Attachment 1.

IUPAC "Critical Evaluation of Data" Meeting São Paulo 2017

Subcommittee on Modeling of Polymerization Kinetics and Processes

Division IV (Polymers)

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Motivation/Scope of the Subcommittee

Modeling and mechanistic studies into free-radical polymerizations are important for science and industry, but often completely different model assumptions and parameter values are reported for ostensibly the same systems. The projects of the IUPAC Subcommittee "Modeling of Polymerization Kinetics and Processes" aim to rectify this situation through international collaboration, by producing **critically evaluated kinetic parameters**, whose values are reliable and which can be used by the international polymer community. Moreover, **reliable methodologies** have been established by the IUPAC Subcommittee.

Benchmark propagation rate coefficients, k_p, have been obtained for styrene, many methacrylates, butyl acrylate, methacrylic acid, and vinyl acetate by critical evaluation and also by independent experiments. These efforts are currently extended to termination rate coefficients, initiation rate parameters, and reversible-deactivation radical polymerization kinetics.

Overview of the Subcommittee

- Currently, 44 members from 16 countries mainly from academia (36 out of 44).
- Formed in ~ 1990. Typically 3-5 projects active at a time.
- 16 total publications, dating from 1988 to 2017.
- 2767 total citations (01July 2017 from Web of Science database)

Why successful? A recognized need by the community

Radical Polymerization Rate Coefficients: The Basic Mechanisms

Initiation	$I \xrightarrow{k_d} 2\,f\,P_1$	Propagation	$P_n + M \xrightarrow{k_p} P_{n+1}$
Termination	$P_n + P_m \xrightarrow{k_{t,c}} D_{n+m}$	Transfer to Monomer	$P_n + M \xrightarrow{k_{tr}^{mon}} D_n + P_1$
	$P_n + P_m \xrightarrow{k_{t,d}} D_n + D_m$	Transfer to Solvent	$P_n + S \xrightarrow{k_{tr}^{sol}} D_n + P_1$

$$-\frac{d[M]}{dt} = k_p[M]P_{tot} \qquad (DP_n)_{inst} = \frac{k_p[M]}{(k_{td} + 0.5k_{tc})P_{tot} + k_{tr}^{mon}[M] + k_{tr}^{sol}[S]} \qquad P_{tot} = \left(\frac{2fk_d[I]}{(k_{tc} + k_{td})}\right)^{1/2}$$

- Typical measured quantities (rate, average chain length) are dependent on ratios of rate coefficients
- Individual coefficients are needed in order to generalize and extend representation to multicomponent systems

Why successful? A recognized need by the community

Individual rate coefficients: Polymer Handbook (1988)

