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Polymerization of Styrene in Water-Alcohol-Ionic Surfactant Solutions

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ABSTRACT

The stability regions of styrene and polystyrene W/O microemulsions stabilized by sodium dodecyl sulfate with pentanol or butyl cellosolve as cosurfactant were determined. The polystyrene microemulsions showed considerably smaller stability regions than the ones with the monomer. Hence, early phase separation (turbidity) was encountered in polymerizing styrene within the microemulsion region. The maximally permitted conversion percentage of styrene in the low-water region was directly related to the solubility of the polymer in the cosurfactant. The high solubility of polystyrene in butyl cellosolve gave better stability than the microemulsion containing pentanol, showing the microemulsion concept to be useful in order to prepare hydrocarbon polymers containing ionic compounds.

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INTRODUCTION

Emulsion polymerization is usually carried out in a macroemulsion, an opaque system with particle size in the range 1 to 10 μm. The properties of these systems have been well characterized and a rich variety of information is available [1-3].

Extension of the field toward systems with smaller particle sizes has recently been made and two new types of polymerization systems can be recognized.

Vanderhoff and Ugelstad [4-9] have recently prepared emulsions with much smaller particle sizes ($\simeq$ 0.1 to 0.2 μm) by using ionic surfactants and a low amount of long-chain fatty alcohols as cosurfactants. These emulsions are called "mini-emulsions" to distinguish them from the much larger size "macroemulsions" and the very small size "microemulsions." The latter display a particle size of 0.005 to 0.1 μm and are transparent.

Microemulsions have been extensively studied since their introduction by Schulman [10]. They are essentially transparent oil/water systems stabilized by a combination of an ionic surfactant and a cosurfactant in the form of a medium chain length alcohol. The opinion of their "true" nature has varied [11-26], but the fact that the inverse micellar solution of water and surfactant in the cosurfactant may be diluted with hydrocarbon to a W/O microemulsion is now well recognized [23-26]. These W/O microemulsions are thermodynamically stable.

Polymerization in microemulsion systems has been attempted to a limited extent. Microemulsions have been polymerized, and electron microscopy photos claimed to reflect their structure before polymerization [27]; other results showed polymerization in a methyl methacrylate microemulsion to lead to instability [28] in spite of the fact that the polymer in that case is soluble in the monomer.

Hence, monomer/polymer solubility is not the complete answer to microemulsion stability. Our recent results [29] have shown that addition of the polymer also caused drastic changes in stability in the nonpolar styrene/polystyrene system with excellent mutual solubility of monomer and polymer. It was found that at least two factors influenced the stability of a W/O microemulsion containing styrene and its polymers. In addition to the entropy effect [30-39] that would be expected, the styrene oligomer beginning with the dimer also had an effect on the stability. These results indicate the possibilities to form stable W/O microemulsions to be limited, and the objectives of the present publication are to establish the connection between solubility of an added polymer and the stability of a system having been polymerized in situ. The influence of the solubility of the polymer in the cosurfactant will also be described.

On the other hand, polymers have been used to stabilize microemulsions [40-44], and the mechanism for such stabilization has been discussed by making comparisons with the stabilizing action of polymers in macroemulsions [45].

It appears obvious that microemulsions with polymers present manifold scientific problems, and since their stability is also very important industrially, we found an investigation on the influence of the presence of a polymeric substance on the solubility regions of a monomer microemulsion to be of pronounced interest.

We chose the styrene/polystyrene microemulsion, considering the mutual solubility of the two components and the industrial importance of the system. The present paper describes the effect of polystyrene on the stability of W/O microemulsions and compares these results to those obtained by polymerization of styrene in ionic surfactant-alcohol medium of low water content.

EXPERIMENTAL

Materials

Pentanol and ethylene glycol monobutyl ether (butyl cellosolve, $C_4H_9OCH_2CH_2OH$) of pure grade were used as received from Fisher Scientific Co. Sodium dodecyl sulfate (SDS, $C_{12}H_{25}SO_4Na$) supplied by BDH was twice recrystallized from absolute ethanol. Water was doubly distilled. Styrene from Eastman was used directly for solubility study at 50°C. For polymerization, the purified styrene was distilled at 45°C/10 mmHg. The initiator was azobisisobutyl nitrite (AIBN) from Eastman. Polystyrene of an average molecular weight of 22,000 was obtained from Aldrich Chemical Co.

