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Emulsion Polymerization

Emulsion Polymerization: Some Nonionic Emulsifier Effects

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Summary

The colloidal properties of aqueous solutions of surface active materials have been found to have profound effects on the properties of latexes produced via emulsion polymerization. It has been observed that depending on the polymerization temperature and the concentration of the ingredients it is possible to create either an oil-in-water or a water-in-oil emulsion at the beginning of the reaction. This may, as the polymerization proceeds, undergo phase inversion and lead to two constant rate regions and a bimodally distributed particle size latex.

Introduction

It is only recently that nonionic surface active materials have gained importance commercially as the sole polymer colloids stabilizers. In the past they have been extensively used in emulsion polymerization in combination with ionic emulsifiers to stabilize latexes. As of now, a large number of the nonionic surfactants employed in polymerizations are chemically either polyoxyethylenated alkyl phenols or alcohols. There are advantages in the use of this type of materials alone in the polymerization system since their degree of surface activity can easily be adjusted by changing the length of the polyoxyethylene portion of the molecule, i.e. changing the hydrophile-lipophile ratio of the surfactant. Nonionic surface active materials are stable to pH changes of the medium, and are more compatible with most polymers than are the ionic surfactants. These materials can be employed for the preparation of either oil-in-water or water-in-oil type of emulsions.

There are a number of investigations reported in the literature on the mechanism and kinetics of polymerization carried out in the presence of a variety of nonionic surfactants. Without giving a complete review of the field, it is of interest to mention that, for example, Helin et al.[1] came to the conclusion that, with chloroprene and styrene-butadiene as monomers, the nonionic emulsifiers were unsatisfactory because of low polymerization rates and quite variable stabilizing qualities. Their attempts failed to correlate the so-called "solubility index" (which was a reflection of the surfactants water solubility) and the surfactants performance as a stabilizer in polymerization. They reported the existence of maxima in conversion rates in the copolymerization of styrene-butadiene at 50°C with alkyl phenoxy polyoxyethylene ethanol, but almost constant conversion rates at 5°C.

In the emulsion polymerization of styrene at 60°C with AIBN as the initiator and OS-20 (the reaction product of 20 moles of ethylene oxide with a mixture of higher aliphatic alcohols, usually octadecyl) as the surfactant Gritskova et al.[2] found that the average diameter of the latex particles formed was several times larger than the average diameter of particles with ionic emulsifiers. The rate of polymerization increased steadily both with the initiator and surfactant concentration over a considerable range, but remained almost constant beyond a certain critical concentration.

Similar studies by Dudukin et al.[3] with OP-10 (condensation products of 10-12 moles of ethylene oxide with a mixture of mono- and dialkylphenols with an alkyl residue containing 8-10 carbon atoms), Pluronic F-68 (product of oxyethylation of propylene oxide polymers), and Proxanol P-228 (similar to the Pluronics) as surfactants at 50°C resulted in average particle sizes again larger by one order of magnitude than the corresponding dimensions of particles obtained in ionic systems, did not depend on the initiator concentration, and decreased with an increasing ratio of the emulsifier to monomer. The molecular weights of the polymers decreased with increasing initial concentration of the initiator, and increased with increasing emulsifier concentration. Unfortunately their analyses were based on studies limited to below 30% conversion.

Vil'shanskaya and Yurzhenko[4] studied the emulsion polymerization of styrene in the presence of NPE-n (condensation product of n moles of ethylene oxide with nonylphenol) at 60°C They found that for n = 4 to 13, the average particle size and rate of polymerization did not depend upon the emulsifier concentration. While for n = 30, both the molecular weight and the rate of polymerization increased with increasing emulsifier concentration.

Experimental

Polymerizations were carried out in 4 oz. glass bottles and rotated end-over-end at 60 rpm using the following general basic recipe: 275.0g water, 100g styrene (or variable), 15.0g surfactant, tridecyloxypoly(ethyleneoxy)ethanol (Emulphogene BC-840), 0.94g $K_2S_2O_8$. Polymerization temperature 50°C or variable. Conversions were obtained gravimetrically. The particle size distributions of latexes were determined primarily by hydrodynamic chromatography (HDC) calibrated with the help of electron microscopy (EM).

