

# Emulsion polymerization of styrene in a continuous stirred reactor

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The emulsion polymerization of styrene has been carried out in a continuous stirred reactor at 50°C. Polymerization rates were initially very high but declined subsequently. These rates did not always attain a steady value, but sometimes oscillated with time. Size analysis of the polymer particles showed that particle nucleation almost stopped soon after start-up. A new generation of particles appeared later in the process. The average number of radicals per particle was usually, but not always, >0.5. The time-average polymerization rate was only weakly dependent on the initiator concentration but varied with the first power of the emulsifier concentration.

## INTRODUCTION

Many commercial emulsion polymerization processes are carried out in batch reactors. By using a batch reactor it is possible to accommodate the time sequence of the physical and chemical events which usually occur in these processes, i.e. particle nucleation, polymerization reactions and particle growth.

As the annual output of polymeric materials increases more attention is given to the use of continuous reactors. However, the use of continuous stirred reactors for heterogeneous processes presents conceptual problems which do not arise with batch reactors. The dispersed particles in a continuous stirred reactor are subject to distributions in age, size and composition<sup>1</sup>. This is not the case in a batch reactor where particle nucleation is complete in the early stages of the process. Although continuous emulsion polymerization is used industrially, very little published information is available at present. That work which has been published reveals the nature of the difficulties which must still be overcome<sup>2</sup>.

In the present work the emulsion polymerization of styrene has been carried out in a continuous well-mixed reactor. The rate of polymerization and the size distribution of polymer particles have been studied as functions of reactant concentrations. In some circumstances the polymerization rate did not reach a steady value but oscillated with time.

## EXPERIMENTAL

### Materials

Styrene was freed from inhibitor by washing with aqueous sodium hydroxide. Ammonium persulphate (BDH) was

used as a radical initiator. Sodium lauryl sulphate (Albright and Wilson) was used as an emulsifier.

### Apparatus

The reactor was a cylindrical stainless steel jacketed vessel (maximum capacity  $3 \times 10^{-3} \text{ m}^3$ ) equipped with a mechanical agitator. The reactor contents were maintained at  $50^\circ \pm 0.1^\circ \text{C}$  by passing water through the jacket. The temperature of this water was regulated by an automatic control valve which caused hot and cold water supplies to be mixed in the correct proportions. Liquid reactants were fed to the reactor from reciprocating metering pumps (connected with high density polyethylene tubes). The emulsified product left the reactor via a vertical overflow pipe which passed through the base of the reactor. The effective capacity of the reactor was determined by the height of the pipe above the reactor base. Experiments with an electrolyte tracer showed that the reactor behaved as a 'well-mixed vessel' under normal operating conditions.

### Polymerization procedure

A batch of styrene was pre-emulsified in an aqueous solution of sodium lauryl sulphate (pH maintained between 9 and 11 with sodium hydroxide). This emulsion was fed to the reactor by a metering pump. A second pump was used to supply an aqueous solution of ammonium persulphate. The supply vessel which contained the emulsified styrene was stirred throughout the period of the experiment. A nitrogen atmosphere was maintained throughout the reaction system. The 'start-up' procedure was as follows. The reactor was filled to its operating capacity with an emulsion which contained no initiator; all other ingredients were present in the desired quantities. The reactor was then heated until the temperature of its contents reached 50°C. When the temperature of the reactor was steady, the pumps were started. This was regarded as the starting time of the polymerization process.

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## Analytical procedure

Samples of the reactor effluent were analysed periodically. The polymer content was determined gravimetrically after precipitation in methanol. Size analysis of the polymer particles was achieved by using an electron microscope. Latex samples were diluted with excess water and sprayed on to carbon supports. Size distributions were obtained from enlarged photographs of the particles. Hand counting was necessary because automatic methods were unsatisfactory when the particles were small and overlapping. Intrinsic viscosities of the polymers were measured in benzene at 25°C.

