Recent Travels in $k_t$-Land

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Until a few years ago, a presentation such as this would instead have been entitled “Recent Travails in $k_t$-Land”. What has changed in the last half-decade is the advent of the SP-PLP-EPR technique. It couples single-pulse pulsed-laser polymerization (SP PLP) with highly time-resolved EPR spectroscopy. The result is unrivalled access to chain-length-dependent termination rate coefficients, $k_{t,i,i}$, in radical polymerization. Where once it was a constant source of exasperation to measure termination rate coefficients, $k_t$, now one may obtain highly satisfying results using SP PLP EPR. In particular this is the case for small chain lengths, as illustrated in Fig. 1. This shows radical concentration, $c_R$, in the milliseconds immediately after a laser pulse induces polymerization. By fitting these results, one obtains $k_{t,1,1}$, the rate coefficient for termination between radicals of unity degree of polymerization, and $\alpha$, the power-law exponent in the variation of $k_{t,i}$ with chain length, $i$, at small $i$. No other currently available technique can deliver these highly important parameters with such authority.

This presentation will report on results from a recent sabbatical year in Göttingen, where the only SP-PLP-EPR setup is located. The monomers studied are shown in Scheme 1. They are (1) a series of $n$-alkyl acrylates, and (2) a fluorinated methacrylate. These were of interest in that: (1) Previous $k_{t,i}$ results for acrylates were ambiguous due to the likelihood of mid-chain radicals being present. In the current study this uncertainty was eliminated by working at temperatures too low for backbiting to occur; and (2) Previously only ‘standard’ methacrylates had been studied, and so the effect of fluorination – which is known to alter miscibility and conformation – remained to be established.

1 J. Barth, M. Buback, Macromol. React. Eng. 2010, 4, 288-301

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Research interests: radical polymerization kinetics, mechanisms, modeling and synthesis