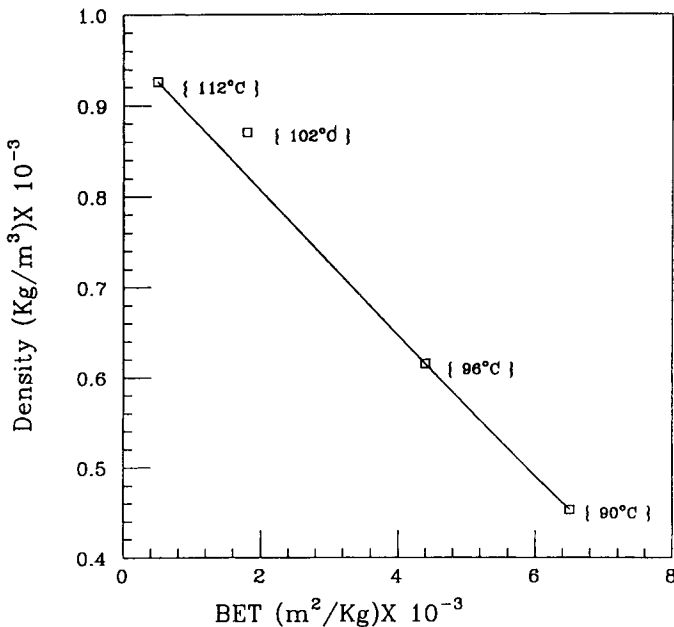


Fig. 14. Correlation of the density and BET data for the coagulated latex particles.

coagulated latex particles processed at temperatures above the glass transition temperature. Moreover, the density of coagulated particles is also found to increase with the increase in applied shear rates, other processing variables remaining unchanged. More compact aggregates are obtained when coagulation takes place at higher rotor speed of the mixer. Even more interesting is the effect of coagulation temperature on the density of the coagulated latex particles. A sharp increase in the density of the coagulated particles with the temperature is observed until the processing temperature reaches the glass transition temperature of the polymer. Above the glass transition temperature, the particle density approaches the density of the polymer. Thus a significant reduction in the porosity of the particles can be obtained by processing the latex at temperatures above the glass transition temperature of the polymer.

This result on particle morphology has been further supported by the specific surface area measurements, which show that both the inner and outer porosity of the particles reduce as the coagulation temperature increases. BET analysis on powdered latex samples show a decrease in specific surface area by an order of magnitude, for about 6500 to 500 m<sup>2</sup>/kg, when the process temperature is increased from 90 to 112°C, remembering that the glass transition temperature of the polymer is 102°C. A one-to-one correlation has been found to exist between the density and specific surface area of the coagulated particles at all process conditions as shown in Figure 14.

## CONCLUSIONS

In conclusion, a coagulated product of a desired particle size distribution can only be obtained by selecting proper coagulation temperature, the screw

speed, and the screw design. Our work has shown that the coagulation temperature controls the average particle size and sets the limit on the PSD, while the fine tuning of PSD can be achieved through the structure of the turbulent flow. The specific observations can be summarized as follows:

1. The most effective processing means to control the particle size and the particle morphology is the coagulation temperature.
2. The maximum rate of increase of the mean particle diameter of the coagulated latex has been found to occur in the neighborhood of the glass transition temperature.
3. Changes in the hydrodynamics, introduced by the variations in the channel depth and rotor speed, proved to be only of secondary importance.
4. By coagulating well above the polymer glass transition temperature an order-of-magnitude drop in the specific surface of the coagulated particles occurs.
5. A one-to-one relationship between the particle density and specific surface has been found for all conditions.

This work has been supported by grants from the DSM Research BV, The Netherlands.

### References

1. R. G. Nichols and F. Kheradi, in *Proceedings of the 2nd International Conference on Reactive Processing of Polymer*, University of Pittsburgh, Pittsburgh, 1982.
2. I. A. Valioulis, *Adv. Colloid Int. Sci.*, **24**, 81 (1986).
3. Th. F. Tadros, *Plast. Rubber Proc. Appl.*, **3**, 151 (1983).
4. R. H. Ottewill, in *Emulsion Polymerization*, I. Piirma, Ed., Academic, New York, 1982.
5. H. Sonntag and K. Strenge, *Coagulation and Stability of Disperse System*, Halsted, New York, 1969.
6. W. R. Schowalter, *Adv. Colloid Int. Sci.*, **17**, 129 (1982).
7. G. R. Zeichner and W. R. Schowalter, *AIChE J.*, **23**, 243 (1977).
8. L. A. Spielman, *Mathematical Models and Design Methods in Solid-Liquid Separation*, A. Rushton, Ed. NATO ASI Series E No. 88, Nijhoff Publ., Dordrecht, 1985.
9. H. N. Stein, E. H. Logtenberg, A. J. G. van Diemen and P. J. Peters, *Colloids Surfaces*, **18**, 223 (1986).
10. K. Higashitani, R. Ogawa, G. Hosokawa and Y. Matsuno, *J. Chem. Eng. Jpn.*, **15**, 229 (1982).
11. L. A. Utracki, *J. Colloid Int. Sci.*, **42**, 185 (1973).
12. J. T. Lin, M. S. El-Aasser, C. A. Silebi and J. W. Vanderhoff, *J. Colloid Int. Sci.*, **110**, 305 (1986).
13. V. Lowry, M. S. El-Aasser, J. W. Vanderhoff, A. Klein and C. A. Silebi, *J. Colloid Int. Sci.*, **112**, 521 (1986).

Received June 28, 1989

Accepted July 10, 1989