

Critically Evaluated Database of Kinetic Parameters for Free-Radical Polymerization

S. Beuermann and M. Buback

Institute of Physical Chemistry, Georg-August-University Goettingen

Poster presented at the
IUPAC Congress/General Assembly
July 2001

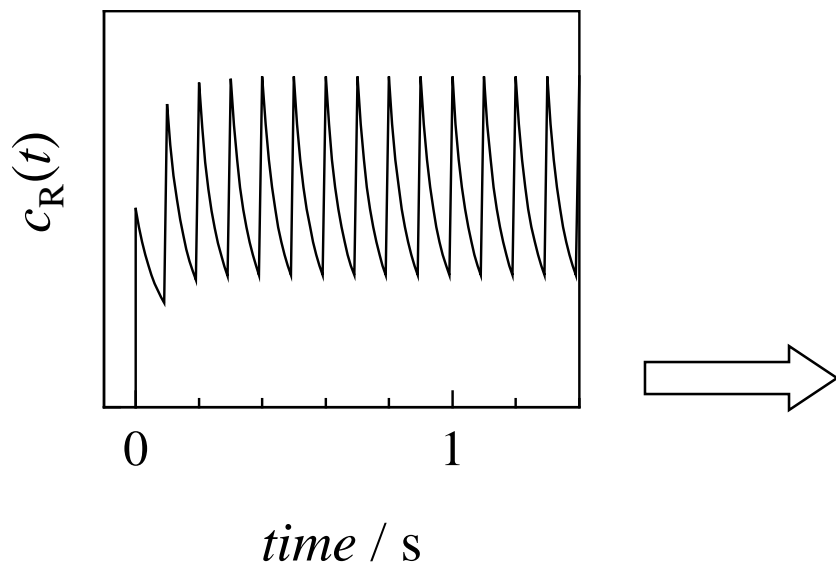
Introduction

Modeling free-radical polymerization is important for science and industry, but often completely different model assumptions and parameter values are reported for ostensibly the same systems. Several IUPAC projects are underway to rectify this situation through international collaboration, by producing **critically evaluated kinetic parameters**. Most of the activities so far have focussed on propagation rate coefficients, k_p , but termination rate coefficients, k_t , have also been addressed.

Pulsed-laser-assisted techniques are perfectly suited for measuring reliable rate coefficients of free-radical polymerization. Two such methods are of particular importance: The PLP-SEC method uses pulsed-laser polymerization (PLP) in conjunction with size-exclusion chromatography (SEC) analysis of the polymeric material. Analysis of the molecular weight distribution enables the unambiguous determination of k_p . Within the second method, SP-PLP, polymerization induced by a single laser pulse (SP) is monitored via on-line infrared or near-infrared spectroscopy with a time resolution of microseconds. The measured trace of monomer conversion vs. time provides access to k_t .

