IUPAC- Polymer Division IV

Subcommittee on Modelling of Polymerization Kinetics and Mechanisms

Member list: A. Anastasaki, C. Barner-Kowollik, S. Beuermann, M. Buback, M. Busch, P. Castignolles, M. Coote, D. D'hooge, M. Drache, C. Fellows, M. Gaborieau, A. Goto, M. Grady, Y. Guillaneuf,, S. Guillaume, D. Guironnet, S. Harrisson, A. M. van Herk, J. P. A. Heuts, K.-D. Hungenberg, R. A. Hutchinson, T. Junkers, A. Kajiwara, D. Konkolewicz, B. Klumperman, I. Lacík, P. Lacroix-Desmazes, J. R. Leiza, P. Lovell, K. Matyjaszewski, G. Moad, M. Monteiro, D. Moscatelli, A. N. Nikitin, S. Perrier, G. T. Russell, E. Sato, D. A. Shipp, J.-P. Vairon, H. Vale, P. Vana, J. Vorholz, E. B. Wysong, S. Yamago, P. B. Zetterlund, I. Zapata, S. Zhu

CO-CHAIRS : Tanja Junkers and Simon Harrisson

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

INTRODUCTION

Modeling and mechanistic studies into free-radical polymerizations are important for science and industry, but completely different model assumptions and parameter values are often reported for ostensibly the same systems.

The projects of the IUPAC Subcommittee "**Modeling of Polymerization Kinetics and Processes**" aim to harness international collaborations to establish standard methodologies for data generation and produce reliable, critically evaluated kinetic parameters for use by the international polymer community.

Benchmark propagation rate coefficients, k_p, have been obtained for styrene, many methacrylates, butyl and methyl acrylate, vinyl acetate, and methacrylic acid by critical evaluation of literature data and bespoke experiments. These efforts have been extended to termination rate coefficients, initiation rate parameters, backbiting, copolymerization and reversible-deactivation radical polymerization kinetics. A **machine accessible databank** for kinetic coefficients has also been launched. These projects rely on accurate and reproducible molecular weight data, typically obtained using size exclusion chromatography (SEC). Thus, a new project will study the reliability and reproducibility of the SEC technique, and provide best practices for the reporting SEC analyses.

PROJECTS

Project Number	TGL	Project Title
2009-050-1-400	G. Moad	Critically evaluated rate coefficients associated with initiation of radical polymerization
2013–051–1–400	G. T. Russell	Critically Evaluated Rate Parameters for Chain-length-Dependent Termination Kinetics in Radical Polymerization of Styrene and Methyl Methacrylate
2017-028-1-400	R. A. Hutchinson, T. Junkers	Critically evaluated rate coefficients for backbiting in acrylate radical polymerization
2019-023-1-400	A. M. van Herk	Experimental methods and data evaluation procedures for the determination of radical copolymerization reactivity ratios
2019-045-1-400	T. Junkers	Development of a Machine Accessible Kinetic Databank for Radical Polymerizations
2022-030-2-400	T. Junkers, S. Harrisson	Accuracy of size exclusion chromatography in relation to polymer synthesis and polymerization modelling
2018-009-2-500	D. Shaw (ISCED Interdisciplinary Project)	Guidance for the Compilation, Critical Evaluation and Dissemination of Chemical Data

MONOMER DATABASE

IUPAC Monomer Database:

www.sql.polymatter.net

Or get the app!

BENCHMARKED k_p DATA

Benchmarked activation energies and pre-exponential factors of propagation rate coefficients in free radical polymerization

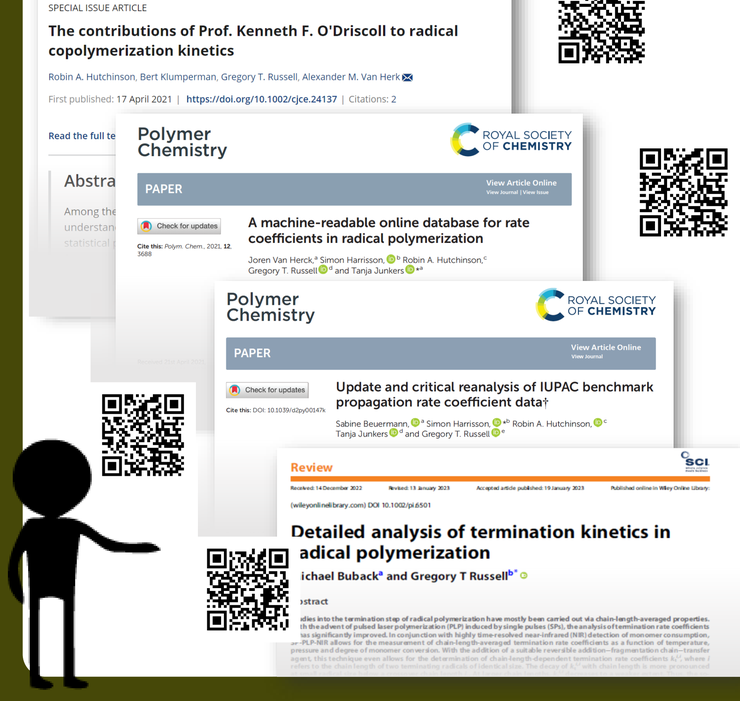
Revised IUPAC benchmark values[b]