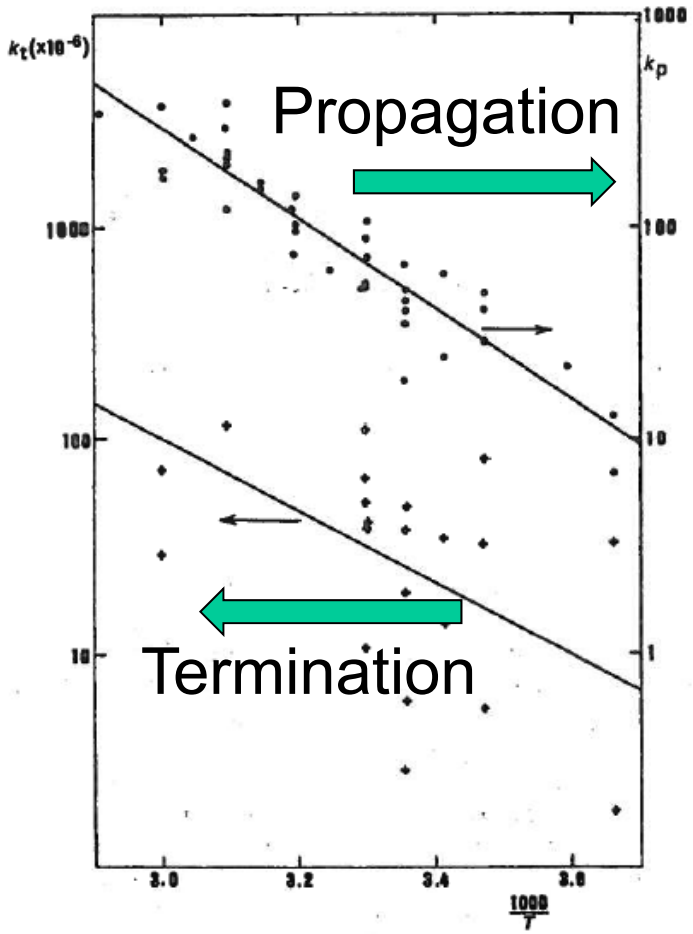

Figure 1. Arrhenius plots of all bulk polymerization data for styrene for k_p (•) and k_t (+). Solid lines are least squares obtained by assuming all points to be of equal value.

The two monomers styrene and methyl methacrylate

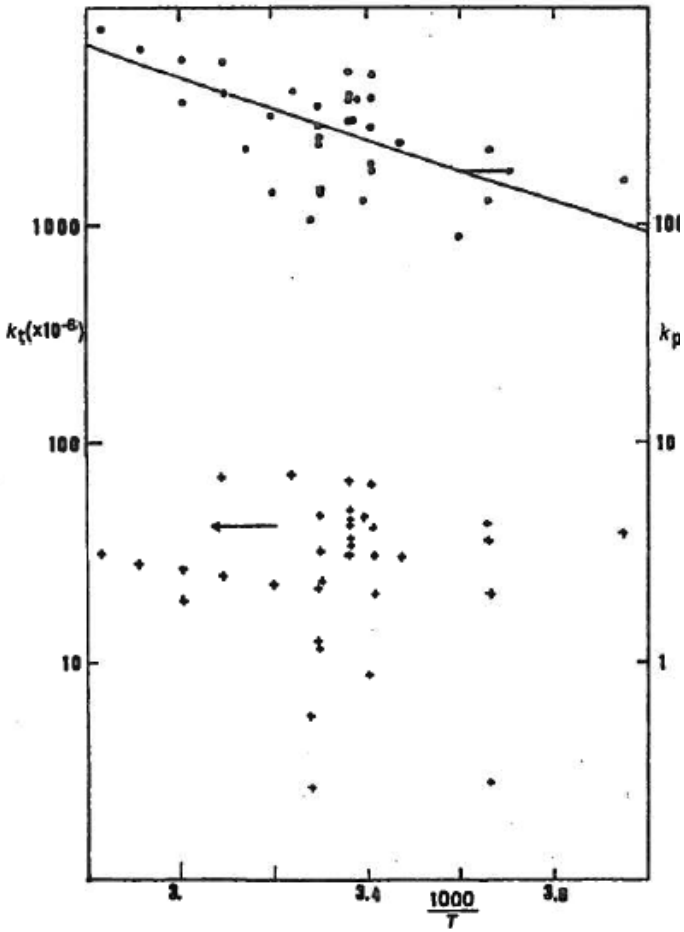

Figure 2. Arrhenius plots of all bulk polymerization data for methyl methacrylate for k_p (•) and k_t (+). Solid lines are least squares obtained by assuming all points to be of equal value. The line for k_t is not shown since a horizontal line for a temperature independent k_t could be a better representation.

Order of magnitude scatter for styrene and methyl methacrylate monomers.

Even worse for other systems (very unreliable).

But individual rate coefficients needed for modeling!

Definition of the problem: The "dilemma" papers

"Consistent values of rate parameters in free radical polymerization systems"
162 citations (0 since Jan 2016)
M. Buback, L. H. Garcia-Rubio, R. G. Gilbert, D. H. Napper, J. Guillot, A. E. Hamielec, D. Hill, K. F. O'Driscoll, O. F. Olaj, J. Shen, D. Solomon, G. Moad, M. Stickler, M. Tirrell, M. A. Winnik, *J. Polym. Sci., Polymer Letters Ed.* **26**, 293-297 (1988).