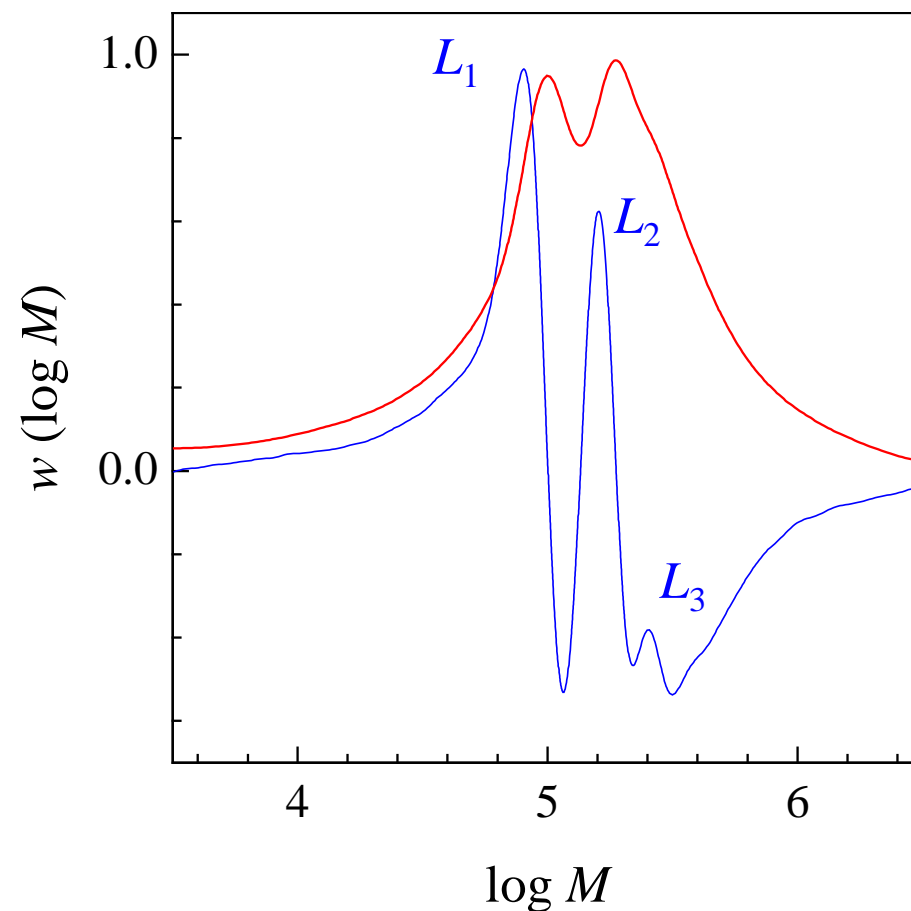
PLP-SEC technique

butyl methacrylate
90°C, 25 Hz, 1 mmol/L benzoin



$$L_i = i \cdot k_p \cdot c_M \cdot t$$

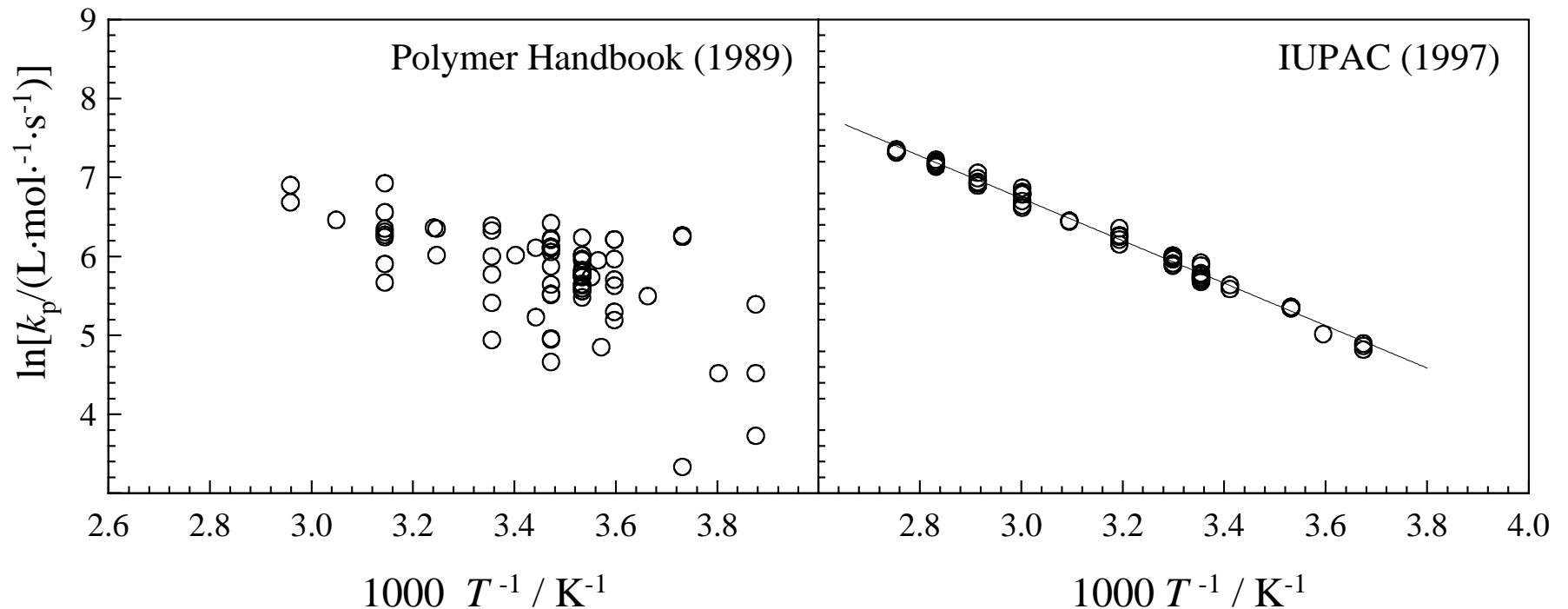
L_1 : number of propagation steps between two successive laser pulses



O. F. Olaj, I. Bitai, F. Hinkelmann, *Makromol. Chem.* **188**, 1689 (1987); O. F. Olaj, I. Schnöll-Bitai, *Eur. Polym. J.* **25**, 635 (1989)

