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Notes

Entry of Hydrophilic Radicals into Latex Particles

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Emulsion polymerization is used to produce a wide range of specialty polymers such as coatings, adhesives, binders for nonwoven fabrics, and additives for papers, textiles, and construction materials. In most commercial processes, the reaction system consists of monomer-swollen polymer particles dispersed in an aqueous medium, and water-soluble initiators are used. Polymerization mainly occurs in the polymer particles, and the kinetics and the polymer microstructure depend on the number of radicals per particle, which in turn depends on the rates of radical entry, radical exit, and termination.

Radicals are produced by decomposition of the initiator in the aqueous phase. Because they are hydrophilic, it is commonly accepted that they cannot enter directly into the polymer particles, but they have first to polymerize in the aqueous phase to a certain chain length to become surface-active. This mechanism is supported by both theoretical[1−3] and experimental[4−7] studies. Recently, this mechanism has been challenged by some clever experiments carried out by Tauer et al.[8] These authors swelled latex particles with a reddish RAFT agent and an inert solvent and observed that the latex discolored upon addition of potassium persulfate (KPS). Because there was no monomer in the system to form surface-active oligomers, they concluded that sulfate ion radicals directly enter into the polymer particles.

In the course of an investigation on the formation of volatile organic compounds in the production of *n*-butyl acrylate (BA)-containing latexes, we found some results that at first sight supported Tauer's conclusion. The addition of KPS to a devolatilized (i.e., without any monomer) BA/vinyl acetate (VAc)/acrylic acid (AA) (63.5/33.5/3 w/w) latex led to the formation of 1-butanol, presumably from the butyl acrylate units in the polymer chain through a mechanism that involves a hydrogen abstraction from the tertiary carbon of the butyl acrylate unit.[9] These results seem to indicate that sulfate ion radicals were able to enter into the polymer particles. However, a different hypothesis may be proposed. It is known[10] that the decomposition of KPS lowers the pH because of the following reaction:

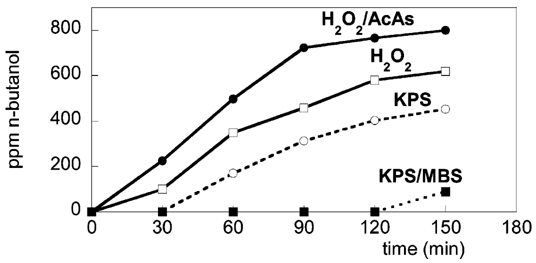

Figure 1. 1-Butanol formation during the addition of initiator.

$$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet -}$$

$$SO_4^{\bullet -} + H_2O \rightarrow HSO_4^{-} + HO^{\bullet}$$

In these reactions hydroxyl radicals, which are much less hydrophilic than the sulfate ion radical, are formed. One may speculate that these radicals are the ones responsible for the effects observed by Tauer et al.[8] and by us.

To clarify this point, a BA/VAc/AA (63.5/33.5/3 w/w) latex prepared using KPS as initiator was heated overnight at 90 °C to completely decompose the initiator. Then, it was thoroughly devolatilized by steam stripping. The amount of residual monomer was checked by headspace gas chromatography, and no monomer could be detected. The pH of the latex was about 2.5. The latex was divided into four parts, and a different initiator system was added to each part. The initiators included two thermal systems (KPS and H_2O_2) and two redox systems, KPS/sodium metabisulfite (MBS) (molar ratio: 1/1) and H_2O_2/ascorbic acid (AsAc) (molar ratio: 2/1). H_2O_2 and H_2O_2/AsAc were used to directly produce $HO^{\bullet}$ radicals at different rates (faster for the redox system). On the other hand, KPS/MBS was used because with this system sulfate ion radicals are formed:

$$S_2O_8^{2-} + S_2O_5^{2-} \rightarrow SO_4^{\bullet -} + SO_4^{2-} + S_2O_5^{\bullet -}$$

and MBS scavenges the hydroxyl radicals through the following reaction scheme:[11]

$$S_2O_5^{2-} + H_2O \leftrightarrow 2HSO_3^{-}$$

$$4HSO_3^{-} + O_2 \rightarrow 4SO_3^{\bullet -} + 2H_2O$$

$$HO^{\bullet} + SO_3^{\bullet -} \rightarrow H^{+} + SO_4^{2-}$$

Therefore, when using the KPS/MBS system, no hydroxyl radicals are expected to exist in the system. The thermal initiators were added as a shot at the beginning of the process, whereas the redox systems were semicontinuously fed (using separate streams) for 90 min. The total amount of initiator was 1 wt % based on the total weight of latex. The experiments were carried out at 60 °C, samples were withdrawn from the reactor, and the 1-butanol was analyzed by headspace gas chromatography. The final pH of the latexes were as follows:

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KPS, pH = 1.86; KPS/MBS, pH = 1.84; H_2O_2, pH = 2.5; H_2O_2/AsAc, pH = 2.1.

Figure 1 presents the evolution of the concentration of 1-butanol during the four runs. It can be seen that the rate of 1-butanol formation depended on the initiator system used. These differences were not due to a pH effect because all latexes presented a similar pH. Figure 1 shows that no 1-butanol was detected during the addition of KPS/MBS, namely, when no hydroxyl radicals were present in the reactor. On the other hand, high concentrations of 1-butanol were observed when hydroxyl radicals were directly formed from the initiator (H_2O_2 and H_2O_2/AsAc systems). Because of the similarity of the pH, these results suggest that in the absence of monomer hydroxyl radicals accounted for most of the radical entry, whereas the contribution of sulfate ion radicals was negligible. It is worth pointing out that in the presence of monomers polymerization with the monomer dissolved in the aqueous phase is the most likely fate of both sulfate ion and hydroxyl radicals, and hence relatively hydrophobic radicals account for most of the radical entry.

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