Polymerization in Gel-Like Emulsions

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Synopsis

Polymerization of styrene in gel-like emulsions (concentrated emulsions which have a volume fraction of monomer greater than 0.74), by using sodium dodecylsulfate as emulsifier and small amounts of water, was carried out with an oil-soluble initiator, AIBN. Both higher conversions and higher molecular weights of the polymer were obtained as compared to the polymerization in bulk. The higher "rigidity" of the monomer in the interior of the cells of the gel is responsible for the increased rate of polymerization and molecular weight. The polymer particles thus obtained have diameters in the range of 0.1 to 0.3 μm, depending upon the conditions of preparation of the gel. The effects of the concentration of the initiator, the concentration of surfactant, the monomer volume fraction, termperature, and ionic strength of the aqueous solution have been investigated.

INTRODUCTION

Because of its various advantages, emulsion polymerization has attracted a tremendous attention. In the conventional emulsion polymerization, monomer droplets are dispersed in an aqueous phase containing micellar aggregates of surfactant. The dispersed phase represents a relatively small volume fraction of the system and the micellar aggregates constitute the sites of the polymerization process. Gel-like emulsions with volume fractions of the dispersed phase as high as 0.99 have been reported however, and studied in some detail.[1-5] Lissant[1] has demonstrated that droplets of these concentrated emulsions are deformed into polyhedral cells. The continuous phase has a very low volume fraction and is in the form of a network of thin liquid films that separate the polyhedral drops. The adsorption of the surfactant on the surface of these drops ensures the stability of the concentrated emulsion.

The use of a concentrated emulsion of a hydrophobic monomer in water to perform polymerization may be of interest for the following reasons:

First, the gel-like structure of the emulsion suggests a lower mobility of the monomer in each of the cells of the emulsion. This means that the so-called gel effect, which leads to the delay in the bimolecular termination step, will take place from the beginning and not only after the extent of polymerization becomes sufficiently large. As a result, high rates of polymerization and molecular weights are expected.

Second, a better control of the size of the obtained polymer latexes becomes possible, since the size of latexes depends on the size of the cells of the gel, which, in turn can be controlled by employing the appropriate surfactant and surfactant concentration or by changing the pH and/or the ionic strength.

CCC 0021-8995/88/040907-17$04.00

EXPERIMENTAL

Materials

Styrene (Aldrich) was distilled and stored in a refrigerator. Azobisisobu-tyronitrile (AIBN, Alfa) was recrystallized from methanol. Sodium dodecyl-sulfate (SDS, Aldrich) and sodium chloride (Baker) were used as received. Water was deionized and distilled.

Instrumentations / Procedures

A typical procedure for the preparation of a concentrated emulsion is as follows: A small amount of aqueous solution containing sodium dodecylsulfate (SDS) was placed in a single neck flask (100 mL capacity) equipped with a mechanical stirrer. Monomer containing the initiator AIBN was added to the aqueous solution, under stirring, through an addition funnel. Care was exercised to prevent phase separation during addition, by adjusting the stirring rate and the addition rate of the monomer. The whole preparation process of the gel was accomplished within 10–15 min at room temperature.

The prepared emulsions were transferred to preweighed centrifuge tubes of 15 mL capacity, which were sealed with rubber septa. A mild centrifugation (1500 rpm, less than 1 minute) was employed to pack the concentrated emulsions into the tubes when necessary. Polymerizations were conducted in a temperature-controlled water bath in the presence of air. The AIBN concentration was 1.50×10^{-2} mol/L, unless specified otherwise. After polymerization, the concentrated emulsion was dispersed by adding water into the tube and agitating with a spatula. The aqueous system was then poured into methanol and the precipitated polymer was separated by filtration. The collected polymer was dried and further purified by dissolution in chloroform followed by precipitation in methanol.

The molecular weight of the resulting polymer was determined by employing gel permeation chromatography (GPC) equipment comprising 500 Å, 10^4 Å, 10^5 Å, and 10^6 Å pore size columns (Waters, Ultrastyragel) in series. The mobile phase was methylene chloride, the flow rate was 1 mL/min, and the wavelength of the detector was 254 nm. The purified and dried polymer was completely dissolved in chloroform (0.1 g/L concentration) and injected in the GPC. The GPC was calibrated using monodisperse polystyrene standards (Polymer Laboratories, U.K.) of molecular weight 10^4–12×10^6. The band broadening was disregarded in the calculation of the molecular weight. Since the concentrated emulsion produces a certain amount of bulk phase during polymerization, the molecular weight of the polymer formed in the gel phase was evaluated by subtracting the molecular size distribution that corresponds to bulk polymerization (which was determined on the basis of a curve obtained for polymer prepared by bulk polymerization). The polymer latexes prepared by the present procedure were examined with a JEOL 100 U Transmission Electron Microscope. Copper grids coated with nitrocellulose films were employed as substrates and the system already dispersed in water was further diluted with water and deposited on the substrate.

RESULTS AND DISCUSSION

Figure 1 compares the polymer conversion in gel polymerization and in bulk polymerization for various polymerization times and for the same concentration of AIBN and temperature. It clearly demonstrates that the polymerization rate reflected in conversion is much higher for the concentrated emulsion procedure. The molecular weight distribution of the resulting polymers obtained by both methods are shown in Figure 2. The molecular weight of the polymer prepared by gel polymerization is higher than that produced by polymerization in bulk by more than an order of magnitude. Therefore, it becomes evident that both higher rates and higher molecular weights are obtained in the concentrated emulsion procedure than in bulk polymerization. One may be tempted to assume that the surfactant participates in the acceleration of polymerization. To verify this, polymerization was carried out in concentrated emulsions without initiator. The negligible amount of polymer thus obtained indicates that there is no direct involvement of the surfactant in the polymerization process.