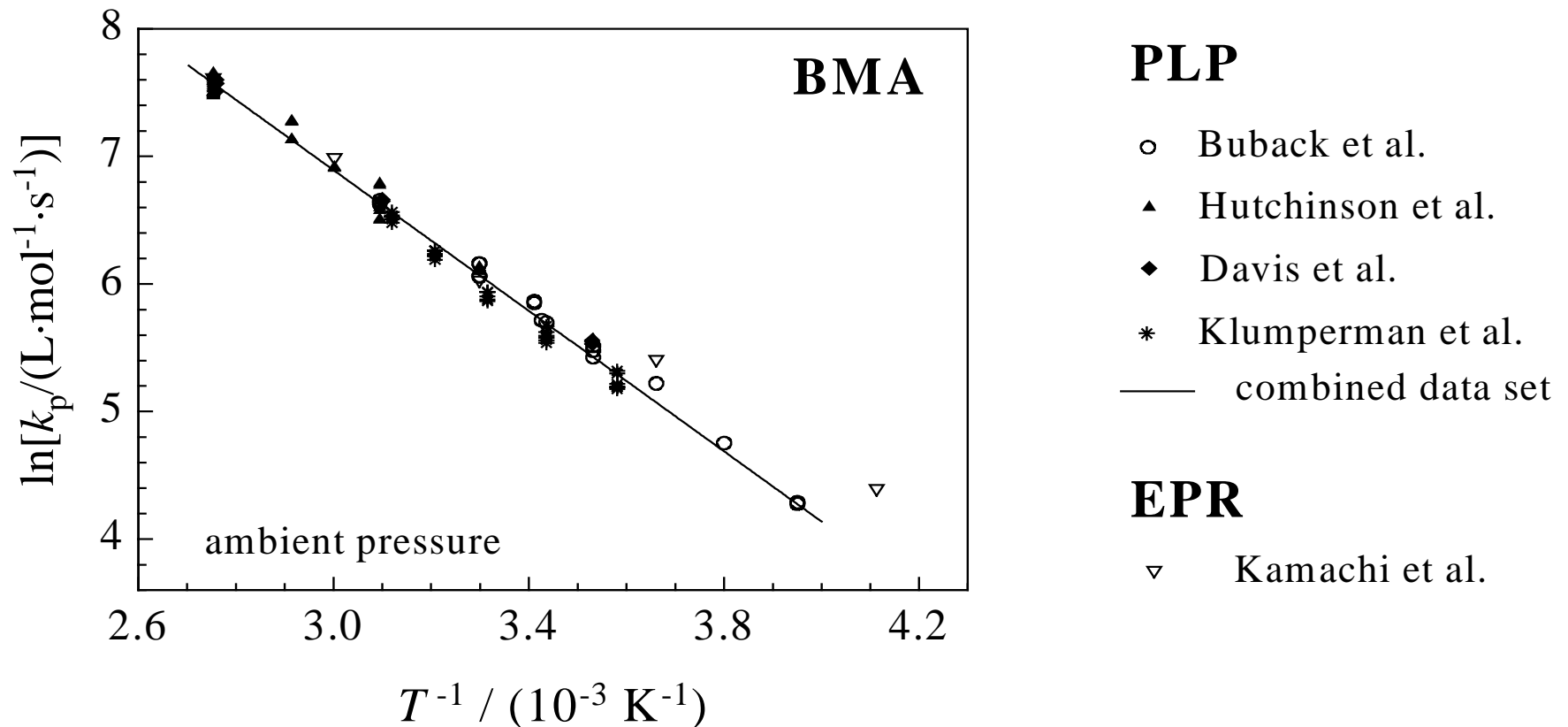
S. Beuermann, M. Buback, T. P. Davis, R. G. Gilbert, R. A. Hutchinson, A. Kajiwara, B. Klumperman, G. T. Russell, *Macromol. Chem. Phys.* **201**, 1355 (2000)

