### NOTE

# The Influence of 4-*tert*-Butylcatechol on the Emulsion Polymerization of Styrene

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### **INTRODUCTON**

In industry, commercial available monomers for the polymerization processes contain an inhibitor to prevent undesired autopolymerization before their use in the polymerization. In laboratory work on the kinetics of emulsion polymerization the inhibitor is usually removed by distillation. In industrial practice, however, distillation is seldomly used for inhibitor removal. The presence of the inhibitor in the reaction mixture will influence both the course of the reaction and the product properties. Huo et al.<sup>1,2</sup> have shown that monomer soluble components such as 4-tert-butylcatechol (TBC) have a significant effect on the conversion time history and particle size in emulsion polymerizations, obeying Smith-Ewart case II kinetics. In this contribution, the influence of TBC on the emulsion polymerization of styrene and on the product properties is elucidated.

TBC may oxidize into 4-*tert*-butyl-1,2-benzochinon (TBBC), which forms long-living radicals. These TBBC radicals influence the course of the emulsion polymerization process. This research note presents a TBBC radicals forming mechanism and proposes two different ways in which the TBBC radicals can influence the emulsion polymerization process. Comparison of emulsion polymerization experiments with and without TBC combined with simulations with a mechanistic model excludes one of the proposed mechanisms.

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### THEORY

### **Mechanism of Forming TBBC Radicals**

If styrene is not distilled before application as a monomer, TBC will be present in the reaction mixture. TBC may oxidize into TBBC during storage of styrene or extraction with sodium hydroxide. During the sulfateinitiated emulsion polymerization of styrene, oxidation of TBC by the persulfate radicals is also possible in the weakly alkaline continuous phase. TBBC is soluble in styrene and is readily absorbed by the particles. TBBC can act as a radical acceptor, so radical transfer from a growing chain to TBBC may occur. This radical transfer is analogous to chain transfer to rosin acid soap, as reported by Titov et al.<sup>3</sup>. Because the TBBC radicals are relatively stable due to conjugation,<sup>4</sup> probably most of the TBBC is converted into TBBC radicals. The resulting (oligomeric) carbonium ions  $R^+$  react with water into an alcohol at the surface of the particles. The mechanism of the formation of TBBC radicals has been illustrated in Figure 1.

## Influence of TBBC Radicals on the Emulsion Polymerization Process

As a result of the radical transfer to TBBC, the chain growth in the particles stagnates. As a consequence, particle growth will retard. The TBBC radicals, which desorb from the particles because of their charge, can react in different ways. Figure 2 proposes a reaction of TBBC radicals, which occurs preferentially in the aqueous phase. This reaction again consumes sulfate radi-

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**Figure 1** Mechanism of the formation TBBC radicals in the polymer particles during the emulsion polymerization of styrene with the presence of TBC in the reaction mixture.

cals, converting the TBBC radicals back into TBBC. These TBBC molecules may be taken up by the particles once more and transformed into TBBC radicals again, and so on. According to this mechanism, the average number of active radicals available will be lower during the whole emulsion polymerization process than in the absence of TBBC. The total effect of this "inhibition" mechanism is a decrease in the initia-



**Figure 2** The "inhibition" mechanism of the TBBC radicals, consuming persulfate radicals in the aqueous phase during the emulsion polymerization of styrene.



**Figure 3** The "desorption" mechanism of the TBBC radicals, reacting with monomer or oligomer molecules in the aqueous phase.

tor efficiency and a lower particle number in the latex product.

The TBBC radicals can also react with monomer and oligomer molecules in the aqueous phase (see Fig. 3). TBBC might even be built into the oligomer chain. So, the monomer or oligomer radicals are formed from the little reactive TBBC radicals. These monomer and oligomer molecules contribute in the emulsion polymerization process in the usual way. This mechanism is characterized by a high radical desorption rate, and is further regarded as the "desorption" mechanism. Considering the ab initio emulsion polymerization of styrene, relatively high radical desorption rates, according to the "desorption" mechanism, retard the particle growth. As a consequence, the nucleation period lasts longer because less emulsifier is needed for colloidal stabilization of the already existing particles. So, there is more emulsifier available for micellar nucleation. Therefore, the net effect of the "desorption" mechanism is a higher particle number in the product latex.

### **EXPERIMENTAL**

The chemicals used in this study were distilled water, commercially grade styrene, supplied by DSM, sodium lauryl sulfate (emulsifier), sodium persulfate (initiator), and sodium hydroxide (pH buffer), all laboratory grade and supplied by Merck. The following concentrations were used, all expressed in kmol/m<sup>3</sup><sub>water</sub>: emulsifier: 0.126, initiator: 0.0105, and monomer 5.00. The temperature was  $50.0 \pm 0.1^{\circ}$ C, the pH was 10.5, and the impeller speed was 500 rpm. The batch reactor used was a 1.2 dm<sup>3</sup> stainless steel vessel, equipped with a six-bladed Rushton turbine impeller and four baffles. Experiments with and without TBC present were carried out.