## RESULTS

Soon after start-up the conversion of polystyrene reached a relatively high value. The polymerization rate declined subsequently and in some experiments a steady rate was then observed. In other experiments the polymerization rate oscillated with time. These oscillations usually but not always, decayed to produce a steady state. The time required for this decay was usually about 8 times the mean space-time for the reactor contents. Figure 1 shows typical plots of conversion against time. Table 1 shows the conditions used in the experiments and the conversions obtained. In most cases the mean space-time was 30 min and the reactor volume 1.5 l. For a space-time of 60 min

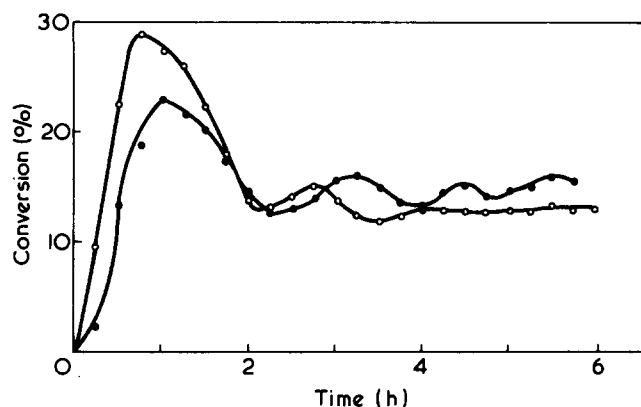


Figure 1 Conversion (% polymer) as a function of time: ● Experiment 3; ○ Experiment 13 (see Table 1)

the reactor volume was adjusted to 2.6 l. The reactor volume was measured when agitation was occurring. In all experiments the weight ratio of water to styrene was 2.87. Table 1 shows the amplitude of the oscillations immediately after the 'peak' conversion.

In order to obtain meaningful estimates of particle size distributions it was necessary to examine samples containing large numbers of particles (usually between 600 and 2000). In the early stages of the polymerization the particle sizes were small. However, just before the time when the initial 'peak' in conversion occurred, the very small particles usually disappeared and the average particle size increased. When the polymerization process had been running for a period of time equal to about 4–6 times the reactor space-time, small particles began to reappear. At this stage the frequency distribution of particle sizes became bimodal. Subsequently, some small particles were always present and the distribution lost its bimodal features. Figure 2 shows how the size distributions changed during a typical polymerization experiment. Table 2 shows average sizes of particles which were present in the later stages of the experiments and at the 'peak' conversions. The particle sizes which are recorded were those observed with the electron microscope: the particles would have been larger than this when they were in the reactor because they would then contain unreacted monomer.

## DISCUSSION

It can be seen that a steady value of the monomer conversion is not always obtained. Ley and Gerrens<sup>4</sup> also obtained oscillatory behaviour, but only at high conversions (in contrast to the present findings). These workers did not use the start-up procedure that was used in the present work. Their reactor was filled with a polymer latex before the pumps were started. Under these conditions no initial 'peak' in conversion was observed. Gershberg and Longfield<sup>5</sup> reported unsteady behaviour but in their work the initiator was premixed with the feed emulsion and higher temperatures were used.

The reasons for oscillations in conversion have been discussed by Brooks<sup>3</sup> who pointed out that the surfactant micelles will participate in two competing rate processes; the nucleation of new particles and dissolution into the

Table 1 Conversions in continuous emulsion polymerization at 50°C. Space-time 30 min

Run No.	Emulsifier concentration (mol/l × 10 <sup>2</sup> )	Initiator concentration (mol/l × 10 <sup>2</sup> )	Peak conversion (%)	Steady conversion (%)	Amplitude of oscillation (% conversion)	Frequency of oscillation (min)	Duration of oscillation (min)	Time of peak conversion (min)
1	3.07	7.87	27	14	2	75	330	45
2	3.07	2.55	23	13.5	2	75	330	60
3	3.07	2.55	23	14	3	90	330	60
4	2.30	5.11	29	12 <sup>b</sup>	4	90	c	45
5	2.30	5.11	29.5	12 <sup>b</sup>	3.5	75	330	45
6	3.07	4.20	23	12	—	—	—	45
7	3.07	0.93	9.5	7	1.5	105	300	90
8	0.75	5.0	11	6	—	—	—	60
9	5.0	4.0	38	29	—	—	—	45
10	6.0	10.0	50	45.5	1	90	c	45
11	6.0	5.0	—	42 <sup>b</sup>	—	—	—	—
12	2.30	2.50	17.5	11	3	90	250	60
13	2.30	7.5	29	13	1.5	90	180	45
14 <sup>a</sup>	2.85	7.59	74	35 <sup>b</sup>	10	90	—	120
15 <sup>a</sup>	2.70	7.20	72	31 <sup>b</sup>	—	—	—	120