Unlike conventional emulsion polymerization, in which the polymer latexes grow during polymerization, the size and shape of the latexes in concentrated emulsions is principally determined by the preparation of the gel. The monomer droplets separated by the thin films of aqueous phase are sufficiently stable for their deformation during polymerization to be only moderate. Nevertheless, some contraction is expected to occur due to the density difference between monomer and polymer.
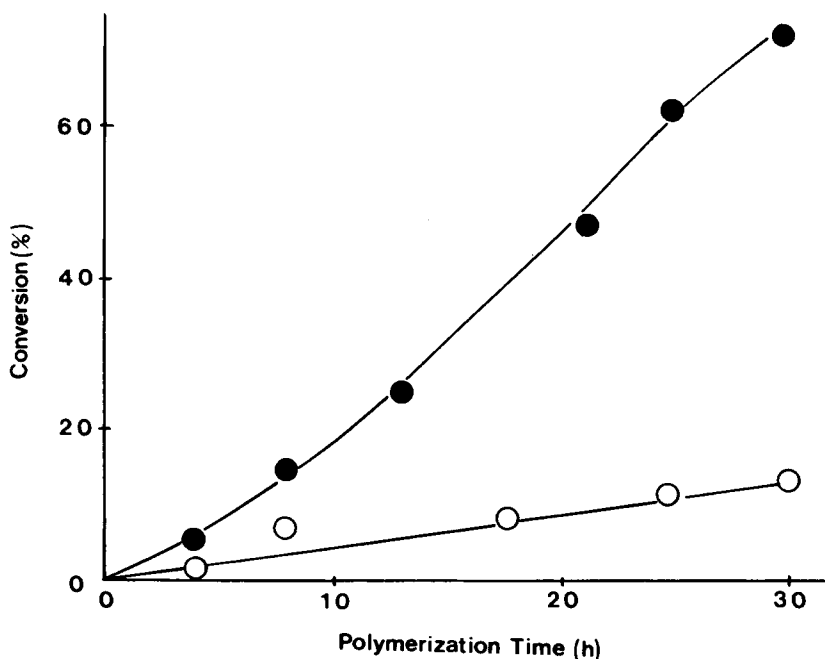

Fig. 1. Plot of polymer conversion against polymerization time (SDS 0.3 g, water 3 mL, styrene 40 mL, 40°C). (●) Gel; (○) bulk.
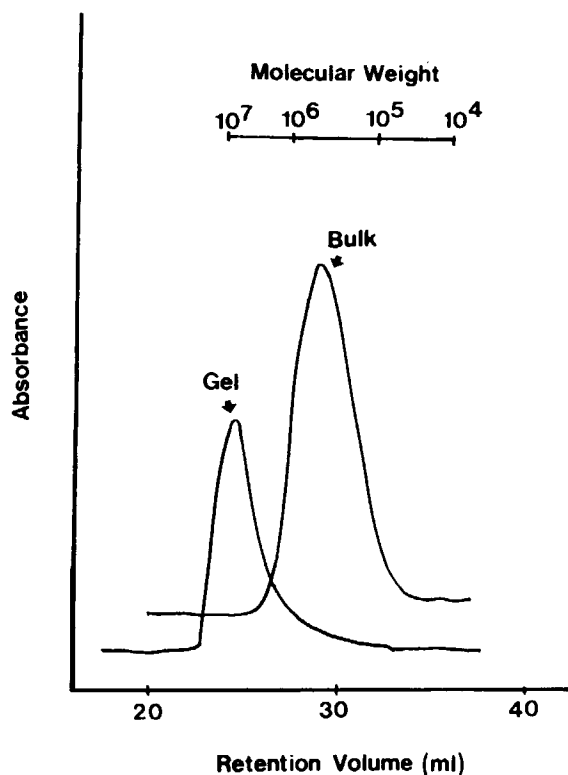
Fig. 2. Molecular weight distribution of polymer in concentrated emulsion polymerization and in bulk polymerization (SDS 0.3 g, water 3 mL, styrene 40 mL, 40°C, 30 h).
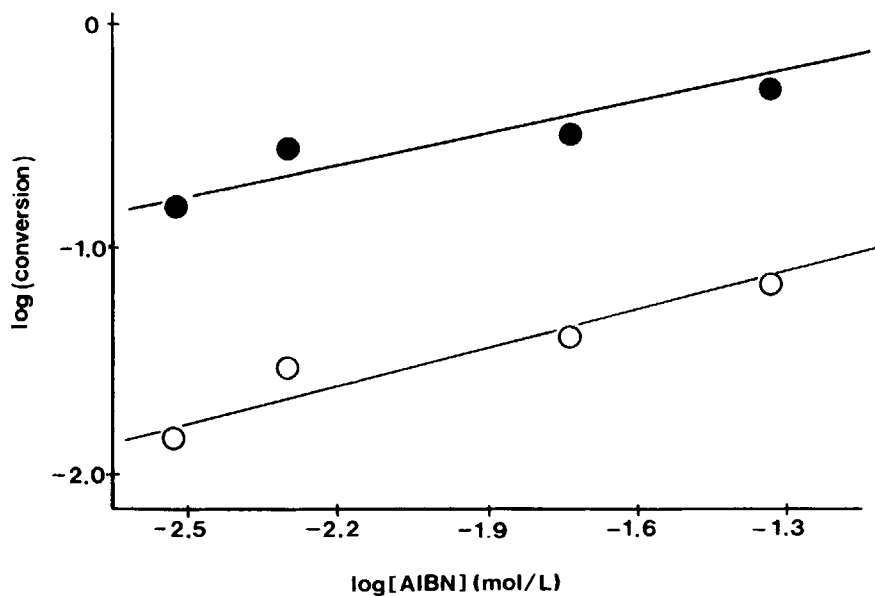

Fig. 3. Plot of log (conversion) against log[AIBN] (SDS 0.3 g, water 2 mL, styrene 15 mL, 40°C, 10 h). (●) Gel; (○) bulk.
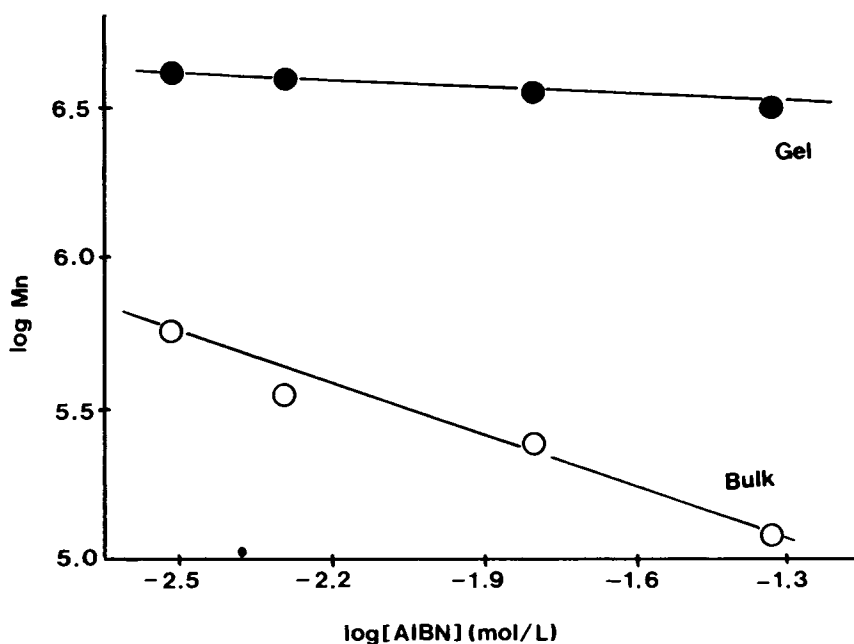
Fig. 4.   Plot of log M_n against log[AIBN] (SDS 0.3 g, water 2 mL, styrene 15 mL, 40°C, 10 h). (●) Gel; (○) bulk.