During the emulsion polymerization samples were taken from the reactor to determine the conversion by gravimetry and the weight-average particle size by dynamic light scattering using a Malvern autosizer IIc. Dynamic light scattering only gives a relative measurement of the particle diameter.



**Figure 4** Experimentally observed and simulated conversion time history.  $\Box$ ,  $\bigcirc$ ,  $\triangle$ , and  $\diamond$  = Experiments with TBC present in the reaction mixture (100 ppm).  $\blacksquare$ ,  $\bigcirc$ , and  $\blacktriangle$  = Experiments without TBC present in the reaction mixture regular weight line = simulation of a "normal" emulsion polymerization with an initiator efficiency ff of 0.5<sup>5,6</sup> and a desorption rate coefficient  $k_{des0}$  of  $2.4 \cdot 10^{-17}$  1/s<sup>5,7</sup>. Heavy weight line = Simulation of the "inhibition" mechanism with ff = 0.3 and  $k_{des0} = 2.4 \cdot 10^{-17}$  1/s. Light weight line = Simulation of the "desorption" mechanism with ff = 0.5 and  $k_{des0} = 5 \cdot 10^{-17}$  1/s.

Simulations with a dynamic mechanistic model describing the emulsion polymerization of styrene<sup>5</sup> were respectively carried out with a lower initiator efficiency for the "inhibition" mechanism and a higher desorption rate for the "desorption" mechanism with respect to the usual values.

### **RESULTS AND DISCUSSION**

Figure 4 shows the experimentally observed and simulated conversion time histories. Apart from the induction period caused by oxygen, the differences between the observed conversion time histories are within the experimental error. No straightforward conclusion can be drawn from the conversion time curves of the experiments with and without TBC. The pseudoretardation in interval I and the acceleration of the polymerization in intervals II and III as described by Huo et al.,<sup>1,2</sup> cannot be observed and simulated particle numbers are presented as a function of conversion. The simulated particle numbers have been determined by the volume average parti-

cle size, while the experimentally observed particle numbers have been determined with dynamic light scattering. So, the observed particle numbers of the experiments with and without TBC are a relative measure for the simulated particle numbers according to the different mechanisms. In agreement with Huo et al.,<sup>1,2</sup> the experimental results collected in Figure 5 reveal that the particle number at complete conversion is significantly higher for reaction with TBC than for reactions without TBC. The simulation of the "desorption" mechanism gives a higher particle number than the simulation without TBC and is, therefore, in qualitative agreement with the experimental results. The "inhibition" mechanism would result in a lower particle number, which was not observed. The experimentally observed and simulated particle numbers for polymerizations with and without TBC point to the "desorption" mechanism rather than to the "inhibition" mechanism.

### **CONCLUSION**

In agreement with Huo et al.,<sup>1</sup> emulsion polymerizations of styrene with and without TBC present have



**Figure 5** Experimentally observed and simulated particle number as a function of conversion.  $\Box$ ,  $\bigcirc$ ,  $\triangle$ , and  $\diamond$  = Experiments with TBC present in the reaction mixture (100 ppm).  $\blacksquare$ ,  $\blacksquare$ , and  $\blacktriangle$  = Experiments without TBC present in the reaction mixture. Regular weight line = simulation of a "normal" emulsion polymerization with an initiator efficiency ff of 0.5<sup>5,6</sup> and a desorption rate coefficient  $k_{des0}$  of  $2.4 \cdot 10^{-17}$  1/s<sup>5,7</sup>. Heavy weight line = simulation of the "inhibition" mechanism with ff = 0.3 and  $k_{des0} = 2.4 \cdot 10^{-17}$  1/s. Light weight line = Simulation of the "desorption" mechanism with ff = 0.5 and  $k_{des0} = 5 \cdot 10^{-17}$  1/s.

shown that TBC influences the course of the emulsion polymerization process and the product properties in terms of particle number. TBC strongly enhances radical desorption from the particles. TBC is converted into TBBC radicals, which according to the "desorption" mechanism, react in the aqueous phase with monomer or oligomer molecules.

If styrene is not distilled before the emulsion polymerization, and as a consequence, TBC is present in the reaction mixture, the particle number of the product latex is significantly higher (the particle size is smaller) than in the case of emulsion polymerization of distilled styrene.

For quality control in industrial processes, it will, therefore, be worthwhile to remove TBC before use. At least determination of the TBC concentration in styrene can be recommended.

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