<sup>a</sup>Space-time 60 min. <sup>b</sup>Average value. <sup>c</sup>Oscillation sustained

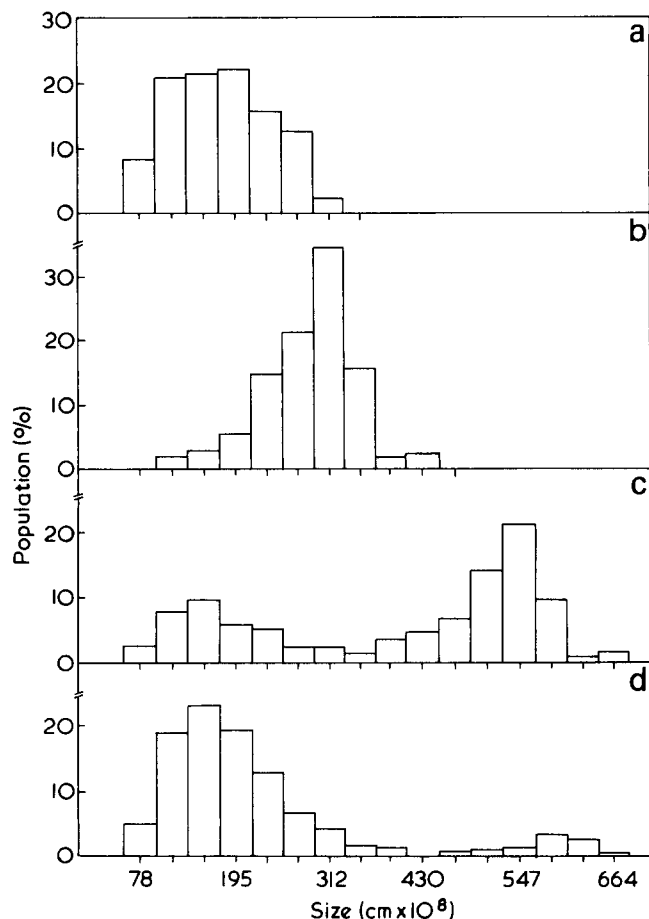


Figure 2 Particle size distribution from Experiment 12 (see Table 1): A, 30 min; B, 60 min; C, 120 min; D, 150 min

Table 2 Average particle radii, radical concentrations and molecular weights. Experiment numbers refer to Table 1

Run No.	Size at peak (Å)	Size immediately after peak (Å)	Final size (Å)	Final $\bar{n}$	Final $MW^a \times 10^{-5}$
1	389	296	313	0.61	—
3	280	193	287	0.64	14.6
5	370	—	—	—	2.57
8	—	—	251	0.26	8.77
9	306	266	339	0.77	—
10	290	—	265	0.44	9.55
12	284	217	—	—	5.70
13	365	315	350	1.08	4.05
14	590	400	500	4.0	—
15	600	—	—	—	—

<sup>a</sup>Viscosity-average

aqueous phase. In the present work the rate of particle nucleation will be very high in the early stages of the polymerization. If the rate at which the particles grow is much larger than the rate at which they leave the reactor, then the absorption surface available to the surfactant in the reactor will increase. Under these conditions the production rate of new particles would be expected to decrease. The results of the particle size analyses show this to be the case (see Figure 2). Soon after start-up a large number of small particles are present. These particles are then reduced in number but grow in size. The absence of very small particles just before the 'peak' conversion occurred showed that particle nucleation had almost ceased at this stage. The

reappearance of small particles after the 'peak' had passed showed that particle nucleation had started again. This explains why the average particle size immediately after the 'peak' (see Table 2) was lower than the average size at the 'peak'. Observation of the subsequent changes in particle size distribution indicated that nucleation rates were reduced again at later stages in the process. These latter reductions were not so distinct as the initial reduction.