Methyl methacrylate homopolymerization in bulk



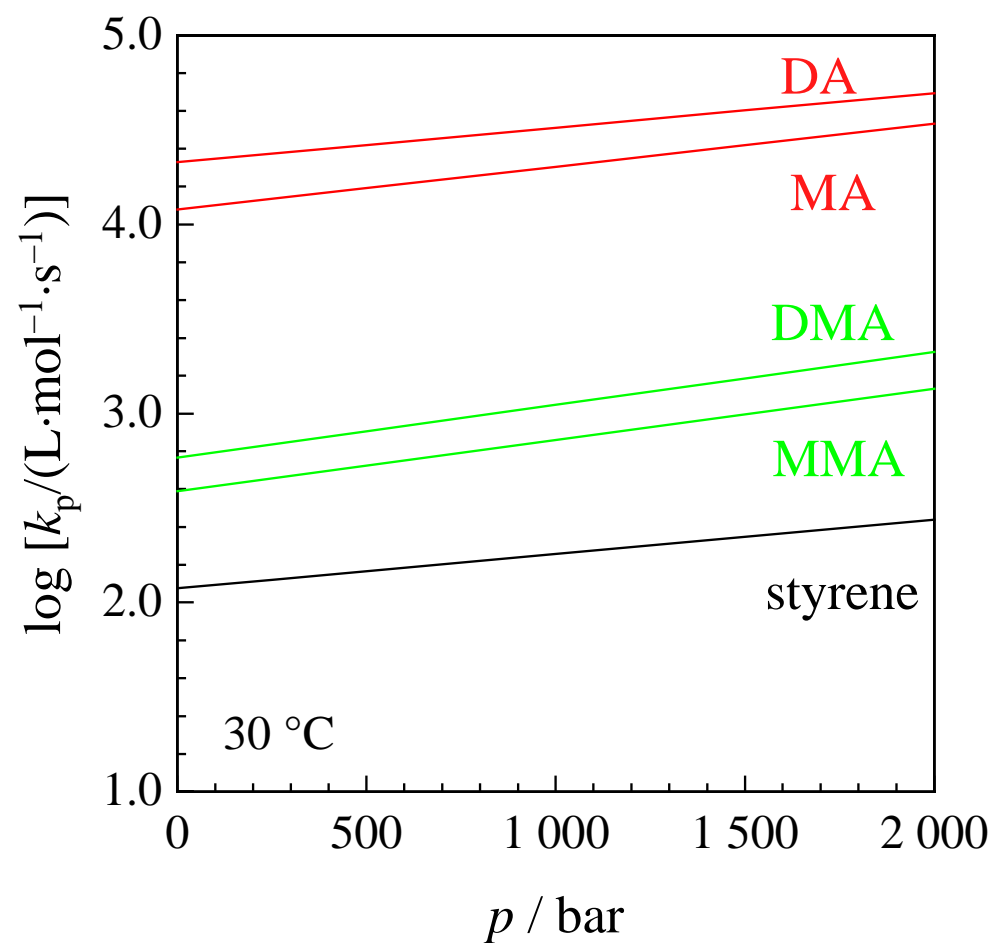
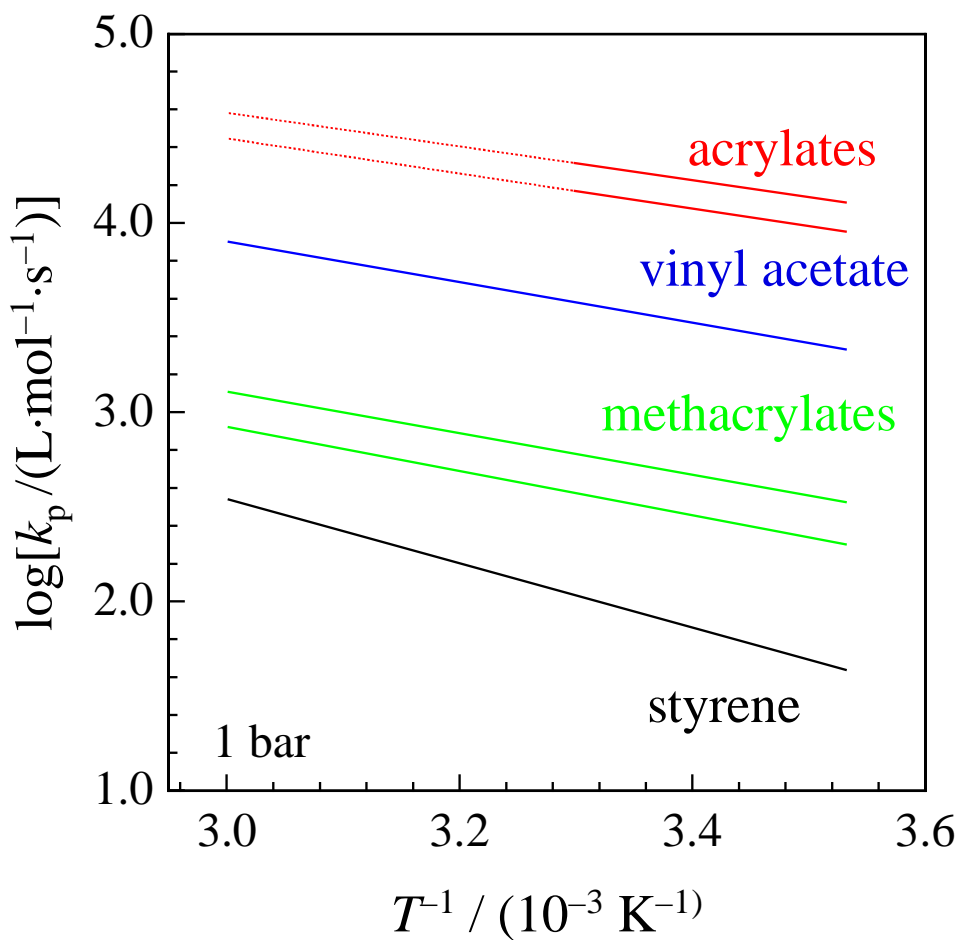
S. Beuermann, M. Buback, T. P. Davis, R. G. Gilbert, R. A. Hutchinson, O. F. Olaj, G. T. Russell, J. Schweer, A. M. van Herk, *Macromol. Chem. Phys.* **198**, 1545 (1997)

