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SHORT COMMUNICATION

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Kinetics of polymerization of styrene-in-water microemulsions

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Abstract The kinetics of polymerization of styrene-in-water microemulsions was investigated using dilatometry. From plots of percentage conversion versus time, the rate of polymerization, R_p, was determined. From log-log plots of R_p versus styrene and initiator [2,2′-azobis(isobutyronitrile), AIBN] concentrations the following relationship was established: $R_p \propto [\text{styrene}]^{1.2} [\text{AIBN}]^{0.46}$. These exponents are similar to those predicted by the theory of emulsion polymerization. The results also showed a rapid conversion in the initial period (interval 1) followed by a slower rate at longer times (interval 2). It was suggested that in interval 1, the main process in nucleation of the microemulsion droplets, whereas in interval 2 propagation is the more dominant factor. The rapid polymerization of microemulsions is consistent with their structure, whereby very small droplets with flexible interfaces are produced.

Key words Polymerization · Microlatex · Kinetics of polymerization

Introduction

In previous publications [1, 2], we have reported investigations of the polymerization of microemulsions that were prepared using nonionic surfactants. Polymerization was carried out using three different techniques, namely thermally, chemically and photochemically initiated polymerization. With thermally initiated polymerization, the microlatices produced were significantly larger than the droplets of the microemulsion precursor. This was particularly the case when the monomer content was higher than 1%. With chemically induced polymerization, the particle size was comparable to that of the microemulsion droplets. This was also the case with photochemically induced polymerization. An explanation of these results was given in terms of the possible changes that may occur as the reaction temperature is increased. With thermally induced polymerization, the reaction temperature was 60 °C when using potassium persulphate initiator (water soluble) and 50 °C when using 2,2′-azobis (isobutyronitrile) (AIBN) (oil-soluble initiator). With chemically induced initiation (using ascorbic acid and hydrogen peroxide), the reaction temperature was lower than 45 °C. The most convenient method of polymerization was the photochemically induced one, whereby the polymerization could be carried out at room temperature.

The microlatices produced were characterized using photon correlation spectroscopy and electron microscopy. The molecular weight of the polymers produced was determined using gel permeation chromatography. The results showed that by controlling the polymerization conditions, it was possible to obtain microlatex particles with nearly the same size as that of the microemulsion droplets. It has also been established that in some cases, the microlatex particle contained only one polymer molecule. Two different mechanisms were proposed to describe the polymerization process, depending on the conditions, monomer content and initiator concentration. At low monomer and initiator concentrations continuous polymerization took place within the microlatex particles by a diffusion process [2]. On the other hand, when the monomer concentration was high or the reaction temperature was close to the cloud-point temperature of the microemulsion, collision between the droplets took place during the polymerization and the resulting latex particles were significantly larger than those of the microemulsion droplets.

To understand the mechanism of polymerization and to study the effect of monomer and initiator content in a quantitative manner, we have carried out kinetics experiments using dilatometry. We should state that the results obtained are limited, since the technique was not straightforward. This paper will give preliminary results which we thought useful to report for further extensive investigations.

Experimental

Materials

The monomer (styrene), the nonionic surfactants (Synperonic NP4 and NP15, nonylphenol with 4 and 15 mol ethylene oxide respectively), the ionic surfactant (Aerosol OT, sodium dioctyl sulphosuccinate) and the initiator (AIBN) were the same materials as used before [2]. Water was doubly distilled in all-glass apparatus.

Yield of polymerization

This was obtained by measuring the free monomer remaining in the microlatex dispersion using gas chromatography.

Procedure for kinetics measurements

The kinetics of polymerization was followed by dilatometry. An all-quartz cylindrical vessel (13.85 cm^3), in which a water-jacketed UV lamp could be fitted was used. This was connected to a precision capillary of 1-mm diameter (1-m length). The microemulsion was directly introduced in the dilatometer using a syringe. The liquid was forced through the device until all air bubbles were removed. The vessel was then covered with aluminium foil to protect the sample from any radiation and was left to stand for about half a hour until the level of the liquid in the capillary became constant. The liquid level was determined using a cathetometer. The polymerization kinetics was followed by recording the variation of the height of the liquid in the capillary as a function of time. Measurement were performed every 3–4 min during the first 20 min and then every 15 min for a duration of at least 2 h. The temperature at the dilatometer wall was monitored using a thermocouple with an accuracy of ±0.1 °C.