To acquire a sound basis for the understanding of the polymerization in concentrated emulsions, the effects of various parameters, such as the concentration of the initiator, the monomer volume fraction ϕ (the internal phase ratio), the concentration of the surfactant, the temperature, and the concentration of electrolyte will be presented.

Effect of Initiator

Concentrated emulsions containing 0.75 and 0.88 volume fractions of monomer with a wide range of AIBN concentrations were polymerized at 40°C. A relatively low temperature was used for polymerization in order to minimize the coalescence of the emulsion droplets during polymerization. (This problem is discussed below.) Bulk polymerization was also carried out for each AIBN concentration for comparison.

Figures 3 and 4 plot log conversion and log M_n (where M_n is the number-average molecular weight) against log[AIBN] for both kinds of polymerization. In the entire range of initiator concentration, polymerization in concentrated emulsions leads to higher conversions and molecular weights with a polydispersity in the range of 1.52–1.87. The slopes of the log–log plots of conversion and number-average molecular weight against initiator concentration provided by Figures 3 and 4 are listed in Table I. For bulk polymerization, the slopes for conversion and number-average molecular weight are very close in absolute value, but have opposite sign. This complies with the kinetics of polymerization, formulated on the basis of the steady-state approximation, when one assumes that the conversion for a given polymeriza-

TABLE I
The Slopes in the Log–Log Plots of Conversion and Number-Average Molecular Weight
Against the Initiator Concentration in Gel and Bulk Polymerization

Monomer volume fraction	Gel[c]		Bulk	
	Conversion	M_n	Conversion	M_n
0.75[a]	0.54	−0.22	0.53	−0.44
	(0.9687)[e]	(0.9867)	(0.9996)	(0.9923)
0.88[b, d]	0.42	−0.11	0.62	−0.57
	(0.9864)	(0.9868)	(0.9949)	(0.9977)

[a] Polymerization condition: 40°C, 18 h.
[b] Polymerization condition: 40°C, 10 h.
[c] Water 2 mL, styrene 15 mL, SDS 0.3 g.
[d] Centrifugation was employed at 1500 rpm for 1 min prior to polymerization for efficient packing of the concentrated emulsion into a reaction tube.
[e] The value in parenthesis signifies the correlation coefficient.

tion time is proportional to the rate of polymerization. Figure 1 indicates that the latter condition is satisfied. However, in the case of concentrated emulsions, the above relationship between the two slopes is no longer valid. While the rate of polymerization increases with increasing initiator concentration in both cases, the extent of decrease of the molecular weight with increasing initiator concentration is much smaller for gel polymerization. The weaker dependence of the molecular weight on the initiator concentration shows that the enhancement in the termination rate, induced by the increase in the initiator concentration, is much less for concentrated emulsion polymerization than for bulk polymerization. Because of the emulsifier layer that surrounds the cells, the "mobility" of the liquid within the cells of the gel is lower than in a bulk liquid. Accordingly, one expects the diffusion of the growing polymer chains to be significantly decreased. The termination rate is, therefore, decreased and the rate of polymerization as well as the molecular weight are increased. In other words, the so-called gel effect, which accounts for the abrupt increase in rate and molecular weight of the polymer in the final stages of bulk polymerization, comes into play from the beginning when polymerization is carried out in a concentrated emulsion.

Effect of the Monomer Volume Fraction ϕ (Internal Phase Ratio)

Figure 5 shows a plot of conversion versus monomer volume fraction. With increasing ϕ, there is a gradual increase in conversion followed by a decrease, with a maximum at about $\phi = 0.9$. This phenomenon can be explained if one assumes that during polymerization some cells of the gel coalesce and form a bulk phase in which the conversion is smaller. Visual observations indeed indicate a separated thin layer at the upper part of the tube after polymerization. Since no appreciable separated liquid phase was observed before polymerization, it is likely that during polymerization some cells do coalesce. Molecular weight distribution curves have been determined for various values of ϕ and plotted in Figure 6. All these GPC curves have a tail at about 29 mL retention volume, which, as one can see from Figure 6, is consistent with the
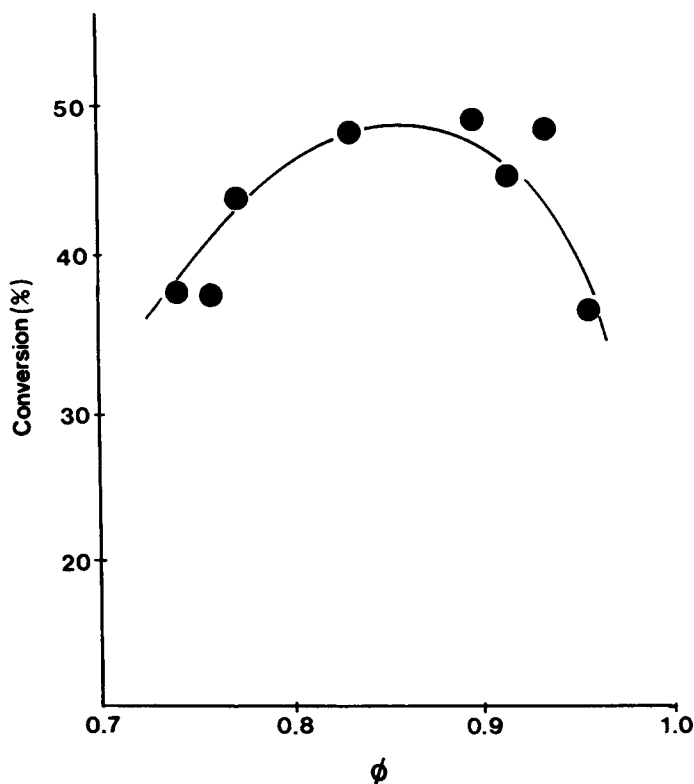
Fig. 5. Plot of polymer conversion against the monomer volume fraction (SDS 0.15 g, styrene 17 mL, 40°C, 24 h).

molecular weight distribution of the polymer prepared by bulk polymerization. Therefore, it is clear that this tail is due to the polymerization in bulk and its area represents the amount of bulk phase resulting from the coalescence of some cells of the gel during polymerization. The weight fraction of polymer produced in the interior of the gel to the total amount of polymer calculated from the GPC area is plotted against ϕ in Figure 7. (In this figure, the amounts of monomer and surfactant have been kept constant, but the amount of water was changed.) This plot is quite similar to that in Figure 5, having its maximum at a value of ϕ of about 0.9. Therefore, one can conclude that the extent of bulk phase formation is an important factor in the overall rate of polymerization. The greater amount of bulk phase formed for values of ϕ greater than 0.9 is probably due to the increased viscosity of the concentrated surfactant aqueous solutions and hence to the higher difficulty in generating a stable gel in such cases.

