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Production of Copolymer Latexes in Continuously Operated Reactors

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Abstract: The outcome of an emulsion copolymerization in terms of the intermolecular chemical composition distribution (CCD) for example strongly depends on the reactor type and the method of operation. It is demonstrated that homogeneous copolymers as well as copolymers with a bimodal CCD can be produced by seeded emulsion copolymerization of styrene and methyl acrylate in a series of CSTRs.

Keywords: Chemical composition distribution · Emulsion copolymerization · Process intensification · Series of CSTRs

Introduction

Control of products of emulsion polymerization processes, *i.e.* latex products, is mainly based on conversion, particle size distribution, molecular mass distribution, degree of branching, and for polymerizations with more than one monomer, on the intermolecular chemical composition distribution (CCD). Material properties such as the glass transition temperature, Youngs modulus and toughness are strongly related to the CCD [1]. Production of copolymer latexes in relatively small continuously operated reactors may become an interesting alternative for large scale (semi-)batch operation used at present. This paper describes the performance of a series of CSTRs in terms of the CCD for the emulsion copolymerization of styrene (S) and methyl acrylate (MA).

Copolymerization

In copolymerization the monomers generally have different reactivities. For a copolymerization of two monomers A and B, reactivities are expressed in reactivity ratios r_A and r_B:

$$r_A = \frac{k_{p,AA}}{k_{p,AB}} \text{ and } r_B = \frac{k_{p,BB}}{k_{p,BA}} \quad (1)$$

$k_{p,AA}$ and $k_{p,BB}$ are the propagation rate coefficients for homopolymerization of the monomers A and B, respectively. $k_{p,AB}$ and $k_{p,BA}$ are the cross propagation rate coefficients. For the monomer pair S and MA the reactivity ratios r_S and r_{MA} are 0.73 and 0.19, respectively [1].

In a batch copolymerization of S and MA, strong composition drift and therefore a broad CCD may be expected for most recipes. This makes the monomer pair S and MA very suitable for the study of the influence of reactor type and method of operation on the CCD.

In a semi-batch process the CCD of the product can be influenced by adjusting the monomer mol fractions at the locus of polymerization by a proper feed rate profile of the monomer(s). By keeping the molar ratio of the monomers at the locus of polymerization at the same value during the complete polymerization process, the CCD of the product will be narrow.

Emulsion Copolymerization in a Series of CSTRs

Homogeneous copolymers, *i.e.* copolymers with a narrow CCD, can be produced in a single CSTR [2]. However, conversions are low. Homogeneous copolymers can also be produced in a series of CSTRs by feeding an additional amount of the more reactive monomer to the tanks 2 up to and including n. Every tank demands a different feed rate. Fig. 1 demonstrates the results for the seeded emulsion copolymerization of S and MA in a series of three equally sized CSTRs, the more reactive monomer S was fed to the second and the third tank. A mechanistic model based on phase equilibria and kinetics has been used for the calculation of the feed rates, see *e.g.* Van den Boomen [3] and Saldivar and Ray [4].

The CCD of the samples taken from the individual tanks were measured with Gradient Polymer Elution Chromatography (GPEC) [5].

Latex products with a predefined bimodal CCD can in principle be produced in a series of two CSTRs. The composition of the copolymer formed in the first tank can be controlled by the feed rates of both monomers and the monomer to water ratio in the tank. The composition of the copolymer produced in the second tank can be controlled by feeding additional monomer with a proper feed rate. A typical example is presented in Fig. 2. The results in Fig. 2 reveal that copolymers with an n-modal CCD can be produced in a series of n CSTRs. The composition the product produced in each CSTR can be controlled by feeding additional monomer to the tank under consideration.

Concluding Remarks

For the production of copolymer latexes continuous emulsion polymerization is an interesting alternative for

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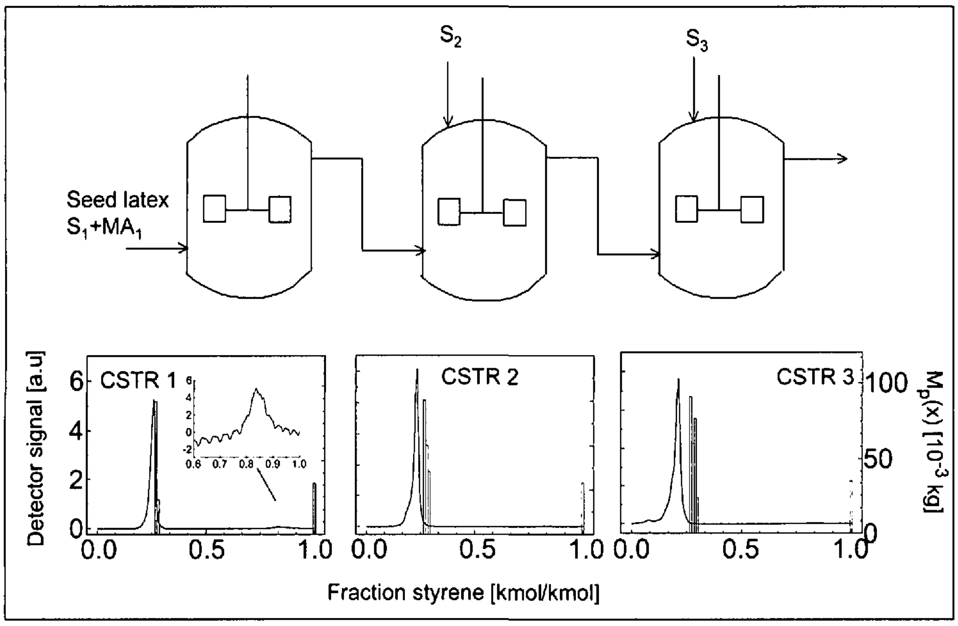