Microemulsion and Solubility of Polystyrene

The transparent microemulsion regions were determined by titration of water to a screw-capped test tube containing pentanol, styrene, and SDS. Vigorous stirring by a Vortex mixer was necessary to ensure rapid homogeneity. Microemulsion containing a certain amount of polystyrene-styrene could readily be prepared in a similar way. The maximum solubilities of polystyrene in the various media were obtained by adding polystyrene stepwise to the media until they became turbid. All the experiments were carried out at 50°C in a water thermostat with a temperature control of ±0.1°C.

Polymerization

AIBN-initiated polymerizations at 50°C were carried out in a series of glass ampules under nitrogen atmosphere. Conversion of polymer was determined by precipitating the reaction mixture in a large excess of methanol. The sampling process was continued at different time intervals until the polymerizing mixture became turbid. The appearance of turbidity was the indication of the beginning of phase separation.

Molecular Weight Determination

The dried polymer was dissolved in the tetrahydrofuron (THF) in 0.2 wt%. The molecular weight of polymer was determined by using a Waters Model 201 liquid chromatograph with 10^3, 10^4 and 10^5 Å M-styragel columns. Polystyrene standards (0.1 wt% in THF) were used for calibration. The flow rate was kept at 1 mL/min.

RESULTS AND DISCUSSION

W/O Microemulsion Solubility Areas

The solubility regions for the structure-forming components of pentanol-aqueous SDS and the microemulsion containing styrene are shown in Fig. 1. The representation in Fig. 1 was chosen in order to facilitate the experimental determinations. The solubility areas were determined with initiation at a line on the SDS/pentanol/styrene triangle with constant content of styrene but varied the pentanol/SDS ratio (Fig. 1). This means that only the water content can be directly read from the diagram. The pentanol and SDS readings should be multiplied by a factor (1 - x/100) in which x means weight percentage of styrene given. The styrene readings should be multiplied by the factor x/100.

The W/O microemulsion regions were a direct continuation of the inverse micellar area of the structure-forming components. Maximum water solubilization was obtained at a weight ratio of cosurfactant/surfactant at 3.2 for both inverse micellar solution and the 25% styrene-microemulsion. This value is similar to that of 50% p-xylene-microemulsion at 30° C, in which the ratio was found to be 3.5 [23, 25]. By further increasing the styrene content from 50 to 75%, the maximum water solubility was markedly reduced from 35 to 10%, both of which occurred at a lower cosurfactant/surfactant ratio of 2. A similar shift of the ratio was also observed for the microemulsions containing benzene-pentanol-aqueous potassium oleate [23]. In such systems [25], no inverse micelles or microemulsions were detected at low concentrations of water (< 15%). Instead, the molecules of surfactant and water were found to exist only in the form of ion pairs or small aggregates in the water-poor region [25].

Pentanol does not mix with a small amount of styrene; the two compounds became miscible when the weight ratio of styrene/pentanol reaches 20/80. In other words, styrene can dissolve pentanol all the way up to a maximum of 400 g pentanol/100 g styrene. The styrene molecules may exert similar interactions with the

