

Large-Molecule Mass Spectrometry: Using a New Technique to Solve Old Problems in Radical Polymerization Kinetics

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As is well known, the advent of large-molecule mass spectrometry (MS) techniques has brought about revolutionary advances in polymer characterisation. Less appreciated is the impact these techniques are starting to have on radical polymerisation (RP) kinetics, where they are helping to solve old and previously intractable problems. Primary amongst these is determination of the mode of termination – i.e., the extent of disproportionation versus combination (see Figure 1) – in RP.¹ This will be the principal topic of this presentation. Figure 2 demonstrates how MS enables direct identification of species formed by each termination pathway. It will be explained how the signal intensities may be used to quantify the mode of termination.¹ This methodology – which includes elimination of errors from mass-related bias in signal intensities – will be illustrated with methyl methacrylate results.

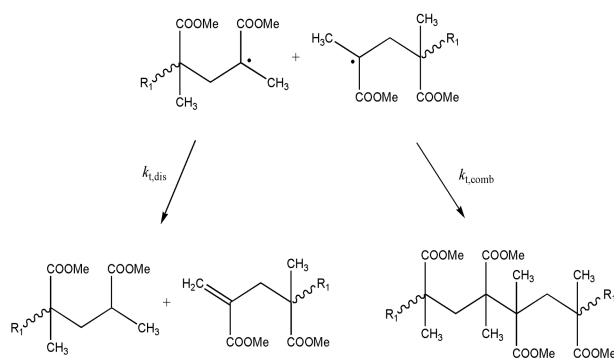


Figure 1. The competing termination reactions of disproportionation, rate coefficient $k_{t,dis}$, and combination, rate coefficient $k_{t,comb}$, in radical polymerization of methyl methacrylate (MMA).

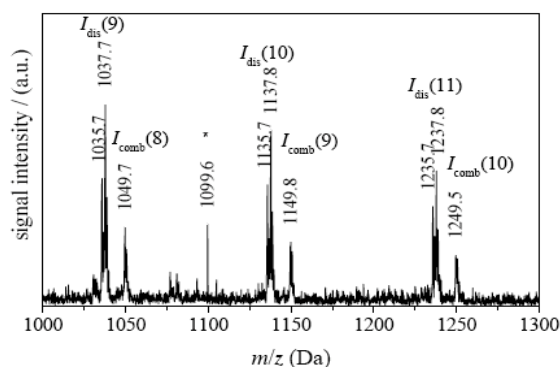


Figure 2. ESI-MS spectrum of poly(MMA).¹ Peaks are for combination ('comb') and disproportionation ('dis') products as indicated. The numbers in brackets are the number of MMA residues.

Another area of RP kinetics in which MS has made waves is that of chain-length dependent propagation.^{2,3} Finally, a novel method for obtaining transfer rate coefficients using MS will be outlined.

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2. Willemse, R. X. E.; Staal, B. B. P.; van Herk, A. M.; Pierik, S. C. J.; Klumperman, B. *Macromolecules* **2003**, *36*, 9797-9803.
3. Heuts, J. P. A.; Russell, G. T. *Eur. Polym. J.* **2006**, *42*, 3-20.