Unfortunately, the temperature initially increased after the polymerization started and this increase continued for the first half hour. The circulating water in the jacket surrounding the UV lamp was not efficient enough to remove the heating effect. As a result, it was necessary to carry out calibration experiments to account for the thermal expansion caused by this heating effect. For this purpose, microemulsions containing 1, 3 and 5% styrene were prepared without the initiator and were placed in the dilatometer. The UV lamp was inserted and the volume increase was recorded as a function of the increase in temperature. Straight lines were obtained for plots of the percentage volume increase versus temperature. The change in volume due to the heating effect was then calculated from the slope of these lines. The volume change during polymerization was then corrected by subtracting the change in height due to the heating effect from the apparent height. The results for the polymerization kinetics were expressed as a percentage conversion of the monomer to the polymer.

Results and discussion

The variation of the percentage conversion with time for microemulsions containing the same AIBN concentration (10^{-2} M) and various amounts of styrene (1, 3 and 5%) is shown in Fig. 1. All the results show the same trend, namely an initial, rapid increase in the conversion rate in the first 40 min or so, followed by a slower rate of conversion. A conversion of the order of 80–90% was obtained after 2 h, indicating that the polymerization process is fairly rapid. The initial rate of polymerization, R_p, was obtained form the slope of the fast rising portion of the curve. Log-log plots of R_p versus styrene concentration were linear (Fig. 2) and linear regression gave the following relationship,

$$R_p \propto [\text{Styrene}]^{1.2} \ . \qquad (1)$$

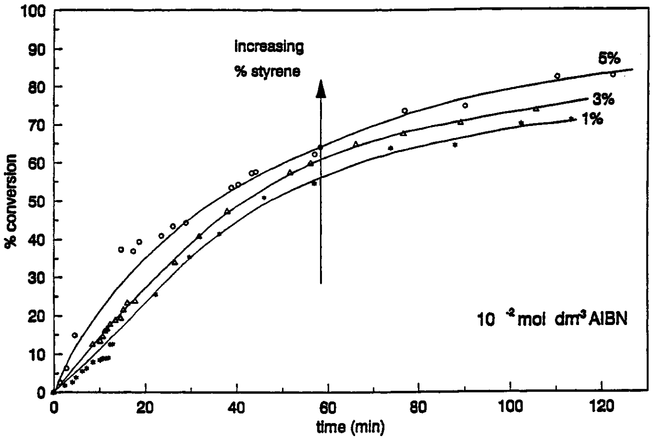


Fig. 1 Influence of styrene content on the percentage of conversion as a function of time with a constant concentration of 2,2′-azobis (isobutyronitrile) (*ABIM*)

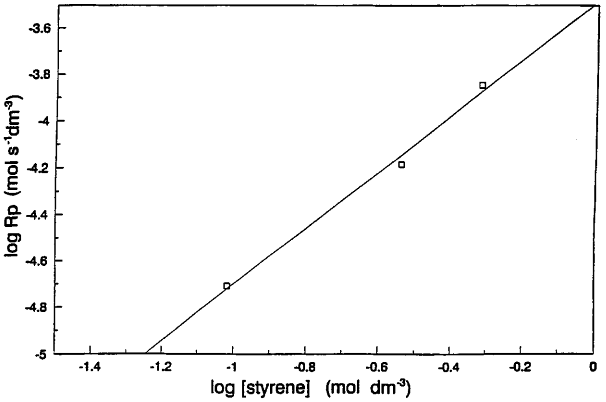


Fig. 2 Dependence of the rate of polymerization on the styrene concentration

The power dependence on styrene concentration is close to unity as normally observed with emulsion polymerization [3]. It should be noted, however, that the line in Fig. 2 contains only three points and more-detailed experiments are required to verify the above conclusions.

Figure 3 shows the variation of the percentage conversion with time for microemulsions containing constant styrene content (1%) but with various AIBN concentrations. Using the same analysis as described before, log-log plots of R_p versus AIBN concentration were obtained (Fig. 4) and the following relationship was established,

$$R_p \propto [\mathrm{AIBN}]^{0.46} \ . \tag{2}$$

This relationship is in agreement with the prediction of Smith–Ewart theory [4] for emulsion polymerization.