Results and Discussion

In their emulsion polymerization studies at 50°C with styrene as the monomer and a nonionic emulsifier of the polyoxyethylene type (Emulphogene BC-840) as the latex stabilizer, Piirma and Chang[5] obtained some unusual results. First of all, the conversion-time plots showed two constant rate regions with a rate inflection of about 40% conversion. The final latexes had bimodally distributed particle sizes, and a study of the molecular weights of the polymers produced showed bimodality in the molecular weight distribution. A thorough study of the development of the properties of the latex with conversion revealed that in the first stages of the polymerization the particle number reached constancy very soon, and the size distribution was unimodal. At approximately 40% conversion a sudden increase in number of particles occurred, which in turn increased the rate of polymerization. These particles were smaller in size, and when separated from the larger ones, the polymer in them was higher in molecular weight. At this point no definite conclusion was reached as to what caused these phenomena to occur, until further studies have finally provided some sensible explanations.

The unusual chemical characteristic of nonionic surfactants of the polyoxyethylene type is their solubility in styrene as well as in water. This partitioning of the surface active material between the two phases creates some unusual circumstances. As the polymerization proceeds, the monomer to water ratio changes and thus liberation of some emulsifier occurs. This in itself could, however, not create a situation where all of a sudden nucleation of new particles takes place, since the liberation of surfactant has to be as slow as polymerization. Subsequently a study has been carried out[6] to determine how the change in styrene to water ratio affects polymerization. The conversion-time plot is shown in Figure 1, where the results again indicate two constant rate regions, which are quite pronounced at higher monomer concentrations, and diminish with decreasing styrene to monomer charge ratio. The hydrodynamic chromatography results (Figure 2) show bimodal particle size distributions for all but the 7.5g (i.e. styrene to water weight ratio 0.136) styrene charge, indicating that the bimodality is somehow connected with the concentration of the organic phase.

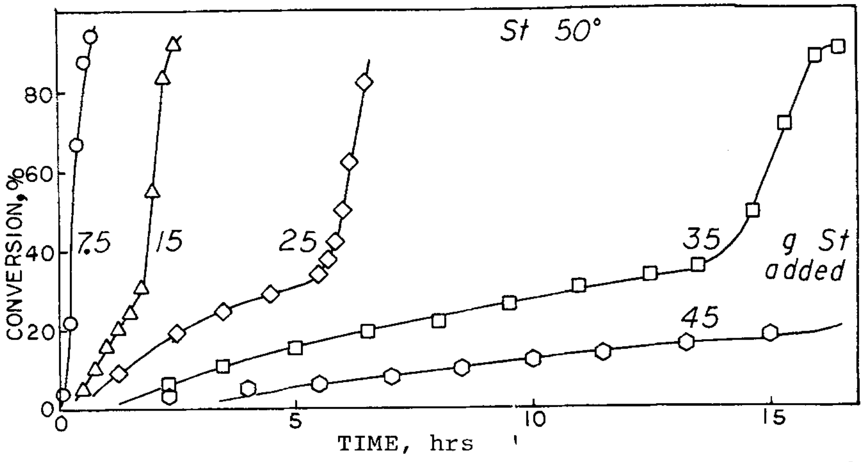

Figure 1. Polymerization of Styrene at 50°C. Water - 55.0g, Emulphogene BC-840 = 3.0g, Potassium Persulfate = 0.188g and Styrene: Variable

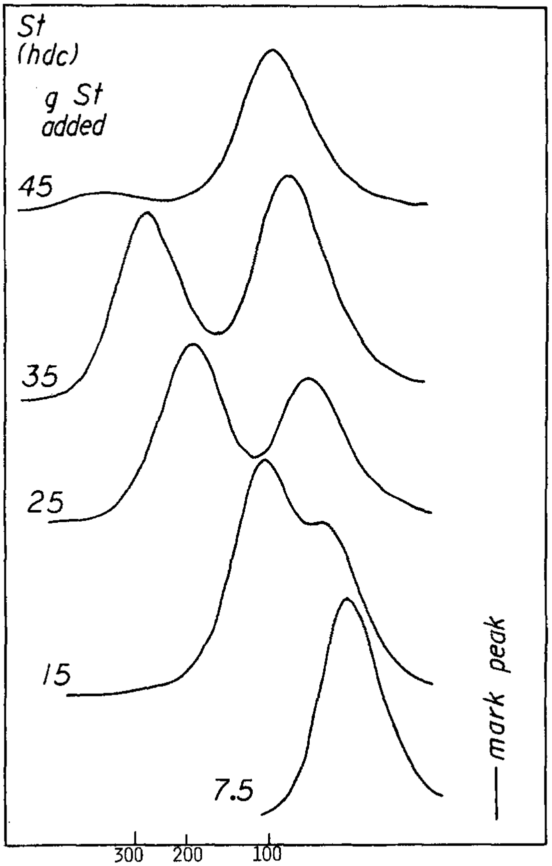

Figure 2. Hydrodynamic Chromatography Analyses of Polystyrene Latexes

The polymerization temperature is another variable which has a profound effect on the occurrence of the two rate regions (Figure 3) and brings about bimodality in the particle size distributions of the final latex as can be seen in Figure 4. At lower polymerization temperatures (from 30° to about 45°) the size distribution is unimodal, with broadening starting to occur at about 47.5° and a bimodal size distribution above that temperature.

