A Novel Reactor for Continuous Emulsion Polymerisation

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Abstract.

It has been demonstrated earlier that a Pulsed Packed Column is a suitable reactor for continuous emulsion polymerisation of styrene. The emulsion polymerisation of vinyl acetate follows a different mechanism, which renders the process more liable to instabilities when carried out in a continuous flow reactor. It was demonstrated that emulsion polymerisation of vinyl acetate in a Pulsed Packed Column can be carried out in a stable manner, and with a sufficient reaction rate, provided the rate of backmixing is limited.

Introduction.

Two mechanisms of emulsion polymerisation have been described in the literature. Mechanism A applies for sparsely water soluble monomers like styrene, mechanism B applies for moderately soluble monomers like vinyl acetate. In both mechanisms the radical chain reaction starts with the decomposition of an initiator in the water phase. According to mechanism A the monomer and small oligomer radicals enter the micelles, so that a nucleus for further polymerisation is formed. This is called micellar nucleation (Smith and Ewart, 1948). The particle formation phase (interval 1) is followed by a period of constant reaction rate in which the particles grow (interval 2). When the monomer droplets have disappeared, the polymerisation proceeds with a decreasing rate because the monomer in the polymer particles is gradually converted (interval 3).

According to mechanism B oligomers grow in the water phase. After reaching the solubility limit, they precipitate and partially stabilized primary particles are formed. This is called homogeneous nucleation (Hansen and Ugelstad, 1978). The particles grow by absorbing and converting monomer, but also by coagulation. Two important effects distinguish mechanism B from mechanism A: chain transfer to monomer followed by radical desorption, which causes additional initiation in the water phase. In the last stage the polymerisation rate decreases.

Emulsion polymerisation is usually carried out in batch reactors, for various reasons: for approaching complete conversion, for limiting the molecular weight distribution, and for preparing different products in the same reactor. It was shown that emulsion polymerisation carried out in a continuous stirred tank reactor (CSTR) may result in much lower particle numbers (per unit volume) and a broader particle size distribution (DeGraff...
and Poehlein, 1971). In addition to this, continuous emulsion polymerisations following mechanism B may show sustained oscillations: the reaction rate and the particle number fluctuate strongly, with a time constant equal to several times the mean residence time. (Kiparissides et al., 1980, Rawlings and Ray, 1987, Penlidis et al., 1989).

It was demonstrated earlier that a Pulsed Packed Column Reactor (PPC) that combines good local agitation with limited backmixing, can be used successfully for continuous emulsion polymerisation of styrene. The particle numbers were the same as obtained in a batch process with the same recipe (Hoedemakers and Thoenes, 1990), provided the backmixing was limited. We have now demonstrated that a PPC can also be used for the continuous emulsion polymerisation of vinyl acetate (obeying mechanism B), and that oscillations can be suppressed sufficiently. In this paper comparative results are reported for a batch reactor, a CSTR and a PPC.

Theory.

In principle, the reaction rate for mechanisms A and B can be expressed by:

\[ R_p = \frac{k_p \overline{n} N C_M}{N_A^n} \]  \hspace{1cm} (1)

This equation shows that if the average number of radicals per particle \( \overline{n} \) is a constant, the reaction rate will be constant as long as the monomer concentration in the particle does not change, i.e. as long as there are separate monomer droplets present in the system. This applies for interval 2 in polymerisations following mechanism A. In the "ideal case" \( \overline{n} = 0.5 \).

In polymerisations obeying mechanism B there are no distinct intervals. Because radical desorption is rapid, small particles have a small chance of retaining radicals, so that \( \overline{n} \ll 0.5 \) (Chem and Poehlein 1987). As particles grow, this chance increases, so that \( \overline{n} \) increases with particle size. This would enhance the reaction rate, were it not that particles coagulate with a certain rate, resulting in a constantly decreasing particle number. It was found that these two effects compensate each other, and that the reaction rate is constant for a long period, as will be shown below.

We suggest the following explanation: It is assumed that chain transfer to monomer in the polymer phase is the rate determining step for radical desorption, which itself is relatively fast, and that bimolecular termination takes place predominantly in the water phase. If this is the case, the total number of radicals in the polymer phase is likely to be independent of the mean particle size and number, and consequently the reaction rate does not change with conversion, within certain limits.

On the basis of theories published by Ugelstad et al. (1967) we developed a kinetic relation for the period of constant reaction rate that does not contain the parameters \( \overline{n}, C \) and \( N \), that all vary with time. This relation predicts the following proportionality:

\[ R_p \sim C^0 B C_{1.5} \]  \hspace{1cm} (2)
which is confirmed by Nomura (1982) and Penlidis et al. (1985).

Experimental.

The chemicals used in this study were: distilled water, distilled commercially grade vinyl acetate, sodium dodecyl sulphate (emulsifier), sodium persulphate (initiator), sodium carbonate (pH-buffer) and sodium chloride (inert electrolyte), all laboratory grade. Unless stated otherwise, the following concentrations were used, all expressed as kmol per m$^3$ water: emulsifier 0.020, initiator 0.020, total sodium ions: 0.10. For batch reactions, the presence of carbonate ions was not essential, for continuous reactions the buffer appeared necessary for improved stability. In all experiments the initial monomer/water ratio was 0.4, the temperature 50 degrees C.

The batch reactor and the CSTR were both stainless steel tanks, equipped with an eight bladed Rushton turbine impeller and four baffles. The volume of the batch reactor and the CSTR were 1.2 and 2.4 dm$^3$, respectively. Unless mentioned otherwise, the impeller speeds were 500 rpm in both reactor types. Great care was taken to remove all traces of oxygen from the reaction mixture before starting the polymerisation.