"Consistent values of rate parameters in free radical polymerization systems. Part II: Outstanding dilemmas and recommendations" **209 citations (5 since 01/16)**

M. Buback, R. G. Gilbert, G. T. Russell, D. J. T. Hill, G. Moad, K. F. O'Driscoll, J. Shen, M. A. Winnik, *J. Polym. Sci., Polym. Chem. Ed*. **30**, 851-863 (1992).

"Consistent values of rate parameters in free-radical polymerization systems"
39 citations (2 since 01/16)

R. G. Gilbert, *Pure App. Chem.* **64**, 1563-1567 (1992).

Why successful? Development of New Experimental Techniques

- New pulsed-laser polymerization (PLP) experimental techniques emerged in the late 1980's and early 1990's

- PLP coupled with off-line MWD analysis, for direct k_p determination
  - first proposed and implemented by Olaj in 1987
  - now employed by several academic and industrial research groups (very active area of research starting in the 1990's)

Now widely referred to as "the IUPAC recommended technique"

- PLP coupled with on-line FTIR analysis, to measure k_t/k_p as a function of conversion
  - first proposed and implemented by Buback in 1987
  - modified techniques (on-line EPR) used to measure chain-length dependencies in the past 10 years

Critically evaluated rate coefficients for free-radical polymerization, 1

Propagation rate coefficient for styrene

Michael Buback[a], *Robert G. Gilbert**[b], *Robin A. Hutchinson*[c], *Bert Klumperman*[d], *Frank-Dieter Kuchta*[a], *Bart G. Manders*[d], *Kenneth F. O'Driscoll*[e], *Gregory T. Russell*[f], *Johannes Schweer*[g]

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[g] Bayer AG, Polymerstrukturforschung — ZF-TPP 5 Gebäude Q 18, D-51368 Leverkusen 1, Germany

(Received: February 16, 1995)

SUMMARY:

Pulsed-laser polymerization (PLP) in conjugation with molecular weight distribution (MWD) measurement has emerged as the method of choice for determining the propagation rate coefficient k_p in free-radical polymerizations. Detailed guidelines for using this technique (including essential internal consistency checks) and reporting the results therefrom are given by the authors, members of the IUPAC Working Party on *Modeling of kinetics and processes of polymerization*. The results for PLP-MWD k_p measurements

Independent data sets from 7 research groups

Consensus reached to establish reporting of experimental details and criteria for evaluation of data

Tab. 1. Critically evaluated values of the propagation rate coefficient k_p for styrene as a function of temperature

