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INTRODUCTION

In industry it may be desirable to perform large scale emulsion polymerizations at a relatively low temperature in order to reduce the rate of heat production and so to provide isothermal reactor operation (Mayer et al., 1994). An important disadvantage of this procedure is that in most cases complete conversion is not obtained. Maxwell et al. (1992) have pointed out that the rate of polymerization at high conversion is hardly enhanced by an increase of the free radical concentration in the continuous phase. Maxwell et al. (1992) and Chen and Lee (1992) have explained this phenomenon by diffusion limitation of the monomer molecules within the polymer particles, which may occur at temperatures below the glass transition temperature \( T_g \). Chen and Lee have also shown that an increase of the monomer diffusion rate in the particles by an increase of the temperature or by the addition of inert diluent enhances the polymerization rate significantly at high conversion. Obviously the addition of inert diluent to the reaction mixture is not preferable in industry since it has to be removed from product at the end of the process.

A very simple procedure to cope with heat transfer limitation in large scale emulsion polymerization is to operate the reactor at a relatively low temperature until the polymerization rate levels off. Subsequently the process temperature is increased in order to allow the monomer molecules to diffuse to the growing chain ends. In this way the rate of heat production is set to an acceptable level during the first step of the polymerization whereas complete conversion is obtained within a short period of time during the second step of the process. Note that the polymer quality can be changed by an increasing temperature profile. A common way to increase the temperature in the later stages of the polymerization is to stop cooling after a certain conversion has been reached. When the product latex has to be concentrated after the polymerization process by increasing the temperature and so evaporating water, no additional measures are necessary to achieve complete conversion.

In this paper it is shown that the above described procedure can be a useful tool in scaling up emulsion polymerization reactors.

EXPERIMENTAL

The chemicals used in this study were distilled water, distilled commercial grade styrene, commercial grade sodium dodecyl sulphate, and laboratory grade sodium persulphate. The batch reactor was a stainless steel tank equipped with an eight bladed Rushton turbine impeller and four baffles. The volume of the batch reactor was 1.2 dm\(^3\) and the impeller speed was 500 rpm. During the polymerization, samples were taken to determine the conversion by gravimetry. The gravimetric procedure for determining the monomer conversion has been checked by analysing the residual monomer content in the latex samples using gas chromatography and an internal standard. The conversions determined by both techniques were found to be in good agreement. The particle concentration has been calculated from the volume averaged particle size which has been determined by transmission electron microscopy.

RESULTS

Figure 1 shows a batch emulsion polymerization of styrene at 50°C. In Fig. 1 it can be seen that the polymerization rate almost equals zero at a fractional monomer con-
version of 0.9. At $t = 165$ min, the reaction temperature was elevated from 50°C to 75°C. The conversion–time plot shows that the enhancement of the reaction temperature leads to complete conversion within an acceptable period of time.

Chen and Lee (1992) observed that at 70°C, a limiting conversion only occurs in systems with large particles $d_p > 200$ nm, but not in systems with small particles as studied in our laboratory $d_p < 150$ nm. Chen and Lee contribute this limitation of conversion to a core-shell morphology of the growing particles, which particularly occurs at high conversion: the polymer radicals have the hydrophobic ends anchoring on the surface and the growing ends within the shell region. The monomer consumed in the shell is expected to be supplied by monomer diffusion from the core of the particles into the shell layer. Since the diffusion distance of monomer from the particle core to the shell increases with the particle diameter, monomer is supplied to the shell layer at a much lower rate for large particles than for small particles. Figure 1 shows that a limiting conversion may also occur in small particles, e.g. $d_p = 68$ nm, when the reaction temperature is relatively low (50°C compared to 70°C for the experiments of Chen and Lee). This result can be explained qualitatively by a decrease of the apparent diffusion coefficient of the monomer in the particles with decreasing temperature.

For latexes with $d_p > 200$ nm, Chen and Lee (1992) observed that the conversion of the product latex was still limited to 0.95 at 85°C whereas complete conversion was obtained at 75°C already for the experiment presented in Fig. 1 with $d_p = 68$ nm. The limiting conversion observed by Chen and Lee (1992) for the latex particles with $d_p > 200$ nm at 85°C cannot be explained by a core–shell morphology of the large particles because of the non-anchored polymer radicals arising from the thermal start inside the particles. The relatively low polymerization rates observed at high monomer conversion might be caused by the fact that the polymerization rate is not determined by the monomer concentration in the particles but by the monomer activity; at high polymer contents, the activity coefficient of the monomer shows a very sharp decrease with increasing polymer content. At present this explanation is being validated.

CONCLUSION

In order to provide both stable and isothermal reactor operation, large scale emulsion polymerization reactors can be operated at a relatively low temperature. When the polymerization rate levels off, complete conversion can be obtained within an acceptable period of time by an increase of the reaction temperature, provided the particles are relatively small, e.g. $d_p < 150$ nm for styrene. The underlying mechanism causing a limiting conversion in emulsion polymerizations performed at a relatively low temperature is, to the best of the authors’ knowledge, not yet well understood. Elucidating this mechanism may provide fundamental criteria for avoiding a limiting conversion in polymerization processes.

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