Butyl methacrylate homopolymerization in bulk

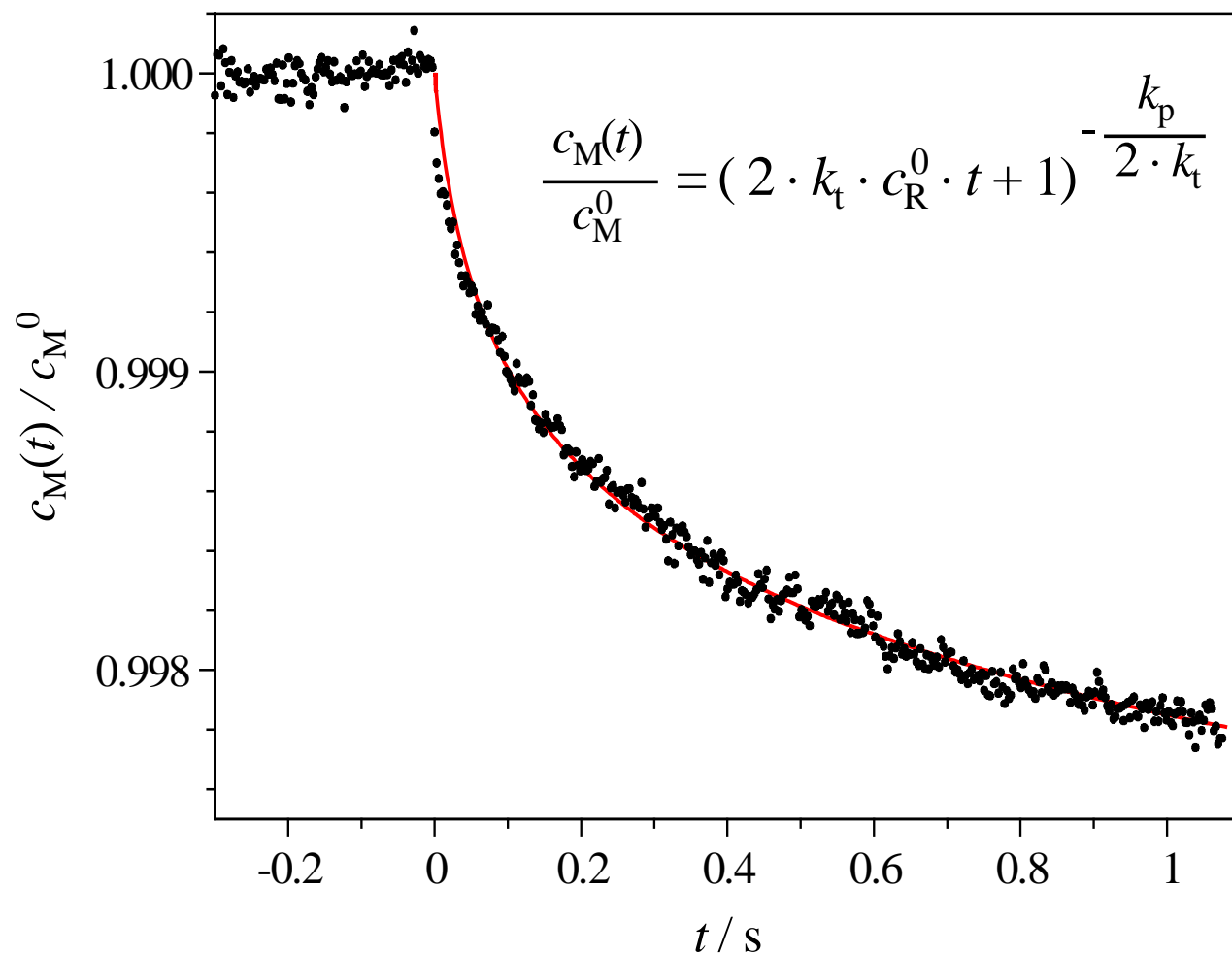


S. Beuermann, M. Buback, T. P. Davis, R. G. Gilbert, R. A. Hutchinson, A. Kajiwarra, B. Klumperman, G. T. Russell, *Macromol. Chem. Phys.* **201**, 1355 (2000)