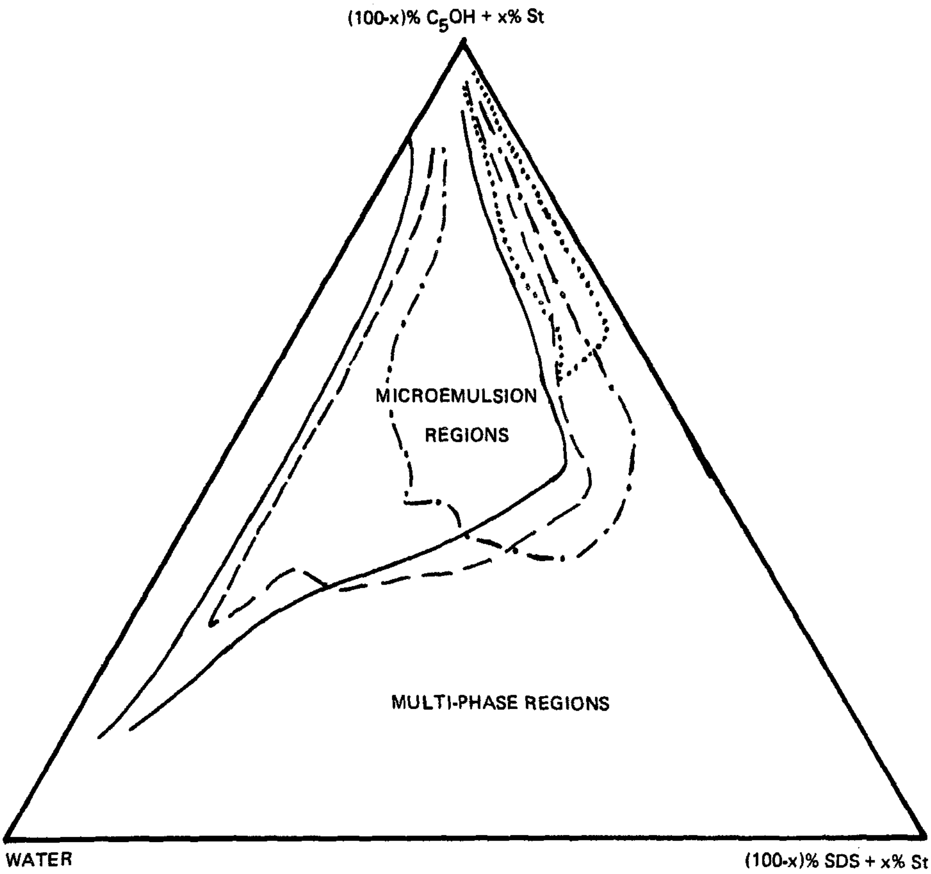

FIG. 1. Styrene (St)/distilled water W/O microemulsion areas stabilized by sodium dodecyl sulfate (SDS) and pentanol (C_5OH). Instructions to read compositions in the diagram are in the text. x = 0 (—), 25 (- -), 50 (– •), 75 (•••).

surfactant/water/cosurfactant complex as benzene [25] by replacing some of the cosurfactant molecules from the complex.

Solubility of Polystyrene

The solubility parameters have been found to be useful guides in the selection of solvents for polymers [46-48]. The total solubility parameter (δ_0) has been related to the components of dispersion force (δ_d), polar force (δ_p), and hydrogen bonding (δ_h) in the form of

TABLE 1. The Solubility Parameters $(\text{cal/cm}^3)^{1/2}$

Compounds	δ_0	δ_d	δ_p	δ_h
Butyl cellosolve	9.5			
	10.25	7.76	3.1	5.9
Pentanol	10.61	7.81	2.2	6.8
Styrene	9.30	9.07	0.5	2.0
Polystyrene	8.6-9.7			

$\delta_0^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$ [45]. In general, a good solvent for a given polymer has a solubility parameter value close to that of the polymer. The solubility parameters for styrene, polystyrene, and the alcohols used are listed in Table 1 from two sources for reference [47, 48].

Styrene itself is a very good solvent for polystyrene. It was found that 100 g styrene could dissolve up to 310 g polystyrene of 22,000 molecular weight. On the other hand, pentanol was a very poor solvent for polystyrene, with the solubility limited to small fractions of a percent, while butyl cellosolve dissolved only about 1 g polystyrene at 50° C.

When alcohol was mixed with styrene in different weight ratios, the solubility of polystyrene was markedly enhanced, as depicted in Fig. 2. However, a significant solubility of polystyrene could only be observed when the styrene content had reached to 50 and 20% in the respective pentanol and butyl cellosolve systems. Beyond that, the solubility curves for polystyrene increased rapidly and quite linearly with an increase of styrene content. Since this solubility has an important bearing on the results of the polymerization studies, two examples will be given in order to illustrate the importance of the difference between the two curves.

If a line, LM, is drawn at 45% alcohol, the initial 55% styrene will be linearly replaced by polystyrene along that line. The limiting solubility of polystyrene will occur at the respective intercepts of a and b. At Intercept a, phase separation will be encountered when 7% polystyrene is present among 48% styrene and 45% pentanol. This is equivalent to 12% styrene being polymerized in a system containing 55% styrene and 45% pentanol. Similarly, a maximum of 59% styrene conversion is compatible with the compositions at Intercept b of the butyl cellosolve system.