During the polymerisation samples were taken for determining the conversion (by gravimetry) and the z-average particle size (using a Malvern autosizer IIc, based on dynamic light scattering).

Figure 1 shows a schematic view of the pilot installation with the PPC. The column (length 5.1 m, internal diameter 0.05 m) was packed with Raschig rings (diameter 0.01 m, bed porosity 0.73), equipped with a water jacket and six sample points. The pulsator was mounted at the bottom. The pulsation frequency ($f$) was varied between 0.87 and 3.5 s$^{-1}$, the stroke length ($s$) in the column was 0.014 m.

Results and discussion.

Batch emulsion polymerisation of vinyl acetate.

In figure 2 the results are given for a typical batch experiment. It appears that the particle number rises in the beginning and then decreases sharply, only to become constant when the conversion hardly increases further. This can only be explained by assuming coagulation. The decrease in particle number coincides with a linear increase in conversion, which indicates a constant reaction rate, for the interval $0.2 < X < 0.8$.

Figure 3 shows that at higher impeller speeds the particle numbers are lower during most of the polymerisation, only towards the end they approach the same value. This indicates that stirring promotes coagulation. At the end the electrostatic stabilisation may be sufficient to prevent further shear coagulation. The reaction rates for both
impeller speeds were not different during the conversion.

Figure 4 shows that higher electrolyte concentrations promote coagulation, while the reaction rate is only slightly affected.

These results show that there is hardly any direct relation between the particle number and the reaction rate.

The results collected in the figures 5 and 6 show that $R_p$ obeys equation (2).

Continuous emulsion polymerisation of vinyl acetate.

Sustained oscillations were found in the CSTR experiments, see figure 7, the time constant was about six times the mean residence time ($\bar{t}$). It is interesting to note that the maxima and minima in the particle number coincide with those of the degree of conversion.
Experimental results obtained in the PPC are reported here for $\tau = 30\ \text{min.}$ and $\tau = 90\ \text{min.}$ Figure 7 shows that the oscillations were suppressed, though some scatter in the particle number did occur. For $\tau = 30\ \text{min.}$ the influence of axial mixing was studied by varying the pulsation frequency. The results are collected in figure 8, together with those for $\tau = 90\ \text{min.}$ at the maximum pulsation frequency ($3.5\ \text{s}^{-1}$). Calculated values of the axial mixing coefficient $E$ are also shown.

Figure 8. Comparison of reactor types: conversions (fig. 8a), particle numbers (fig. 8b). ———: batch, $t = 30\ \text{min.}$; ———: batch, $t \geq 50\ \text{min.}$; ······: CSTR, $\tau = 30\ \text{min.}$; ■: PPC, $\tau = 30\ \text{min.}$, $s = 0.014\ \text{m}$, $f = 0.875\ \text{s}^{-1}$ ($E = 0.084 \times 10^{-3}\ \text{m}^3/\text{s}$), $f = 1.5\ \text{s}^{-1}$ ($E = 0.14 \times 10^{-3}\ \text{m}^3/\text{s}$), $f = 2.7\ \text{s}^{-1}$ ($E = 0.23 \times 10^{-3}\ \text{m}^3/\text{s}$), $f = 3.5\ \text{s}^{-1}$ ($E = 0.30 \times 10^{-3}\ \text{m}^3/\text{s}$); ▲: PPC, $\tau = 90\ \text{min.}$, $s = 0.014\ \text{m}$, $f = 3.5\ \text{s}^{-1}$ ($E = 0.30 \times 10^{-3}\ \text{m}^3/\text{s}$). Axial mixing coefficients calculated according to Hoedemakers (1990).

Apparently the limited axial mixing hardly influenced the degree of conversion and the reaction rate, but the particle number was clearly affected. We suggest the following explanation: as a result of the backmixing particle formation takes place in the presence of larger particles, that grow by coagulation with smaller ones. This results in a lower particle number and an increased reaction rate per particle. As it was shown in batch experiments that the particle number and size did not influence the reaction rate over a wide range of conversions, it was to be expected that residence time distribution, within limits, would not affect the reaction rate.
Conclusions.
- In the batchwise emulsion polymerisation of vinyl acetate the reaction rate remains constant during a large part of the process, despite a strong decrease in particle number during the same time.
- The reaction rate appeared to be proportional to the square root of the initiator concentration, and insensitive to most other process parameters.
- In continuous emulsion polymerisation of vinyl acetate in a CSTR sustained oscillations were observed. In a Pulsed Packed Column Reactor these were suppressed almost completely.
- When the axial mixing in the PPC was varied within limits, the particle number was affected, but the reaction rate was not. This was in accordance with the results of batch experiments.

List of symbols

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\begin{align*}
C & \text{ concentrations } (\text{kmol/m}^3) \text{ of emulsifier (E), initiator (I) and sodium ions (Na}^+\text{) in water or monomer in particles (M)} \\
E & \text{ axial mixing coefficient } (m^2/s) \\
f & \text{ frequency of pulsation } (s^{-1}) \\
k_p & \text{ propagation rate constant } (m^3/kmol.s) \\
n & \text{ average number of radicals in the polymer particles} \\
N & \text{ number of particles per unit of volume of the water phase } (m^3) \\
N_Av & \text{ Avogadro's number } (\text{kmol}^{-1}) \\
R_p & \text{ rate of polymerisation } (\text{kmol/m}^3.s) \\
s & \text{ stroke length of pulsation in the column } (m) \\
t & \text{ time } (\text{min. or s}) \\
X & \text{ conversion} \\
\bar{t} & \text{ mean residence time } (\text{min. or s})
\end{align*}
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References