It is well known that a system consisting of oil, water, and emulsifier will form an emulsion. In case the emulsifying agent is predominantly water soluble, an oil-in-water emulsion results, and the opposite is true with an oil soluble emulsifier, it will promote the formation of a water-in-oil emulsion. In case the emulsifier dissolves to a certain extent in both phases, what type of emulsion is formed depends on a number of factors. Variables such as the chemical structure of the surfactant as represented by the balance between the hydrophilic and the hydrophobic portions of the molecule (HLB) come into effect, the concentration of the surfactant in the system, and the partition of it between the water and the oil phases. The temperature at which the experiments are carried out is also of utmost importance.

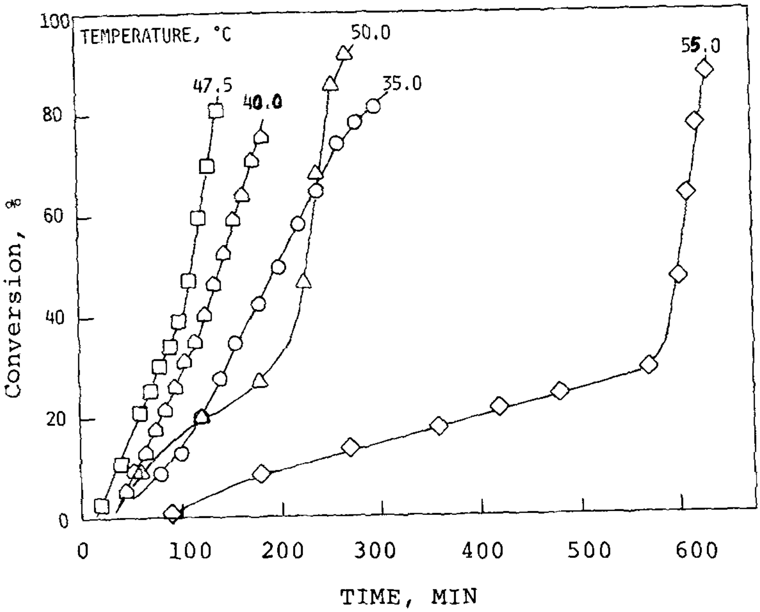

Figure 3. Polymerization of Styrene at Different Temperatures. Water: 55.0g, Styrene: 20.0g, Emulphogene BC-840 = 3.0g and Potassium Persulfate = 0.188g

Shinoda and coworkers[7] have carried out extensive studies on the temperature effect in the formation of types of emulsions in a system of cyclohexane, water, and nonionic emulsifier of the polyoxyethylene nonylphenylethers series. They observed the change of volume fractions of the water phase, cyclohexane phase and their emulsion phase at temperatures from 10 to 100°C. The at lower temperatures stable oil-in-water emulsion separated with increasing temperature into three phases. The temperature at which this occurred Shinoda called the phase inversion temperature (PIT). Above this temperature the emulsion is of the water-in-oil type. Shinoda and Kunieda[7] also studied, at constant temperature, how the polyoxyethylene chain length in the surfactant molecule affects the formation of the type of emulsion. They observed that the short oxyethylene chains (n = 4 to 6) favored the formation of a water-in-oil emulsion which at a specific chain length value gave way to the formation of an oil-in-water cream.

