Recent Travels in k_t-Land

Johannes Barth,[1] Sabine Beuermann,[2] Michael Buback,[1] Gregory T. Russell,[3] Rebekka Siegmann[2]

[1] Institut für Physikalische Chemie, Georg-August-Universität Göttingen, Tammannstrasse 6, D-37077 Göttingen, Germany
[2] Institute of Chemistry, University of Potsdam, Karl-Liebknecht-Str. 24-25, D-14476 Potsdam/Golm, Germany
[3] Department of Chemistry, University of Canterbury, Private Bag 4800, Christchurch, New Zealand

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.[1] 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 α_s, the power-law exponent in the variation of $k_t^{i,i}$ with chain length, i, at small i. No other currently available technique can deliver these highly important parameters with such authority.

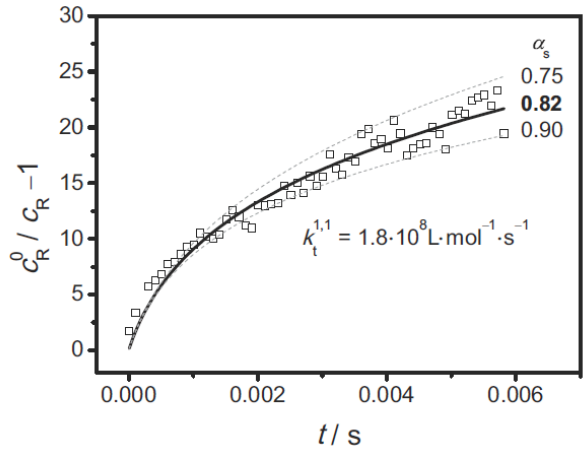
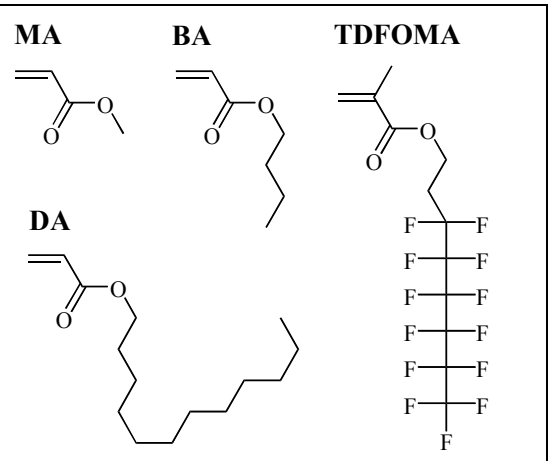


Figure 1. Results[2] from SP PLP EPR of MA (1.5 M in toluene) at –40 °C



Scheme 1. Monomers studied here: three acrylates and 1*H*, 1*H*, 2*H*, 2*H*-tridecafluorooctyl methacrylate

This presentation will report on results from a recent sabbatical year in Göttingen, where the only SP-PLP-EPR setup[1] is located. The monomers studied are shown in **Scheme 1**. They are (1) a series of *n*-alkyl acrylates,[2] and (2) a fluorinated methacrylate. These were of interest in that: (1) Previous $k_t^{i,i}$ 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
[2] J. Barth, M. Buback, G. T. Russell, S. Smolne, *Macromol. Chem. Phys.* **2011**, *212*, 1366-1378

Greg Russell

A/Professor, Dr.
Department of Chemistry, University of Canterbury, New Zealand
Phone: +64-3-3642458 Fax: +64-3-3642110 E-mail: greg.russell@canterbury.ac.nz

Personal History

1991 PhD in Physical and Theoretical Chemistry: Sydney University
1992-4 Alexander von Humboldt Fellow: Göttingen University, Germany
1995-7 Lecturer (in Chemistry): University of Canterbury, New Zealand
1998-2005 Senior Lecturer: University of Canterbury, New Zealand
Since 2006 Associate Professor: University of Canterbury, New Zealand

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