For a line with an initial 75% styrene and 25% alcohol, along NP, the maximum conversion of polystyrene in the pentanol system will show a pronounced increase from 12 to 46.7%, corresponding to Intercept c. The maximum conversion of polystyrene in the butyl cellosolve system, on the other hand, is only moderately increased

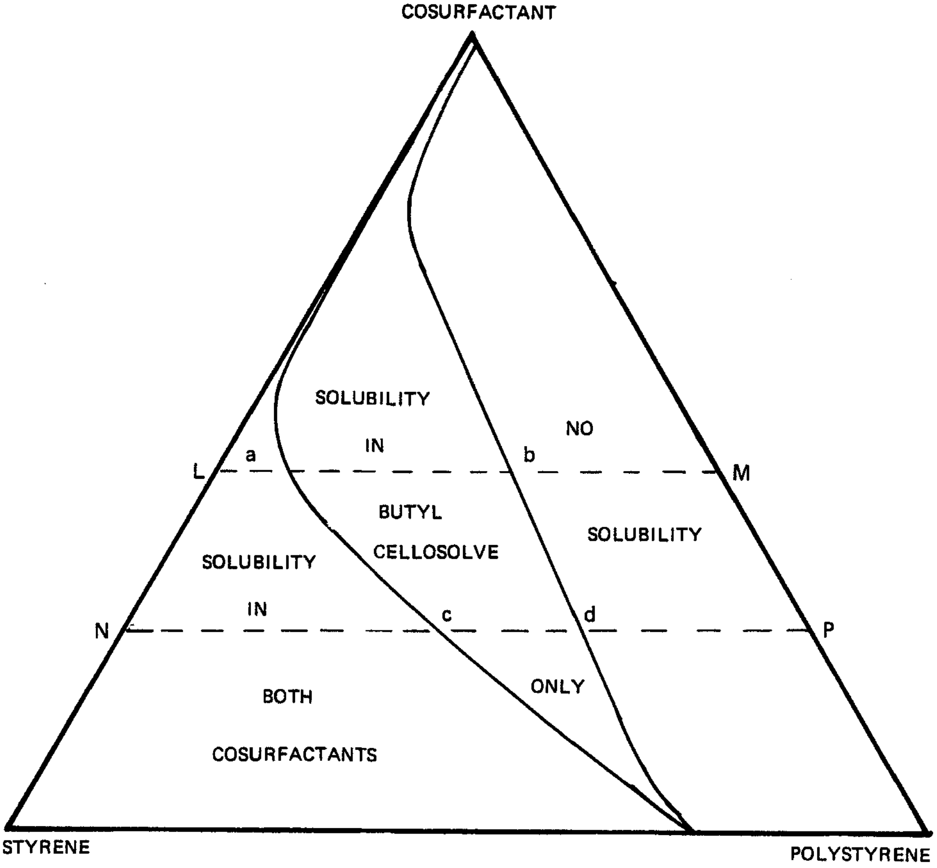

FIG. 2. Replacing pentanol with butyl cellosolve as a cosurfactant gives improved solubility of polystyrene ($\overline{M}_w$ = 22,000).

from 59 to 66.6% at Intercept d. This information will be used in the polymerization study (vide infra).

As W/O microemulsions with high water content were unstable with polystyrene, the investigation was extended to the water-poor region. This region may consist of ion pairs of the surfactant molecules in the organic medium [25]. Figure 3 shows the solubility regions with and without 10% polystyrene in the media containing 75% styrene, aqueous SDS, and either pentanol or butyl cellosolve. As can be seen from Fig. 3, the water content in the solubility regions was reduced to less than half in the presence of 10% polystyrene.