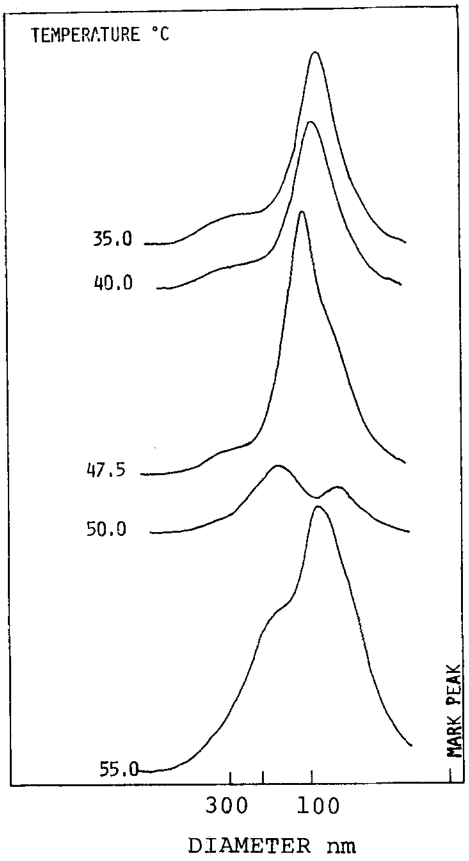

Figure 4. HDC Analyses of Polystyrene Latexes

Using styrene, water and the surfactant Emulphogene BC-840 we carried out experiments similar to Shinoda's and by plotting the different phase volumes against temperature arrived at a diagram as shown in Figure 5. As can be seen, the PIT of the system under study is at approximately 40°C, and since our polymerizations were carried out at 50°C, our starting emulsions most likely are of the water-in-oil type, or maybe even water-in-oil-in-water[8]. As the polymerization proceeds, the oil phase (styrene) is decreasing and the surfactant concentration in water is increasing which will finally lead to a phase inversion to oil-in-water emulsion. A combination of these events will create physical condictions for the nucleation of a large number of new particles which we observe in our polymerizations.

Shinoda and coworkers[7], as mentioned previously, also observed the formation of different types of emulsions with different chain lengths of oxyethylene chains in their surfactant molecules. Using a combination of commercial surfactants of the Emulphogene series, tridecyloxpoly(ethyleneoxy)-ethanol and the Igepal series, alkyl phenoxypoly(ethyleneoxy)-ethanol to create a variety of HLB numbers, polymerization of

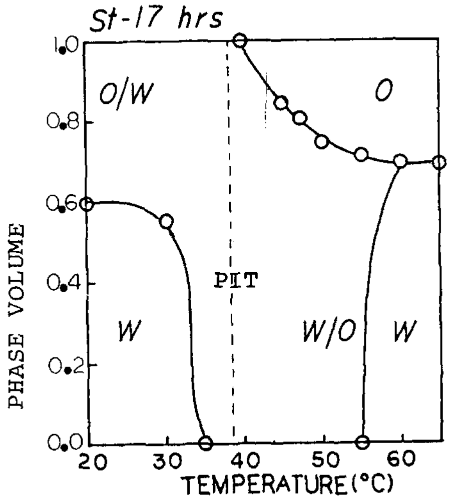

Figure 5. Phase Volume Diagram of Styrene-Emulphogene BC-840 Water System

styrene at 50° were carried out[9]. The electron microscopy studies of the final latexes indicated bimodal particle size distributions with surfactants with HLB numbers between 13 and 16 (Figure 6) indicating that one group of particles was formed during the first constant rate period, and another group of particles was nucleated at the start of the second constant rate.

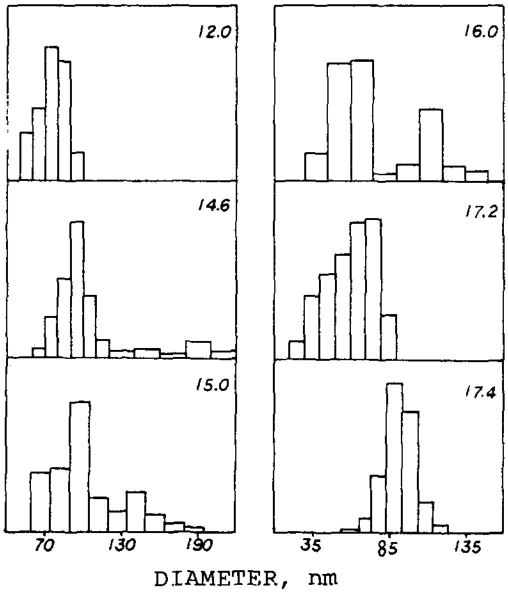

Figure 6. Histograms of Polystyrene Latex Particles Prepared at 50°C with Nonionic Surfactants of Different HLB Values

Conclusions

Based on our studies reported here, it is certain that the type of emulsion created at the start of the reaction plays an important role in emulsion polymerization. It determines or has an influence on the rate of polymerization, and the particle size distribution of the latex. The emulsion phase change during polymerization will create latexes with bimodal particle size distributions. Small changes in the reaction variables such as polymerization temperature, surfactant chemical structure, the solubility of the surfactant in water and styrene, and the charge ratios of all these materials will create tremendous changes in the outcome of the reaction and the final product.

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