Fig. 1. CCD of the seeded emulsion copolymerization of S and MA in a series of three equally sized CSTRs in the steady state. Volume per tank 2.5 dm^3, 6 bladed turbine impeller, 4 baffles, mean residence time in the cascade 5700 s, temperature 50 °C, overall conversion 0.6, additional S feeds into tanks 2 and 3. Solid lines: experimental results with GPEC, histograms: calculated CCD, $M_p(x)$ is the amount of copolymer with composition x calculated with the model [5]. Recipe and feed rates reported by Van den Boomen [5].

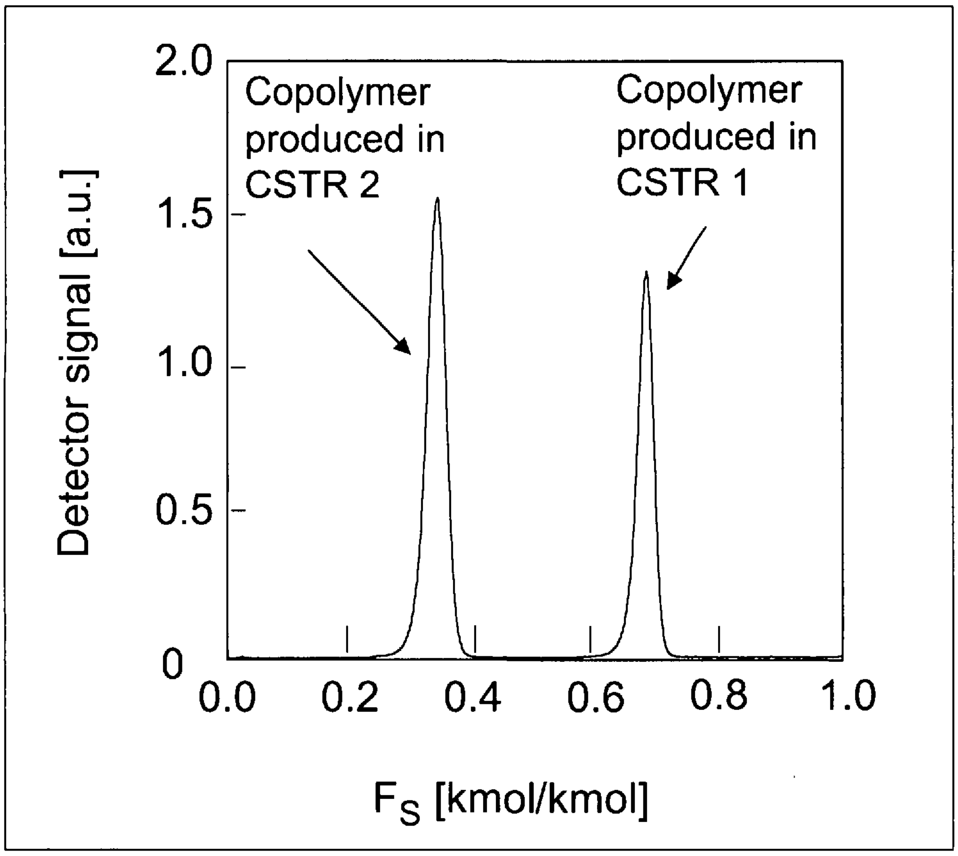

Fig. 2. CCD of the product of a seeded emulsion copolymerization of S and MA in a series of two 2.5 dm^3 CSTRs in the steady state. CCD determined with GPEC. Mean residence time in the cascade 3500 s, additional MA feed into tank 2, temperature in tank 1 50 °C, in tank 265 °C,overall conversion 0.35.

(semi-)batch operation, even for relatively small volume products. Flexibility towards different products is an important issue. A compelling demand is that a change from one product to another only leads to relatively small amounts of off-spec product. For seeded emulsion copolymerization, a series of 5–10 CSTRs seem to be promising.

Continuous emulsion copolymerization in a series of 5–10 relatively small volume CSTRs instead of latex production in actual large scale (semi-)batchwise operated equipment is a promising example of process intensification.

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