The minimum amount of water required was about the same for

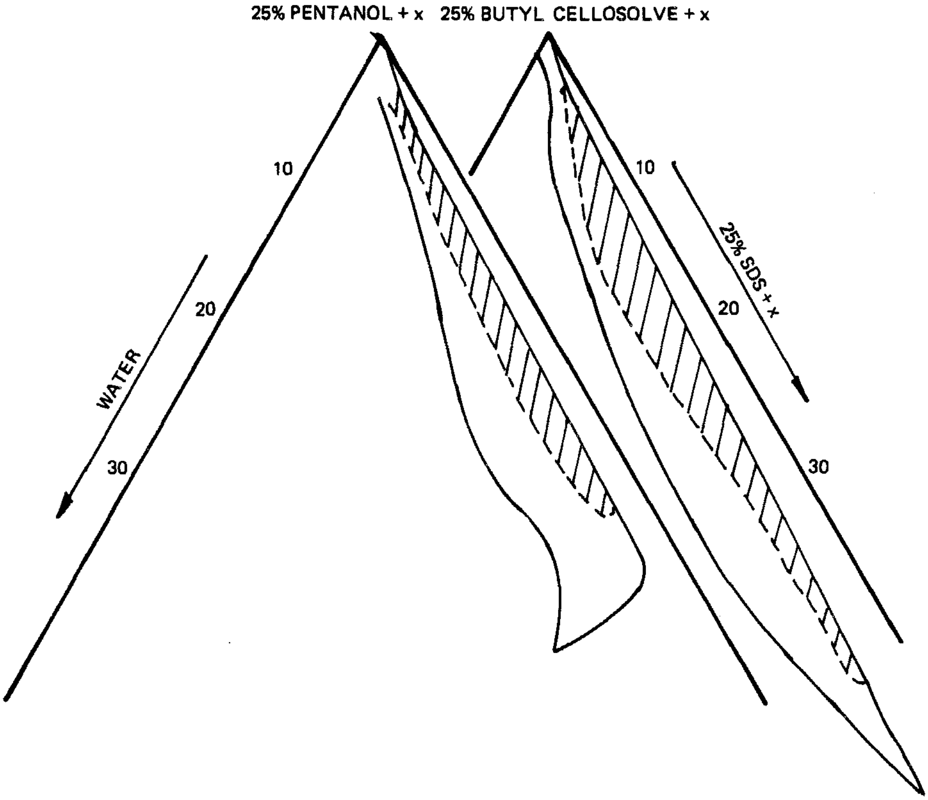

FIG. 3. Solubility areas for styrene and its polystyrene solution. x = 75% styrene (—) and 67.5% styrene + 7.5% polystyrene (cross-hatched areas).

all samples at a given concentration of SDS. It was calculated that about five molecules of water were needed for each molecule of SDS, irrespective of the presence of different alcohols and polystyrene. Furthermore, a similar molecular ratio of water/SDS prevailed along the minimum water boundary as the amount of SDS was increased.

The maximum solubility of polystyrene was determined along this minimum water boundary, OP, as shown in Fig. 4. The absissa, OP, denotes the compositions of this boundary, which are represented by the triangle phase diagram. The maximum solubility of polystyrene is expressed in terms of total styrene units. It is equivalent to % conversion in a polymerization system.

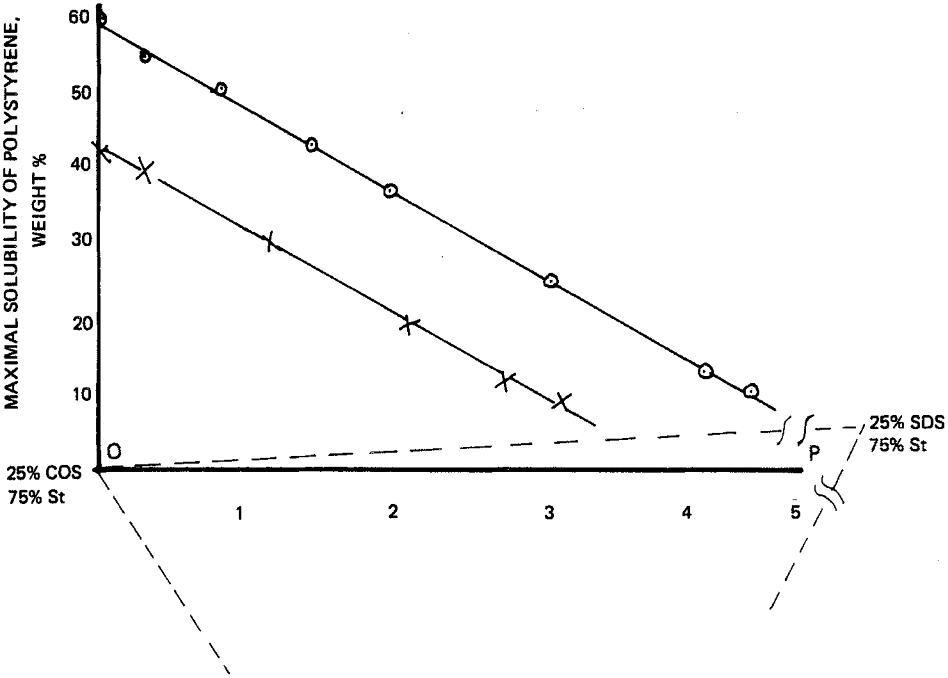

FIG. 4. The presence of water and ionic surfactant caused a reduction of the solubility of the polymer.