Transmission electron micrographs of polymer latexes, prepared from gels with ϕ values of 0.96 and 0.82 and subsequently diluted with water, are presented in Figure 8. Both micrographs contain polymer latexes of about 0.22 μm diameter. However, the micrograph corresponding to $\phi = 0.96$ contains bigger particles of about 0.32 μm in diameter as well, while that corresponding to $\phi = 0.82$ contains smaller particles, as small as 0.12 μm in diameter. It
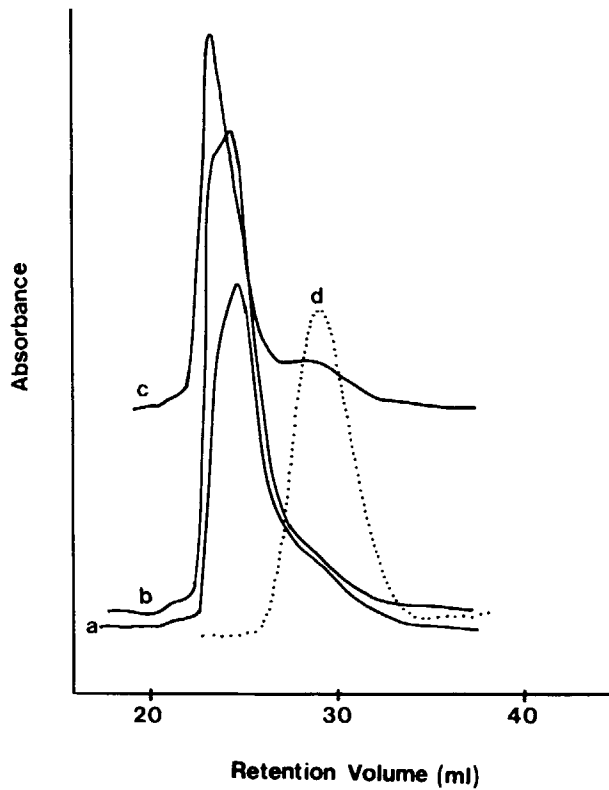
Fig. 6. GPC curves of polymer for various monomer volume fractions (SDS 0.15 g, styrene 17 mL, 40°C, 24 h). (a) $\phi = 0.92$, (b) $\phi = 0.89$, (c) $\phi = 0.77$, and (d) bulk polymerization.
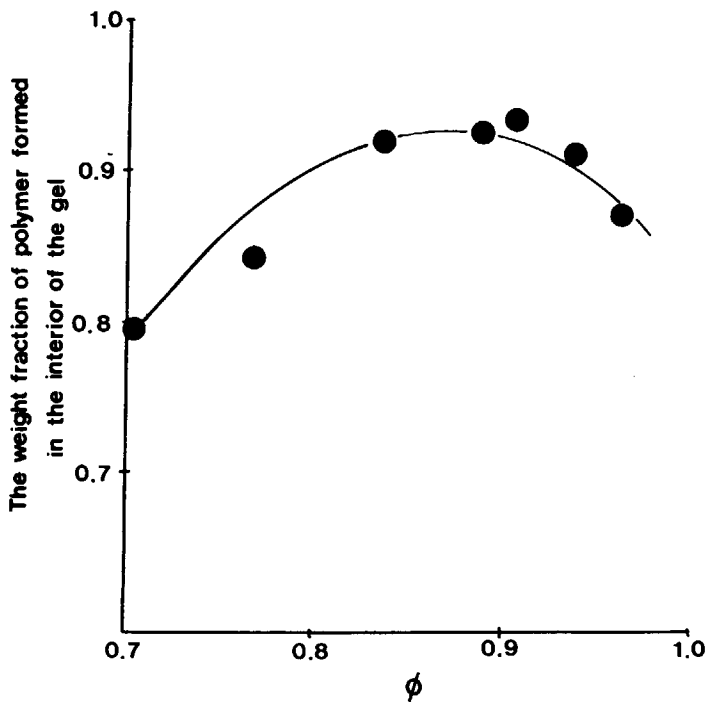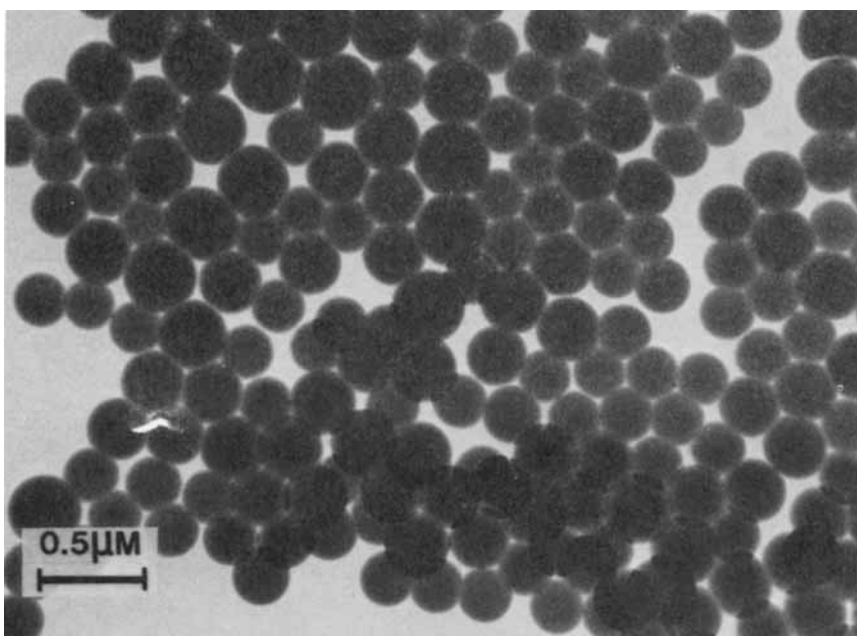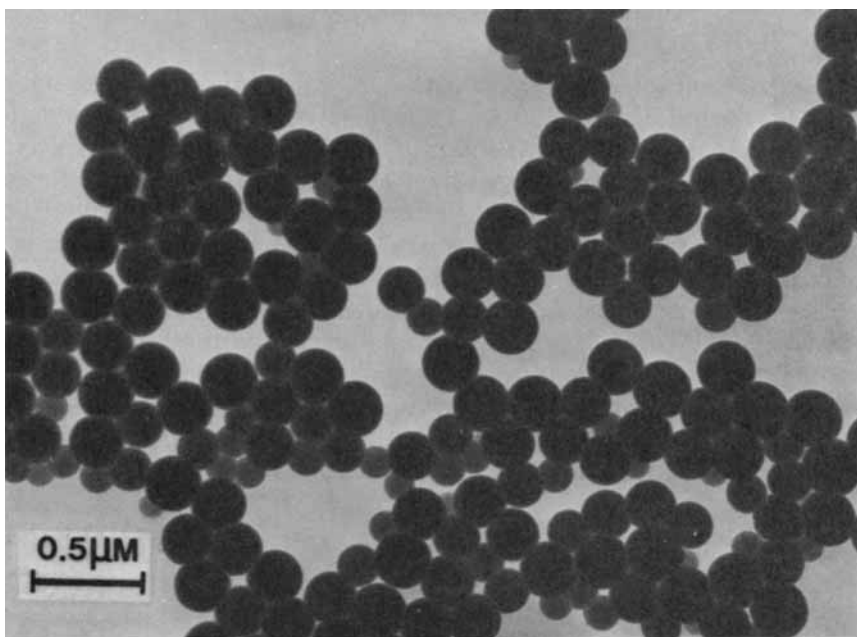