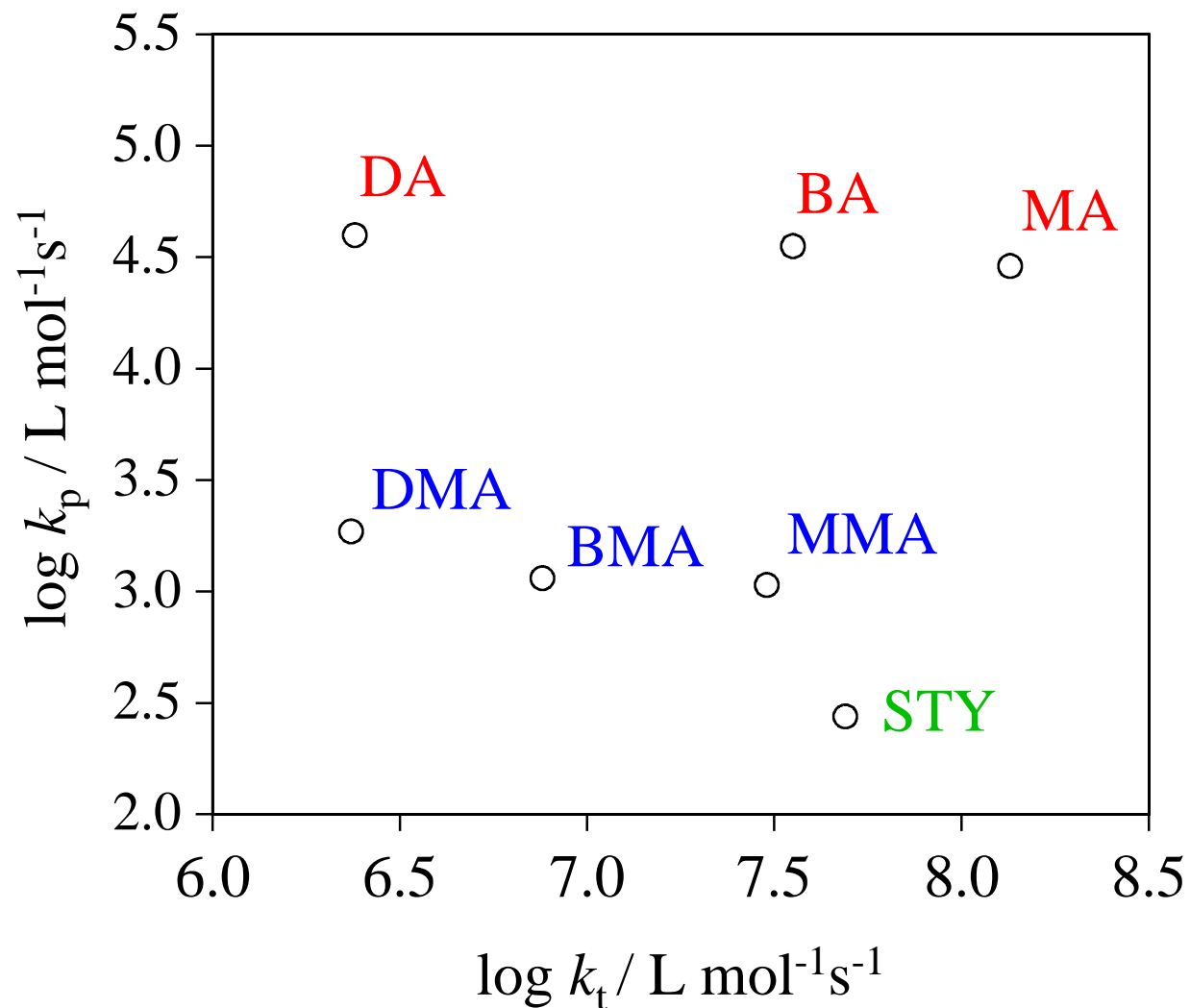
Temperature and pressure dependence of the propagation rate coefficient k_p