	Notation					
	0	1	2	3	4	5
H_2O	0.5	1	1.5	2	2.5	3
SDS	0	2.4	4.8	7.3	9.7	12.1
C_5OH	24.9	22.3	19.8	17.2	14.7	12.1
St	74.6	74.2	73.9	73.5	73.2	72.8

With the addition of 0.5% water to 74.6% styrene and 24.9% alcohol, the maximum solubility of polystyrene was reduced from 46.7 to 41% in pentanol system and from 66.6 to 58% in butyl cellosolve system. This clearly demonstrates the effect of water on the solubility of polystyrene in the styrene-alcohol mixture.

The combining effect of water and SDS caused the maximum solubility of polystyrene to diminish more rapidly along the minimum water boundary, OP, of Fig. 4. The weight ratio of water/SDS along this boundary was fairly constant at about 1/3, which is equivalent to about 5 on a molecular basis. Polystyrene was more soluble in a butyl cellosolve system than in the alcohol system; this fact is reflected in the higher solubility in the butyl cellosolve system with no water and surfactant present. The reduction of solubility with increased water/surfactant content (OP) was approximately similar for the two systems. From the slope, the average diminishing rate of polystyrene solubility was about 15% for each increment of 1% water and 3% SDS. A comparison with the values for pure water shows the influence by the SDS per se to be insignificant. This generalization also included the effect, due to small change in styrene-alcohol compositions. Table 2 summarizes the effect of water, SDS, and the composition change on the maximum solubility of polystyrene.

Polymerization of Styrene

Early phase separation was encountered for polymerizing styrene in the W/O microemulsion region with large amounts of water. Hence, polymerizations were carried out at low water media according to the compositions listed in Table 3. Some of these compositions were similar to those used in the solubility study, as already shown in Table 2.

The maximum conversion of styrene to polystyrene before phase separation was obtained at the onset of turbidity. It is obvious by comparing Tables 2 and 3 that the maximum conversions of styrene were only marginally lower than those predicted by the solubility study. The minor discrepancy could well be due to their differences in molecular weights and molecular weight distributions. As will be shown later, the prepared polystyrenes indeed had higher molecular weights than the one used for the solubility study.

The rates of styrene polymerization were very similar for both alcohol systems and they are represented by one solid curve in Fig. 5. The maximum conversions of styrene for these compositions as numbered in Table 3 are also shown. The average rate of polymerization was about 1.5% conversion per hour during the first 15 h of reaction. Thereafter, as expected, it began to slow down.

Table 4 shows the molecular weights of polystyrene prepared from different compositions and at different conversions. The peak molecular distribution, $\overline{M}_w/\overline{M}_n$, seemed to vary with the percent conversion. At 10% conversion, $\overline{M}_w/\overline{M}_n$ was about 1.5. It increased to about 2 at about 30% conversion.

TABLE 2. The Effect of Water and Surfactant on the Maximum Solubility of Polystyrene at 50°C

	Pentanol					Butyl cellosolve				
Compositions	1	2	3	4	5	6	7	8	9	10
H_2O (%)	0	0.5	0.5	1	2	0	0.5	0.5	1	2
SDS (%)	0	0	1.5	3	6	0	0	1.5	3	6
Alcohol	25	24.9	23.4	22	19	25	24.9	23.4	22	19
Styrene (%)	40	44	48.6	53.2	64.2	25	31.3	37.3	42	52.5
Polystyrene (%)	35	30.6	26	20.8	8.8	50	43.3	37.5	32	20.5
Maximum solubility of polystyrene[a] (%)	46.7	41	34.9	28.1	11.9	66.6	58	50	43.2	28.1

[a] Maximum solubility of polystyrene = (PS/[PS + S]) × 100.

TABLE 3. Styrene Polymerization in the Low Water-Alcohol-Ionic Surfactant Medium[a]

	Pentanol			Butyl cellosolve	
Compositions	1	2	3	4	5
H_2O (%)	0.5	1.0	1.5	0.5	1.0
SDS	0	3.0	4.5	0	3.0
Alcohol (%)	24.9	22	20.5	24.9	22
Styrene (%)	74.6	74	73.5	74.6	74
Time for maximum conversion (h)	31	18	13	47	30
Maximum conversion of styrene before phase separation (%)	39.5	25.3	18.5	56	40.7

[a] Initiator: AIBN at 0.37% of the total polymerizing mixture or at 0.5% of styrene content. Polymerization temperature: 50°C.