Monomer	A (L mol^{-1} s^{-1})	E_A (kJ mol^{-1})	k_p at 25 °C (L mol^{-1} s^{-1})	T (°C)	N[c]
STY[1]	$10^{7.51(19)}$	**31.8(5)**	87(2)	−12–120	16
MMA[2]	$10^{6.50(08)}$	22.8(4)	325(6)	−18–92	19
EMA[3]	$10^{6.53(20)}$	22.9(7)	337(13)	1–91	4
BMA[3]	$10^{6.57(09)}$	22.7(5)	**390(11)**	−20–91	8
DMA[3]	$10^{6.31(15)}$	20.5(8)	522(24)	9–90	3
CHMA[4]	$10^{6.78(15)}$	22.9(8)	585(27)	10–90	3
GMA[4]	$10^{6.85(16)}$	23.4(9)	**558(29)**	20–90	3
BnMA[4]	$10^{6.71(13)}$	22.3(7)	643(30)	6–90	4
iBoMA[4]	$10^{6.77(18)}$	23.1(9)	539(30)	0–91	2
BA[5]	$\mathbf{10^{7.22(11)}}$	17.3(6)	$\mathbf{15.7(5) \times 10^3}$	−65–70	8
MAA[6]	$10^{6.21(18)}$	15.1(1.0)	$3.73(21) \times 10^3$	18–89	2
MA[7]	$10^{7.25(13)}$	17.8(7)	$\mathbf{13.7(5) \times 10^3}$	−26–61	4
VAc[8]	$10^{7.13(12)}$	20.4(7)	$3.62(12) \times 10^3$	5–70	6

[b] reproduced from Beuermann et al., *Polym. Chem.* 2022, 13, 1891-1900
[c] *N* represents number fo independent studies

1 M. Buback, R. G. Gilbert, R. A. Hutchinson, B. Klumperman, F.-D. Kuchta, B. Manders, K. F. O'Driscoll, G. T. Russell and J. Schweer, *Macromol. Chem. Phys.*, 1995, **196**, 3267–3280.
2 S. Beuermann, M. Buback, T. P. Davis, R. G. Gilbert, R. A. Hutchinson, O. F. Olaj, G. T. Russell, J. Schweer and A. M. van Herk, *Macromol. Chem. Phys.*, 1997, **198**, 1545–1560.
3 S. Beuermann, M. Buback, T. P. Davis, R. G. Gilbert, R. A. Hutchinson, A. Kajiwara, B. Klumperman and G. T. Russell, *Macromol. Chem. Phys.*, 2000, **201**, 1355–1364.
4 S. Beuermann, M. Buback, T. P. Davis, N. García, R. G. Gilbert, R. A. Hutchinson, A. Kajiwara, M. Kamachi, I. Lacík and G. T. Russell, *Macromol. Chem. Phys.*, 2003, **204**, 1338–1350.
5 J. M. Asua, S. Beuermann, M. Buback, P. Castignolles, B. Charleux, R. G. Gilbert, R. A. Hutchinson, J. R. Leiza, A. N. Nikitin, J. P. Vairon and A. M. van Herk, *Macromol. Chem. Phys.*, 2004, **205**, 2151–2160.
6 S. Beuermann, M. Buback, P. Hesse, F.-D. Kuchta, I. Lacík and A. M. van Herk, *Pure Appl. Chem.*, 2007, **79**, 1463–1469.
7 C. Barner-Kowollik, S. Beuermann, M. Buback, P. Castignolles, B. Charleux, M. L. Coote, R. A. Hutchinson, T. Junkers, I. Lacík, G. T. Russell, M. Stach and A. M. van Herk, *Polym. Chem.*, 2014, **5**, 204–212.
8 C. Barner-Kowollik, S. Beuermann, M. Buback, R. A. Hutchinson, T. Junkers, H. Kattner, B. Manders, A. N. Nikitin, G. T. Russell and A. M. van Herk, *Macromol. Chem. Phys.*, 2017, **218**, 1600357.

RECENT PUBLICATIONS



PERSPECTIVES

There is a continuing need for **reliable**, **benchmarked kinetic data** which extends beyond radical polymerizations. However, access to equipment and funding is limited.

Accurate and **reproducible** molecular weight determination is fundamental to kinetic studies of polymerizations – a round robin interlaboratory study on size exclusion chromatography is underway. Other planned projects seek to establish benchmarked kinetic parameters for non-radical polymerizations, as well as to develop best practices for data curation and management to faciliate the application of artificial intelligence and machine learning techniques.

GROUP PHOTO

SUBCOMITTEE VIRTUAL MEETING, DECEMBER 5, 2022