Fig. 7. Plot of the weight fraction of polymer formed in the interior of the gel against the monomer volume fraction (SDS 0.15 g, styrene 17 mL, 40°C, 24 h).

(a)

(b)

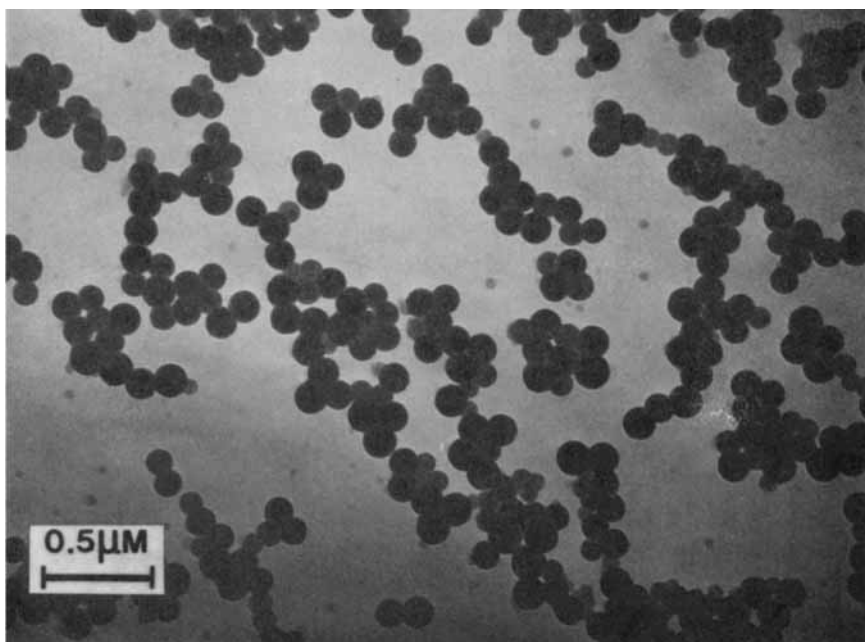Fig. 8. Electron micrographs of polymer latexes (SDS 0.3 g, styrene 35 mL, 40°C, 22 h). (a) $\phi = 0.96$; (b) $\phi = 0.82$.

Fig. 9.   Electron micrograph of polymer latexes obtained in a dilute emulsion of 0.2 monomer volume fraction (SDS 0.15 g, water 20 mL, styrene 5 mL, 40°C, 22 h, under stirring).

is noteworthy that some particles in both micrographs are flocculated, having flat and polyhedral interfaces. It should be pointed out that the deformation of the emulsion droplets to polyhedral shapes as well as the heterogeneity in the particle size distribution have been proposed as explanations for the increased packing efficiency when the internal phase ratio exceeds the critical value of 0.74. This critical value corresponds to the most compact packing of homodisperse spheres. The presence of larger particles in the emulsion with $\phi = 0.96$ can be explained in terms of the increased heterogeneity in the particle size distribution. The presence of the smaller particles in the gel with $\phi = 0.82$ is most likely a result of the polymerization in the aqueous phase, since this system contains a significant fraction of aqueous phase. This explanation is supported by the fact that the size of these polymer latexes is comparable to that obtained in the dilute emulsion with $\phi = 0.2$ (Fig. 9).

Effect of Surfactant

Figure 10 represents GPC curves of the polystyrene prepared in concentrated emulsions of various surfactant concentrations. It clearly shows that the amount of bulk phase decreases with increasing surfactant concentration. Figure 11 shows that, as the surfactant concentration increases, the weight fraction of polymer formed in the interior of the droplet increases first steadily and then levels off, while the conversion shows a linear increase through the entire range of surfactant concentrations. Certainly, the stability of the gel cells depends on the surfactant concentration. Figure 12 is a plot of the molecular weight of polymer produced in the gel phase as a function of the
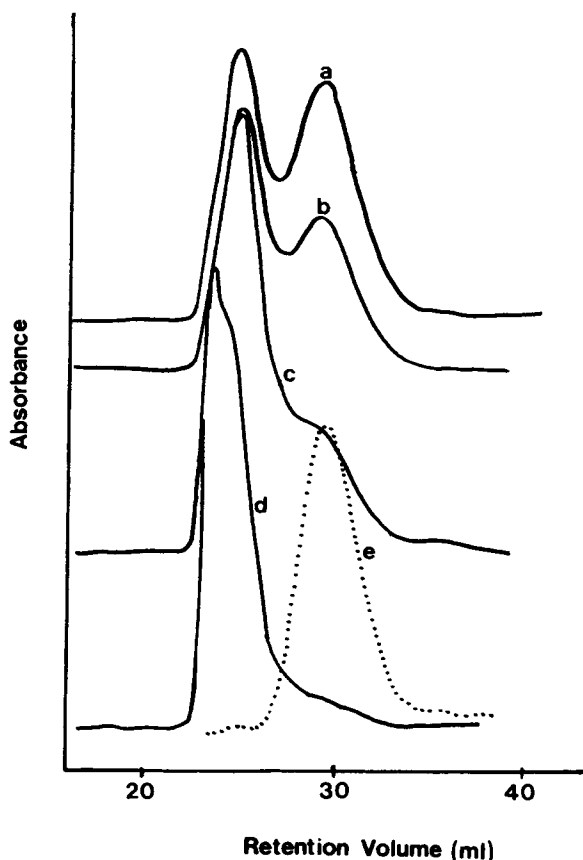
Fig. 10.   GPC curves of polystyrene prepared in concentrated emulsions for various SDS concentrations (water 2 mL, styrene 30 mL, 45°C, 18 h). (a) 1.67×10^{-3} g SDS/mL styrene; (b) 2.50×10^{-3} g SDS/mL styrene; (c) 5.00×10^{-3} g SDS/mL styrene; (d) 1.33×10^{-2} g SDS/mL styrene; and (e) polystyrene obtained in bulk polymerization.