It is well known that radical transfer reactions may occur to monomer, polymer, solvent, and even initiator. The reported values of the transfer constants at 50°C [49] for monomer styrene, polystyrene, and AIBN are $C_m = 0.4 \times 10^{-4}$, $C_p = 2\text{-}14 \times 10^{-4}$ and $C_I = 0$, respectively. No information is available for polystyrene radical transferred to pentanol or butyl cellosolve, but it seems that they have similar transfer constants if one compares $\overline{M}_w/\overline{M}_n$ for Samples 2 and 5 at about 17% conversion (Table 4). Consequently, one is inclined to believe that the significant transfer reactions to polystyrene could be responsible for broadening the molecular weight distribution at higher conversions.

Composition Analysis at Incipient Phase Separation

Phase separation was inevitably encountered for all the polymerizations carried out in this study. It occurred at different percent conversion of styrene, depending on the type of cosurfactant and the amount of water used. Preliminary information on the instability of polymer solution was obtained by analyzing the composition distributions at incipient phase separation.

The recipe in Table 5 was used for polymerization up to 18.5%

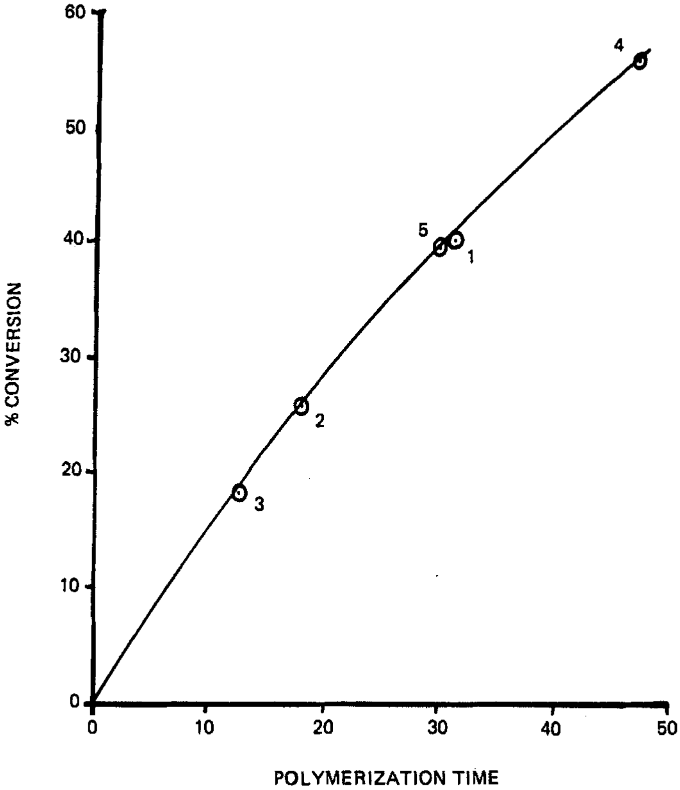

FIG. 5. Times for polymerization in low-water systems at 50°C. Numbers refer to compositions in Table 3.

conversion when the first appearance of turbidity was observed, at which stage oxygen was bubbled with the polymerizing mixture in order to stop further polymerization. It was then centrifuged for 30 min at 8000 rpm. The mixture was separated into three phases, namely, transparent top and middle fractions and a bottom fraction of opaque paste.

Table 5 shows the compositions distributed in these three fractions. The top and middle fractions constituted 27.8 and 69.7% of the total mixture, respectively. Polystyrene was concentrated in the middle fraction. The amount of water and SDS in this fraction was about four times lower than the change in the recipe. On the other hand, the top fraction contained only a trace of polystyrene but twice as much water and SDS as in the recipe. The 2.5% opaque paste consisted of a relatively high amount of polystyrene, water, and SDS.