Figure 3 shows that, when the initiator concentration is constant, the steady (or the eventual time-average) polymerization rate varies linearly with the emulsifier concentration. This is to be expected when the reactor is well mixed and the average number of radicals per polymer particle,  $\bar{n}$ , is constant. It has already been shown<sup>3</sup> that, under these conditions, the adoption of any reasonable model for the nucleation process usually predicts a linear relationship between emulsifier concentration and particle number,  $N$ . Therefore, if  $\bar{n}$  is constant, the polymerization rate will vary linearly with emulsifier concentration. This dependency would still be observed when changes in  $\bar{n}$  are small because the number of particles is expected to depend approximately on  $\bar{n}$  raised to the power  $-2/3$ , [see equations (40) and (42) of ref 3]. Therefore the polymerization rate would only vary with the  $1/3$  power of  $\bar{n}$ .

Gerrens and Kuchner<sup>16</sup> give equations which indicate that the polymerization rate should be almost independent of initiator concentration. De Graff and Poehlein<sup>7</sup> obtained evidence for this independence, although Gershberg and Longfield<sup>5</sup> found that the polymerization rate varied with the square root of the initiator concentration at high temperatures (when radical generation rates would be high). Reasons for this have been suggested<sup>3</sup>. It is clear that any approximations, which lead to the conclusion that the initiator concentration does not affect the polymerization rate must become invalid when initiator concentrations are very low. Figure 4 shows that, when the emulsifier concentration is 0.023 mol/l, the polymerization rate is weakly dependent on initiator concentration. This dependence is almost negligible at the higher emulsifier concentration, until the initiator concentration becomes low. The exact nature of these relationships is difficult to predict<sup>3</sup>.

Table 2 shows that  $\bar{n}$  in the 'steady state' is usually  $> 0.5$ , thus the idealized model of Smith and Ewart (Case II)<sup>8</sup> does not apply. However,  $\bar{n}$  is considerably less than

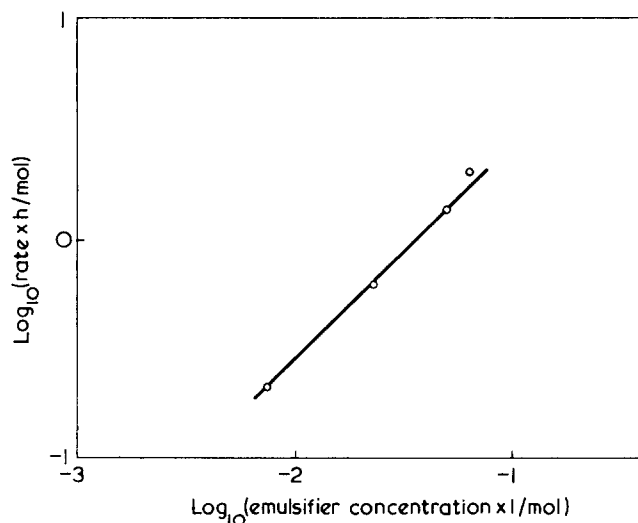


Figure 3 Polymerization rate as a function of emulsifier concentration (persulphate concentration  $5.1 \times 10^{-2}$  mol/l)

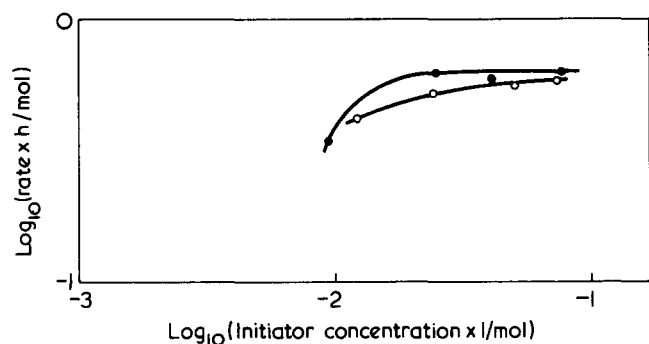


Figure 4 Polymerization rate as a function of initiator concentration. ○, Emulsifier concentration  $2.3 \times 10^{-2}$  mol/l; ●, emulsifier concentration  $3.07 \times 10^{-2}$  mol/l

the values found by Ley and Gerrens at high conversion<sup>4</sup>. The cases in which  $\bar{n} < 0.5$  indicate that radical desorption from the particles is probably taking place<sup>9</sup>. Preliminary work with gel permeation chromatography has indicated the ratio of the weight-average to number-average molecular weight is usually between 6 and 7. This may be an indication that the net transfer rates of radicals to the particles depends

on particle size<sup>3</sup> or that the number of radicals in a particle depends on its size.

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