The results of analysis of the remaining monomer in the microlatex gave values less than 1%, indicating that the polymerization process is virtually complete on the time scale of the reaction (4 h). These results clearly demonstrate that microemulsions provide a suitable method for producing microlatices. The reaction is fairly fast and by control of the conditions latices with sizes approaching those of the microemulsion droplets can be produced [2]. This is understood if one considers the structure of microemulsions. These consist of very small droplets which once initiated prevent any further capture of free-radical molecules. Thus, in this case the polymerization is continuous within the droplet and this explain why in many cases a single polymer molecule is formed after polymerization. Evidence for this was obtained from molecular weight determination (using gel permeation chromatography) as discussed previously [2]. The determination of the free monomer concentration in the latex resulted in a value lower than 1%. This means that the entire volume of the latex particles is occupied by the polymer molecules. In this case it is possible to calculate the average number of molecules, n, per particle from the average radius, r,

$$n = \frac{4\pi r^3 \rho_{\mathrm{PS}} N_{\mathrm{A}}}{3M_{\mathrm{w}}} \ , \tag{3}$$

where ρ_{PS} is the density of polystyrene which was taken to be 1.05 and N_{A} is Avogadro's constant.

The results of the UV polymerized styrene with AIBN initiator showed an average value of n between 1.6 and 11.6. This means that in some cases 1–2

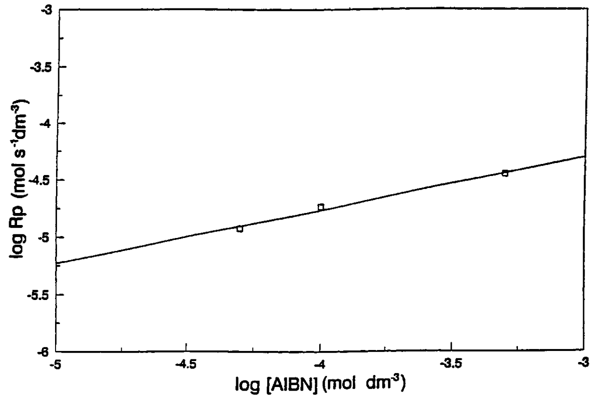
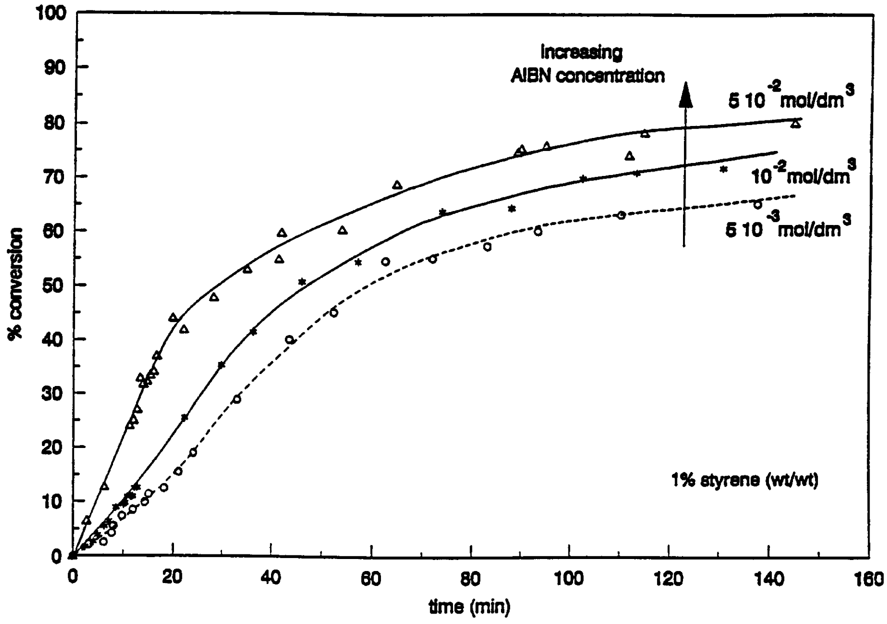


Fig. 4 Dependence of the rate of polymerization on AIBN concentration

Fig. 3 Influence of AIBN content on the percentage conversion as a function of time



molecules per particle are produced. Since the average radius was taken to be the hydrodynamic radius, which is greater than the core radius, it is likely that in some cases there will be only one polymer molecule per particle.

Careful consideration of the percentage conversion versus time curves points towards a two-step polymerization process. In the initial interval nucleation of the monomer droplets is predominant. After this interval, the most dominant process will be propagation of the polymerization, which occurs at a much slower rate than the initial nucleation process. Further studies are required to throw more light on the mechanism of polymerization in microemulsions.

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