TABLE 4. Molecular Weights of Polystyrene

System (cosurfactant)	No.[a]	Reaction time (h)	Conversion (%)	Peak MW	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
Pentanol	1	10	14.5	104,200	82,600	119,600	1.45
		20	28.3	109,600	80,000	123,400	1.54
Pentanol	2	11	16.6	90,200	59,200	95,300	1.61
		18	25.3	105,400	62,200	116,100	1.87
Pentanol	3	8	11.2	94,400	68,000	97,800	1.44
		13	18.5	101,200	57,600	180,800	1.89
Butyl cellosolve	4	16	24.3	95,500	61,300	94,700	1.55
		47	56.0	106,900	67,700	155,100	2.29
Butyl cellosolve	5	12	17.8	97,900	65,800	102,500	1.56
		30	40.7	109,600	62,100	120,900	1.95

[a] The sample numbers are identical to those in Table 3.

TABLE 5. Composition of Polymer Mixtures at Incipient Phase Separation

Compositions	Recipe[a]	Top fraction (clear solution) 27.8%	Central fraction (clear solution) 69.7%	Bottom fraction (opaque paste) 2.5%
Water (%)	1.5	3.3	0.3	14.2
SDS (%)	4.5	12.5	1.2	11.8
Pentanol (%)	20.5	83.6	72.7	58.2
Styrene (%)	73.5	83.6	72.7	58.2
Polystyrene (%)	0	0.6	25.8	15.8

[a] AIBN = 0.37% total polymerizing mixture. Polymerization at 50°C was stopped at 18.5% conversion on the onset of turbidity.

If the oxygen-bubbled mixture was left on standing instead of on centrifugation, a top clear fraction slowly separated from the bottom turbid fraction. The bottom fraction was emulsionlike and water droplets could clearly be seen. When this lower phase was subjected to centrifugation, three fractions were again obtained. However, the transparent fractions were unstable, the middle fraction slowly becoming turbid from the boundary.

DISCUSSION

The results give some information on the behavior of the styrene/polystyrene couple in W/O microemulsion systems stabilized by an ionic surfactant/alcohol cosurfactant combination.

The styrene monomer microemulsions are similar to the conventional W/O microemulsions containing aromatic hydrocarbons [23]. The reduction in maximum water content is moderate for hydrocarbon contents less than 50%, being rapidly accentuated for higher contents. These results may be explained by the equilibria of pentanol molecules as monomers, as dimers, and at the site of the inverse micelles [25].

The polymer, on the other hand, was clearly incompatible with W/O microemulsions. This fact has earlier been observed [28]; it is appropriate to emphasize this incompatibility not to be solely related with the entropy part of the free energy of the polymer. The presence of the styrene dimer also gave a considerable reduction of the water solubilization in W/O microemulsions [29]. The results confirm the suggestion that the results from solubility determinations of the polymer [29] and the stability of a microemulsion during polymerization in situ are directly related.

The present results show that the presence of the polymer also influences the stability not only of the microemulsion but also in the part of the system in which presumably no microemulsion droplets are present; light-scattering and electron microscopy analysis [25] have given no evidence of colloidal size particles in the water-poor part of the system. Since the stability is changed, it appears reasonable to conclude that the polymer also has an influence on the premicellar aggregates. The mechanism for this effect is not the same as the one from the oligomers. These [50] obviously cause the formation of W/O microdroplets at lower water concentrations; in the presence of polymers, on the other hand, no change of aggregate size seems to be indicated.

In the water-poor area a pronounced reduction of the maximum water solubility was observed when 10% of the original 75% styrene was replaced by polystyrene, corresponding to 13% conversion. The reduction of water solubility was similar for pentanol and butyl cellosolve, in spite of the fact that the latter was superior to pentanol as a solvent for the polystyrene.

The water-poor part of the system confirmed the implication of using the water-poor part of a microemulsion as a vehicle to bring polar amphiphiles into a solid polymer. This is possible since the incipient feature of microemulsion systems is the fact that a minimum water/surfactant ratio enables the dissolution of an ionic surfactant in a hydrocarbon. Figure 4 shows a maximum of 12.5% of SDS dissolved in 73.5% styrene plus 12.5% butyl cellosolve with the aid of 2.5% water. Without water the solubility of anionic surfactant is less than 1%. Polymerization led to reduced amounts, in spite of the fact that the solubility parameters are similar for styrene and polystyrene. A conversion of 67% of the styrene gave a product allowing about 2% of the ionic surfactant.

However, this solubility is significant; it is possible to dissolve ionic substances into polystyrene in this manner with limited efficiency. The results in Fig. 5 directly give the rule for the success of such a solubility effort. A cosurfactant with optimum solubility for the polymer should be found since the effect of water to reduce the solubility of the polymer was independent of the initial solubility capacity of the cosurfactant.

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