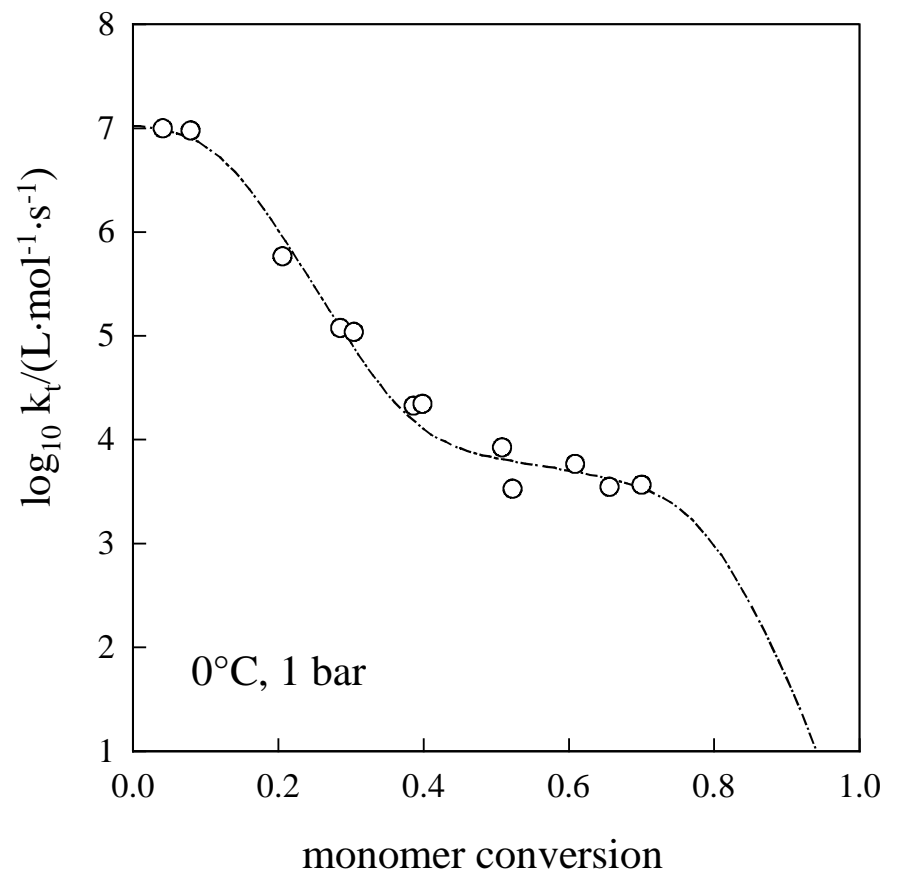
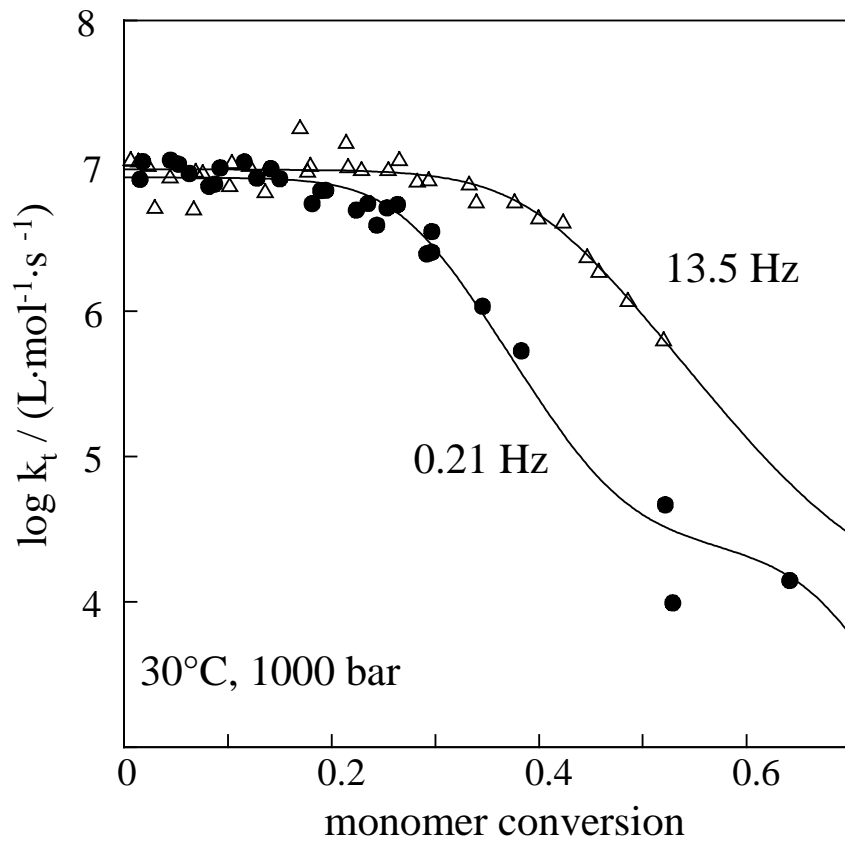
k_t from pulsed laser initiated polymerization in combination with time-resolved NIR spectroscopy