Temp. in °C	k_p / L · mol^{-1} · s^{-1}	t_d/s	Initiator [a]	[initiator] / mmol · L^{-1}	Pulse energy in mJ	Reference
−11.8	13.5	0.5	DMPA	5	30	31)
−11.7	13.5	0.5	DMPA	5	30	31)
−11.2	14.2	1	DMPA	5	30	31)
−10.9	14.62	1	DMPA	5	30	31)
−2.3	23.2	0.5	DMPA	5	30	31)
−2.3	24.1	1	DMPA	5	30	31)
−1.9	24.5	1	DMPA	5	30	31)
−1.3	24.6	0.5	DMPA	5	30	31)
8.5	43.9	0.5	DMPA	5	30	31)
8.5	43.2	0.5	DMPA	5	30	31)
8.7	43.8	1	DMPA	5	30	31)
8.7	43.8	1	DMPA	5	30	31)
20.6	75.5	0.5	DMPA	5	30	31)
21	75.9	0.5	DMPA	5	30	31)
21.3	71.9	0.2	DMPA	5	30	31)
25	77 [b]					26)
25	78 [b]	0.2−8	AIBN	1−5	35	28)
25	84 [b]	0.2	AIBN	5	35	27)
25	78.6 [b]	0.2−8	AIBN	1	35	30)
25	95 [b]	0.1	DMPA	5	varied	21)
29.7	112	0.1	DMPA	5	30	31)
29.8	113	0.2	DMPA	5	30	31)
30	107 [b]	0.1	benzoin	5	40	19)
30	116 [b]	0.1	DMPA	10	3	29)
31.3	114	0.5	DMPA	5	30	31)
35	120 [b]	0.1−10	AIBN, benzoin	5	35	28)
38.8	172	0.2	DMPA	5	30	31)
39.4	168	0.1	DMPA	5	30	31)
39.5	170	0.2	DMPA	5	30	31)
45	168 [b]	0.1−10	AIBN, benzoin	5	35	28)
48.9	240	0.1	DMPA	5	30	31)
49	248	0.2	DMPA	5	30	31)
49.8	229	0.1	DMPA	5	30	31)
50	260 [b]	0.1	benzoin	5	40	19)
50	248 [b]	0.2	DMPA	8	3	29)
50	248	0.2	DMPA	5	30	31)
55	249 [b]	0.1−10	AIBN, benzoin	5	35	28)
58.3	343	0.3	DMPA	5	30	31)
58.4	343	0.1	DMPA	5	30	31)
59.1	344	0.1	DMPA	5	30	31)
59.3	341	0.1	DMPA	5	30	31)
59.7	342	0.1	DMPA	5	30	31)
67.5	477	0.1	DMPA	5	30	31)
68.4	469	0.2	DMPA	5	30	31)
68.6	473	0.2	DMPA	5	30	31)

