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Letter

Comments on: Exit Process and Re-entry Rate in Emulsion Polymerization J.H. Kim and H. H. Lee, *Polymer*, 1996, **37**, 1941.

Dear Sir

In a recent article, Kim and Lee[1] discussed the processes involved in the exit of free radicals from the polymer particles in emulsion polymerization, as well as the re-entry of the exited radicals.

The basic aspects of their formulation may be summarized as follows.

(i) Only monomeric radicals can desorb from the polymer particles.
(ii) The desorbed monomeric radicals may react in the aqueous phase by both propagation and termination or may reenter into the polymer particles.
(iii) The probability of re-entry into particles with no radicals, N_0, was assumed to be much larger than into particles that with one radical, N_1 (a zero–one system was considered).
(iv) The oligomers resulting from the propagation in the aqueous phase of the desorbed radicals cannot enter into the polymer particles.

The rationale behind points (iii) and (iv) is unsound.

According to Kim and Lee[1], the monomeric radical will most likely enter into N_0 because the free radical concentration difference between the aqueous phase and the polymer particle, and hence the driving force for diffusion, is much larger for N_0 than for N_1. However, there is a misconception in the argument because the driving force for the diffusion of the monomeric radicals is not affected by the presence of longer active chains in the particles. This means that only the particles N_1 that contain monomeric radicals are affected by the reduction of the driving force. Simple calculations using the most probable distribution[2] show that for a number average length of the active chains of 10 000, only about one out to 10 000 N_1 particles will contain monomeric radicals. Therefore, only a negligible fraction of N_1 particles is affected by the reduction of the driving force for diffusion. Consequently the probability for re-entry (the notation of the paper[1] will be used and the equation numbered as they are numbered in the paper) is:

$$P_{\mathrm{re}} = \frac{k_{\mathrm{a}} N_c}{k_{\mathrm{P_w}} [M]_w + k_{\mathrm{t_w}} [T] + k_{\mathrm{a}} N_c} \tag{23}$$

This probability is related to the probability that the monomeric radical reacts in the aqueous phase by either propagation or termination, β, used by Asua *et al.*[3]

$$\beta = 1 - \mathrm{P}_{\mathrm{re}}$$

Substituting this equation into eqn (17) gives

$$K_{\mathrm{d}} = k_{\mathrm{ct}} [M]_{\mathrm{P}} \frac{K_0}{\beta K_0 + k_{\mathrm{p}} [M]_{\mathrm{p}}} \tag{17}$$

This equation has already been reported as a limiting case for zero-one systems[3] of the general desorption equation.

Point (iv) is based on the assumption that the oligomers resulting from the propagation in the aqueous phase of the desorbed monomeric radicals cannot enter the latex particles because they are surface-inactive. However, the longer the length of a hydrocarbon chain the larger the decrease of free energy for transfer of the hydrophobic species from aqueous phase to organic phase [4]. This means that, in contrast with what was stated by Kim and Lee[1], the longer the hydrophobic radical the higher the driving force to enter into the polymer particle.

References

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