

Emulsion Polymerization of Styrene with Disproportionated Rosin Acid Soap as Emulsifier

In the industrial production of rubbers and latices, disproportionated rosin acid soap (DRAS) is often applied as an emulsifier. Titov et al.¹ showed that phenanthrene-type cyclic compounds with aliphatic- or aromatic-type double bonds, which are present in DRAS, may act as a chain-transfer agent. As a result of radical transfer to these chain transfer agents, the rate of radical desorption from the particles into the water phase is enhanced. For batch emulsion polymerizations with DRAS as an emulsifier, Mayer et al.^{2,3} showed that limited particle coagulation occurs in interval 2. In spite of the decrease of the particle concentration, the polymerization rate was not significantly influenced. Apparently, the effect of the decrease of the particle number is compensated by the increase of the average number of growing chains per particle. This result is typical for emulsion polymerizations where radical desorption and radical absorption are of the same order of magnitude, i.e., Smith and Ewart case 1 kinetics.^{4,5} Mayer et al.^{2,3} also showed that the polymerization rate in a latex with DRAS as an emulsifier can be predicted over a wide range of operating conditions with the solution of the radical population balance over the particle-size distribution and a proper rate coefficient for radical desorption, k_{des} . The value of k_{des} depends on the concentration of DRAS in the recipe.

However, there is possibly another mechanism by which most experimental results obtained by Mayer et al. can be explained: Nonmonomeric compounds with a double bond which are present in DRAS may react with a growing chain. When the chain-end radical formed in this way propagates at a very slow rate, the characteristic time for propagation may even be considerably longer than the characteristic time for absorption of a second radical and subsequent instantaneous bimolecular termination. This means that a significant number of growing chains are excluded from the propagation process so that the growth rate of the particles is considerably retarded. According to this mechanism, the unsaturated compounds present in DRAS are built into the polymer chains. The total effect is a decrease of the initiator efficiency. Since the rate of radical absorption increases with increasing particle diameter, inhibited radicals are terminated at a faster rate in large particles than in small particles. Additionally, the

increase of the radical absorption rate with increasing particle diameter causes the polymerization process in large particles to be restarted at a faster rate than in small particles. This leads to a more pronounced dependence of the growth rate on the particle diameter, making the polymerization process similar to a process where radical desorption is dominant. Note that the "desorption mechanism" and the "inhibition mechanism" predict a similar molecular weight (distribution).

Whether the "desorption mechanism" or the "inhibition mechanism" will be dominant depends on the ratio of the total rate coefficient for radical transfer k_{tr} and the rate coefficient for propagation of a growing chain end with a nonsaturated compound in DRAS k_{nonsat} . For small values of k_{tr}/k_{nonsat} , the "inhibition mechanism" will be dominant, whereas large values of k_{tr}/k_{nonsat} will lead to the "desorption mechanism."

REFERENCES

1. A. P. Titov, V. V. Kotov, and L. J. Yakovleva, *Int. Polym. Sci. Technol.*, **17**, 27 (1990).
2. M. J. J. Mayer, J. Meuldijk, and D. Thoenes, *J. Appl. Polym. Sci.*, **56**, 119 (1995).
3. M. J. J. Mayer, J. Meuldijk, and D. Thoenes, *J. Appl. Polym. Sci.*, to appear.
4. M. S. El-Aasser and J. W. Vanderhoff, *Emulsion Polymerization of Vinyl Acetate*, Applied Science, London, 1981.
5. J. Meuldijk, C. J. G. van Strien, F. H. A. C. van Door-malen, and D. Thoenes, *Chem. Eng. Sci.*, **47**, 263 (1992).

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