amount of surfactant. The molecular weight of the polymer is found to increase slightly but distinctively with the amount of surfactant. For additional information, electron micrographs of the polymer latexes produced with 3.3×10^{-3} g SDS/mL styrene and 1.3×10^{-2} g SDS/mL styrene are presented in Figure 13. By comparing the two micrographs, one can see that the latexes prepared with a larger amount of surfactant contain smaller particles. One can speculate that a reduction in the cell size provides higher rigidity in the interior of the droplet. This delays the bimolecular termination step and, therefore, leads to a larger molecular weight of the polymer and to an increased rate of polymerization. This could account for the continuous increase in conversion with increasing surfactant concentration while the weight fraction of the polymer formed in the cells of the gel reaches an asymptotic value close to unity. The decrease in size of the latex particles with increasing surfactant concentration is further confirmed by the micrograph of Figure 14, which was obtained for a surfactant to styrene ratio of 2×10^{-2} g SDS/mL styrene. It should be mentioned that the use of amounts of surfac-
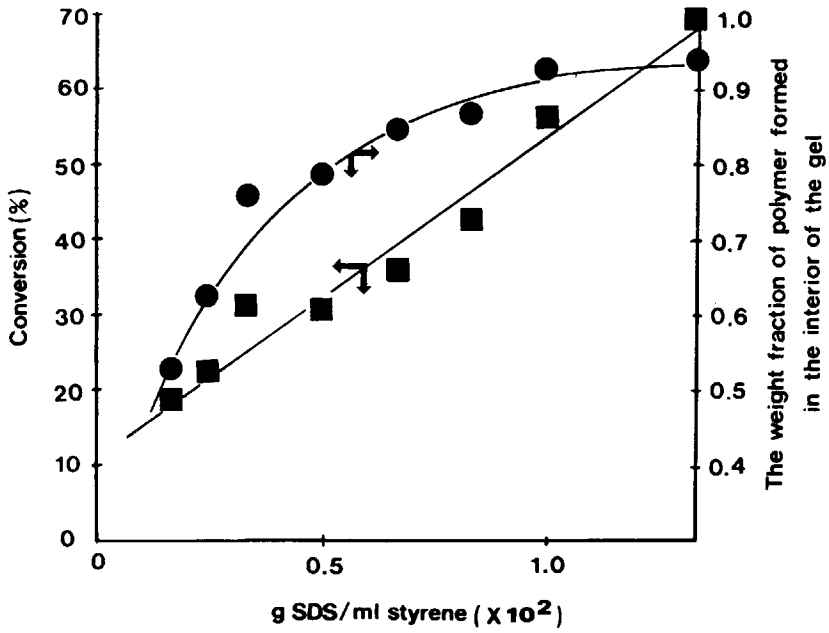
Fig. 11. Plot of polymer conversion and weight fraction of the polymer formed in the interior of the gel as a function of the SDS concentration (water 2 mL, styrene 30 mL, 45°C, 18 h).
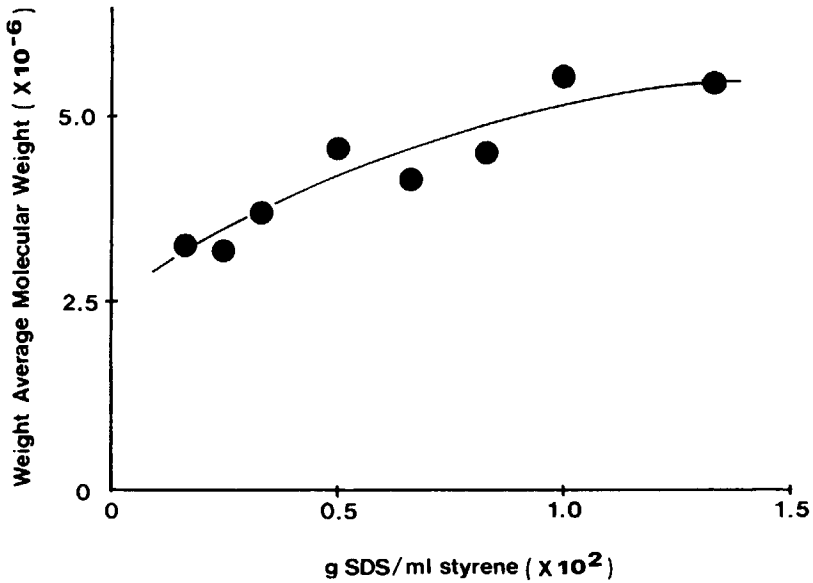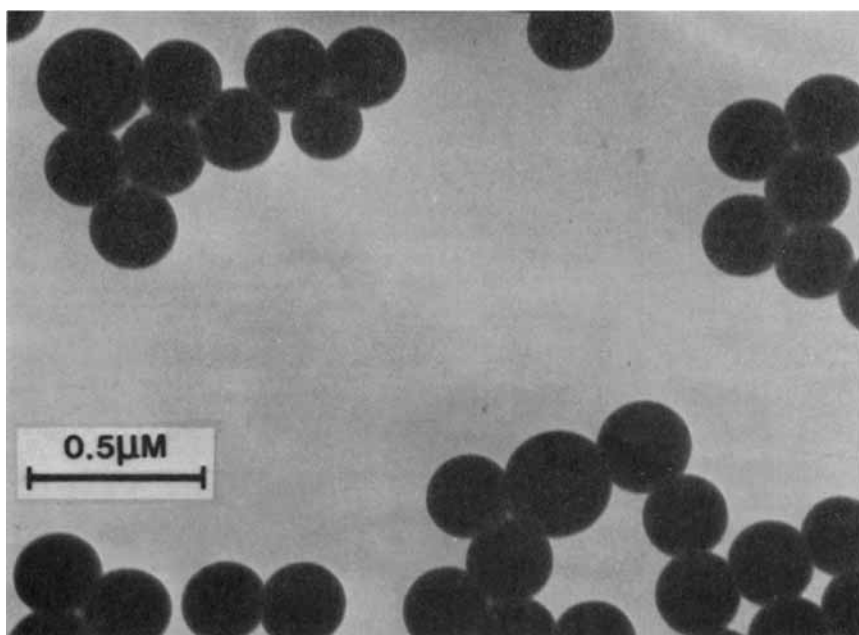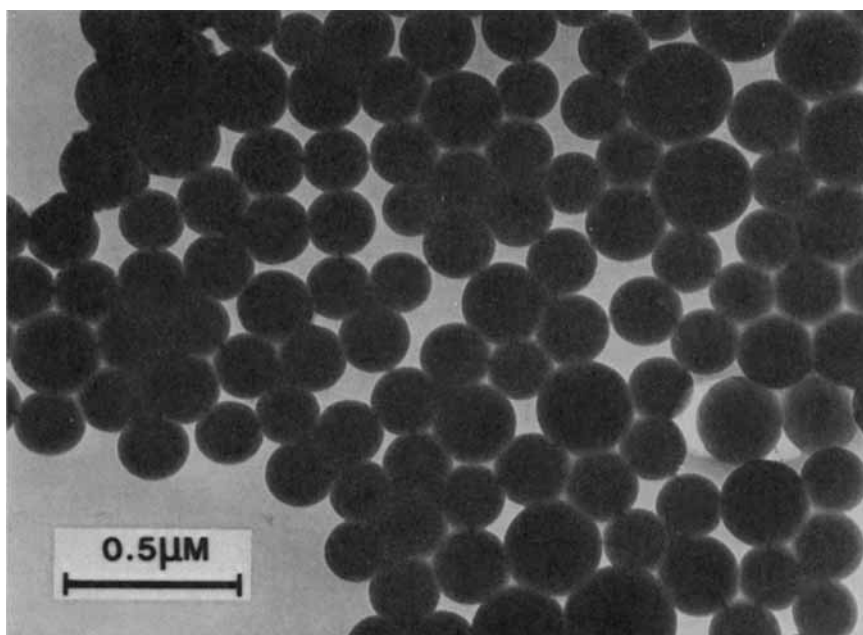