Propagation and termination rate coefficients at 40°C and 1000 bar

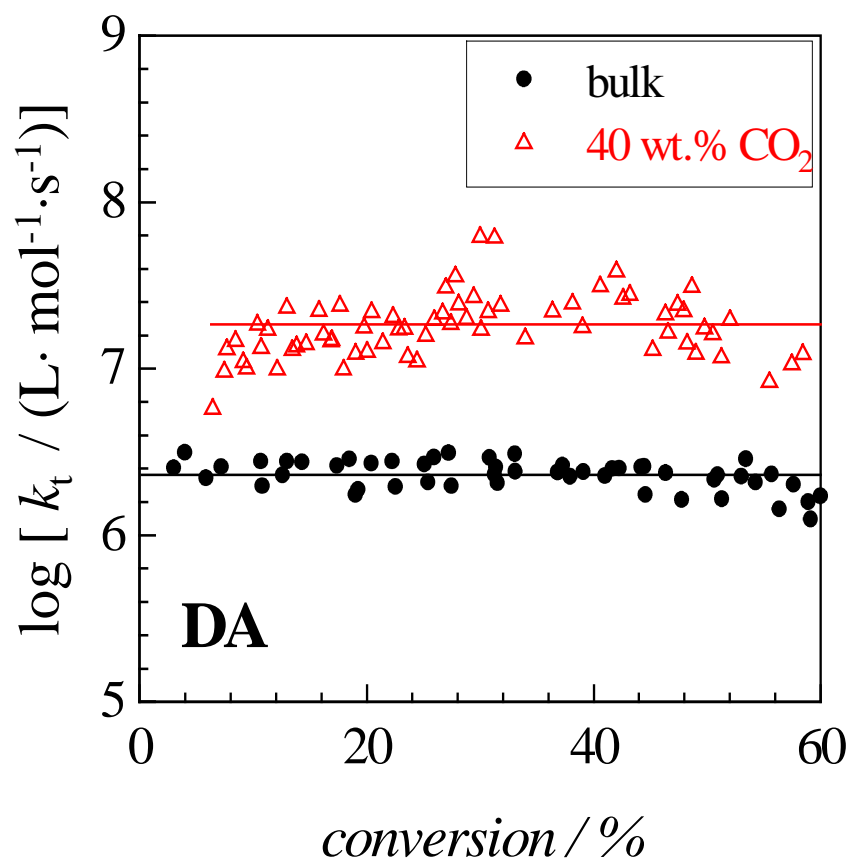
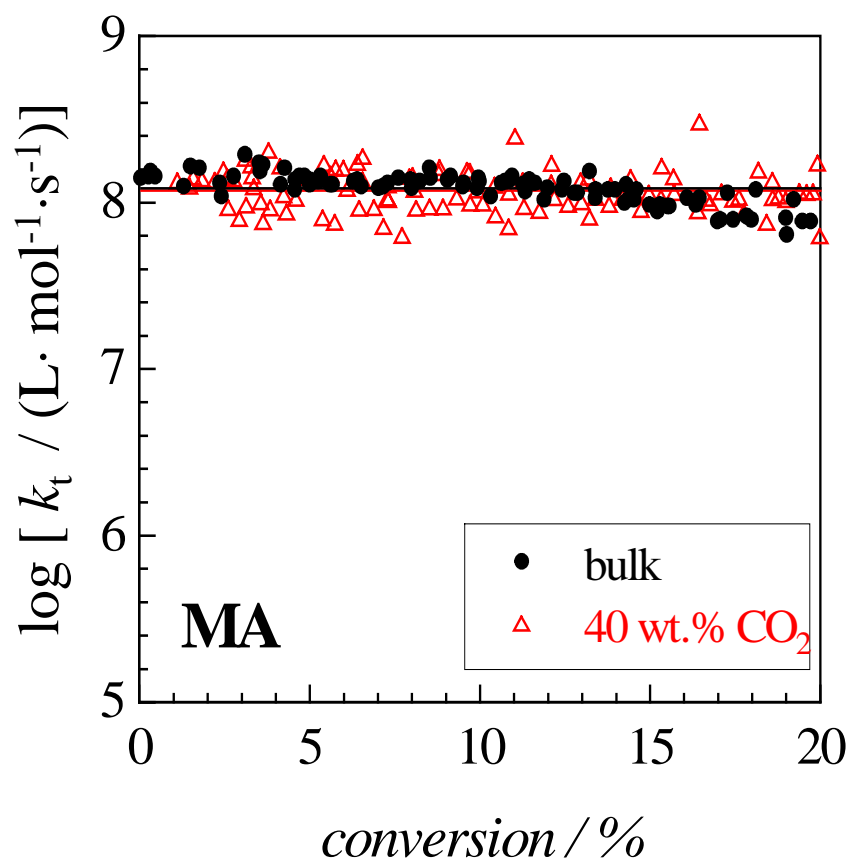


Termination rate coefficients for methyl methacrylate



R. Sack-Kouloumbri, G. Meyerhoff,
Makromol. Chem. **190**, 1133 (1989)

Termination rate coefficients in acrylate homopolymerizations



40°C, 1000 bar