Fig. 12. Plot of the weight average molecular weight of polymer formed in the interior of the gel as a function of the SDS concentration.

(a)

(b)

Fig. 13.   Electron micrographs of polymer latexes obtained with (a) 3.3×10^{-3} g SDS/mL styrene and (b) 1.33×10^{-2} g SDS/mL styrene (water 2 mL, styrene 30 mL, 45°C, 18h).
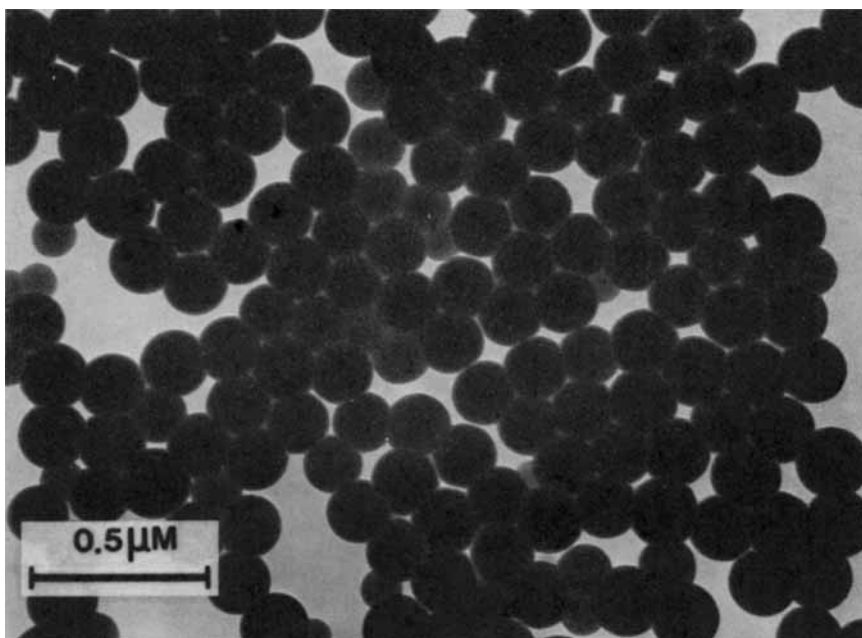
Fig. 14. Electron micrograph of polymer latexes ([AIBN] = 1.55×10^{-2} mol/L, 2.0×10^{-2} g SDS/mL styrene, water 2 mL, styrene 15 mL, 40°C, 10 h).
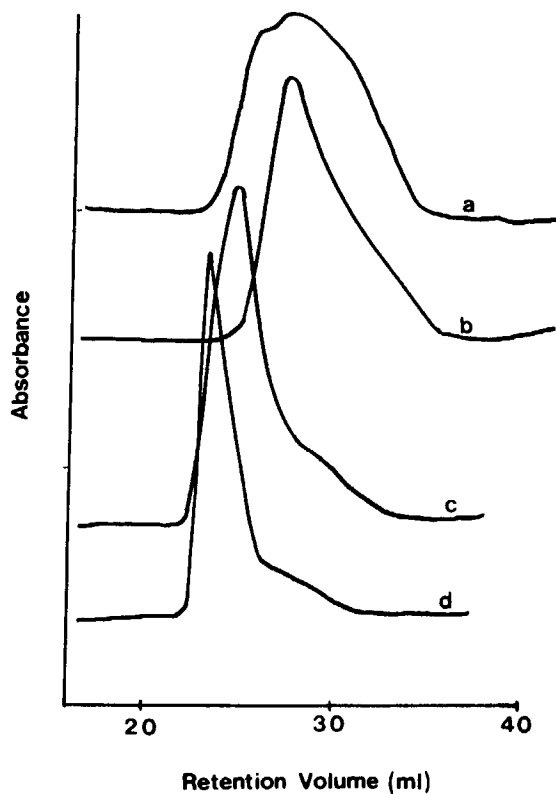

Fig. 15. GPC curves of polystyrenes prepared by the concentrated emulsion procedure at various polymerization temperatures (SDS 0.25 g, water 2.5 mL, styrene 42 mL). (a) 65°C, 20 h (b) 55°C, 21 h (c) 45°C, 24 h, (d) 35°C, 72 h.
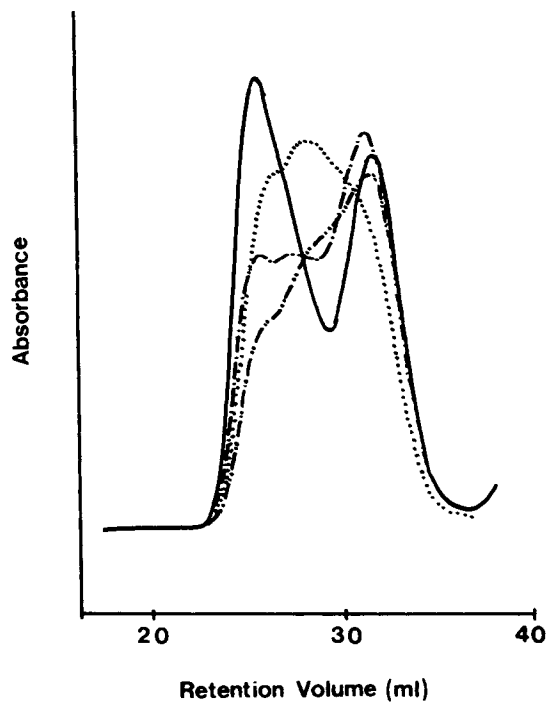
Fig. 16. The change in the GPC curve with polymerizing time at 65°C (SDS 0.25 g, water 2.5 mL, styrene 42 mL: (—) 2 h; (—·—) 4 h; (—··—) 6 h; (···) 8.5 h).
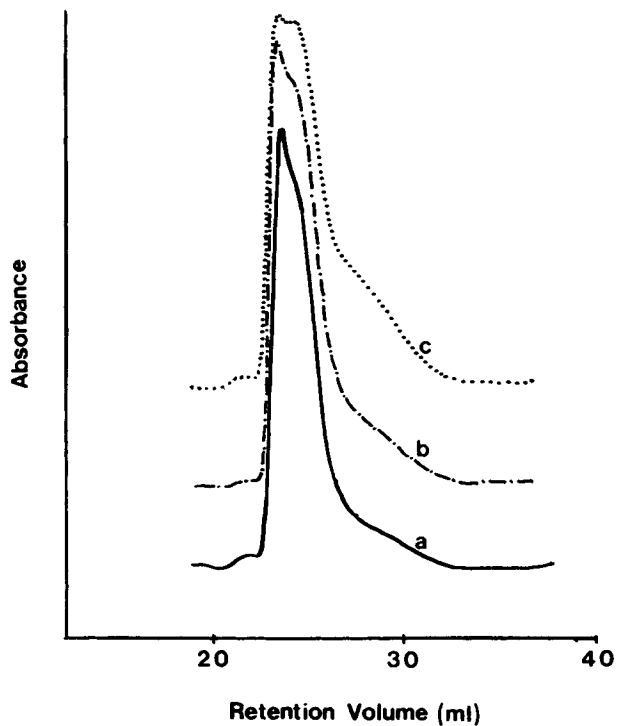

Fig. 17. GPC curves of polystyrene prepared by the concentrated emulsion procedure with various amounts of NaCl (SDS 0.225 g, water 1.5 mL, styrene 22.5 mL, 40°C, 18 h). (a) no NaCl, (b) 0.043M NaCland, (c) 0.22M NaCl.

tant greater than 0.2 g SDS/mL water resulted in the failure to produce gels. This probably happened because of the high viscosity of the highly concentrated aqueous solutions of surfactant which impedes the formation of the cells. Therefore, the use of an excessive amount of surfactant should be avoided in the preparation of the gel.

Effect of Temperature

Figure 15 shows the GPC curves of polystyrenes obtained in concentrated emulsions at various temperatures. The molecular weight distribution is found to broaden because of a greater amount of low molecular weight polymers generated in the bulk as the polymerization temperature increases. This shows that coalescence of cells readily takes place during polymerization, generating a greater amount of bulk phase. The greater the temperature, the greater is the coalescence, and hence the amount of bulk phase formed. Figure 16 shows that the destruction of the cells becomes more significant with increasing polymerization time. Also notable is the trimodal molecular size distribution that appears after 8.5 h. This is most likely a result of the "gel effect" in the bulk.

Effect of Ionic Strength

GPC curves of polystyrenes generated in the presence of various amounts of NaCl are presented in Figure 17. The bulk phase reflected in the tail of the GPC curve increases with NaCl concentration. This can be explained by noting that the double layer-repulsive force between the emulsion cells be-
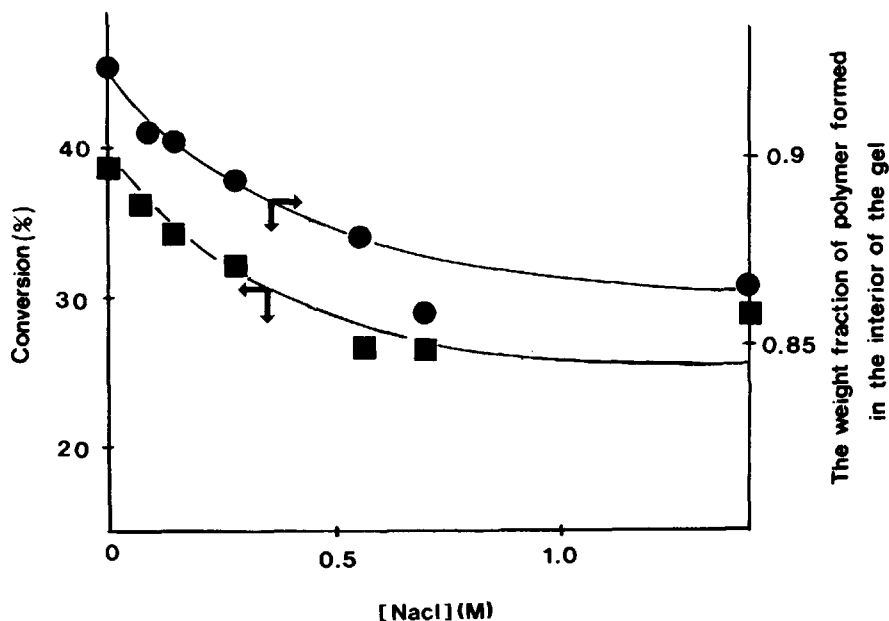

Fig. 18. Plot of polymer conversion and weight fraction of polymer formed in the interior of the gel as a function of the NaCl concentration in the aqueous phase (SDS 0.225 g, water 1.5 mL, styrene 22.5 mL, 40°C, 18 h).

comes weaker with increasing salt concentration. Figure 18 shows that the conversion and the weight fraction of polymer formed in the gel phase decrease with increasing NaCl concentration.

CONCLUSION

The polymerization in the interior of a concentrated emulsion (gel) proceeds much faster and produces higher molecular weight polymers than bulk polymerization. This is attributed to a gel effect induced by the higher rigidity of the monomer in the emulsion cells.

The minimization of the formation of a bulk phase during polymerization constitutes an important factor in the success of this method, since the rate of the process as well as the molecular weight are much lower in bulk polymerization. The results of this study show that a low temperature, the absence of electrolyte, a suitable amount of water, and a sufficient but not an excessive amount of surfactant minimize the occurrence of a bulk phase.

References

1. K. J. Lissant, *J. Colloid Interface Sci.*, **22**, 492 (1966).
2. K. J. Lissant and K. G. Mayhan, *J. Colloid Interface Sci.*, **42**, 201 (1972).
3. H. M. Princen, *J. Colloid Interface Sci.*, **71**, 55 (1979).
4. H. M. Princen, *J. Colloid Interface Sci.*, **75**, 246 (1980).
5. H. M. Princen, *J. Colloid Interface Sci.*, **91**, 160 (1983).
6. E. Ruckenstein and D. Feldman, Invention Disclosure, SUNY Buffalo, Oct. 30, 1986.