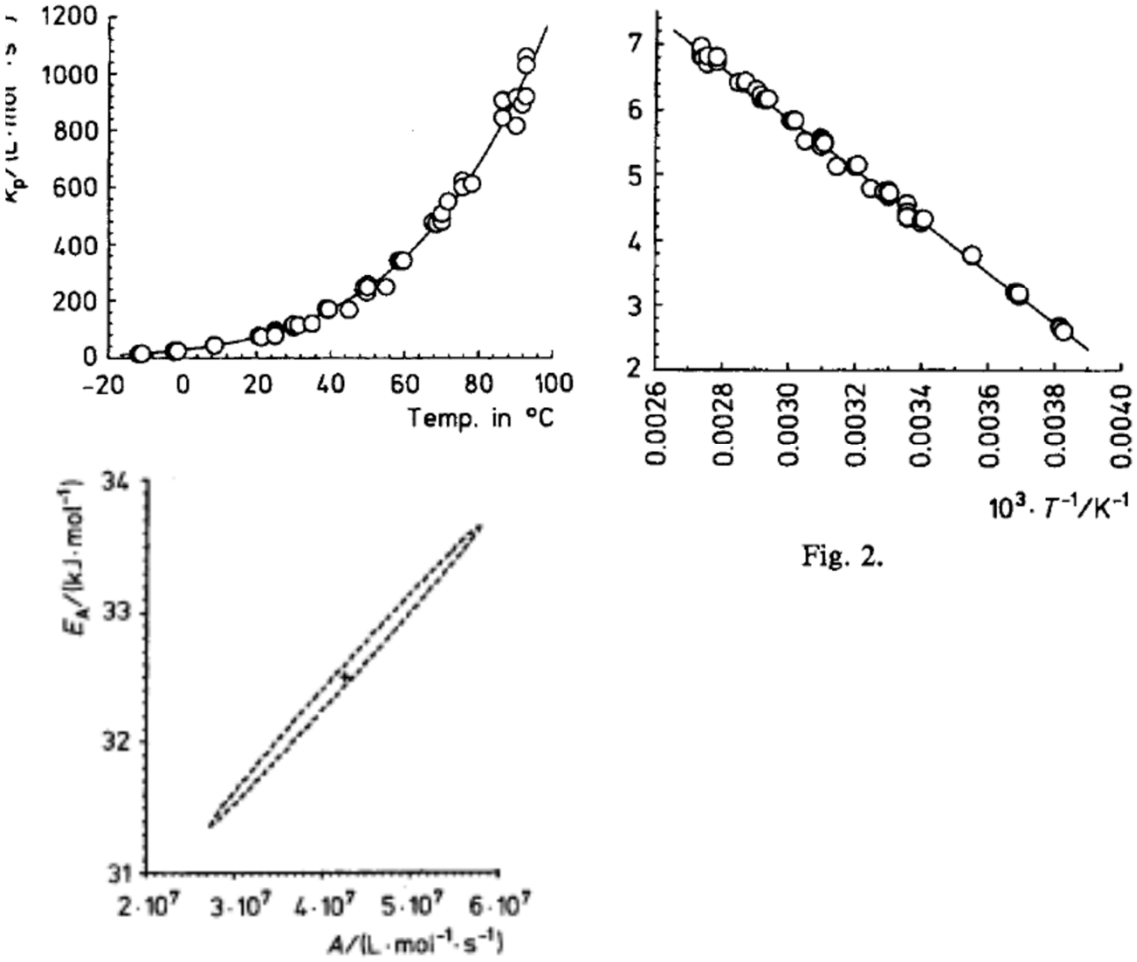


Fig. 2.

$$k_p = 10^{7.630}\ \mathrm{L \cdot mol^{-1} \cdot s^{-1}} \exp\left(\frac{-32.51\ \mathrm{kJ \cdot mol^{-1}}}{R \cdot T}\right)$$

$$-12\,^{\circ}\mathrm{C} \leq \text{temperature} \leq 93\,^{\circ}\mathrm{C}$$

Table of critically evaluated individual data points

Graphical representations, fit of data with error estimates

Publications – Propagation

"Critically evaluated rate coefficients for free-radical polymerization, 1. Propagation rate coefficients for styrene" **584 citations (37 since 01/16)**

M. Buback, R. G. Gilbert, R. A. Hutchinson, B. Klumperman, F.-D. Kuchta, B. G. Manders, K. F. O'Driscoll, G. T. Russell, J. Schweer, *Macromol. Chem. Phys*. **196**, 3267-3280 (1995).

"Critically evaluated rate coefficients for free-radical polymerization, 2. Propagation rate coefficients for methyl methacrylate" **455 citations (34 since 01/16)**

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**, 1545-1560 (1997).

"Critically-evaluated propagation rate coefficents in free radical polymerizations. 1. Styrene and methyl methacrylate" **111 citations (3 since 01/16)**

R. G. Gilbert, *Pure Appl. Chem.* **68**, 1491-1494 (1996).

Publications – Propagation (cont.)

"Critically evaluated rate coefficients for free-radical polymerization - 3. Propagation rate coefficients for alkyl methacrylates" **201 citations (21 since 01/16)**
S. Beuermann, M. Buback, T.P. Davis, R.G. Gilbert, R.A. Hutchinson, A. Kajiwara, B. Klumperman, and G.T. Russell, *Macromol. Chem. Phys*. **201**, 1355-1364 (2000).

"Critically evaluated rate coefficients for free-radical polymerization, 4. Propagation rate coefficients for methacrylates with cyclic ester groups" **84 citations (16 since 01/16)**
S. Beuermann, M. Buback, T. P. Davis, N. García, R. G. Gilbert, R. A. Hutchinson, A. Kajiwara, M. Kamachi, I. Lacík, G. T. Russell, *Macromol. Chem. Phys*. **204**, 1338-1350 (2003).

"Critically evaluated rate coefficients for free-radical polymerization, 5. Propagation rate coefficient for butyl acrylate" **256 citations (31 since 01/16)**
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, A. M. van Herk, *Macromol. Chem. Phys*. **205**, 2151-2160 (2004).

Publications – Propagation (cont.)

"Critically evaluated rate coefficients for free-radical polymerization, Part 6. Propagation rate coefficient of methacrylic acid in aqueous solution"
52 citations (14 since 01/16)
S. Beuermann, M. Buback, P. Hesse, F.-D. Kuchta, I. Lacík, A. M. van Herk, *Pure Appl. Chem.* **79**, 1463-1469 (2007).

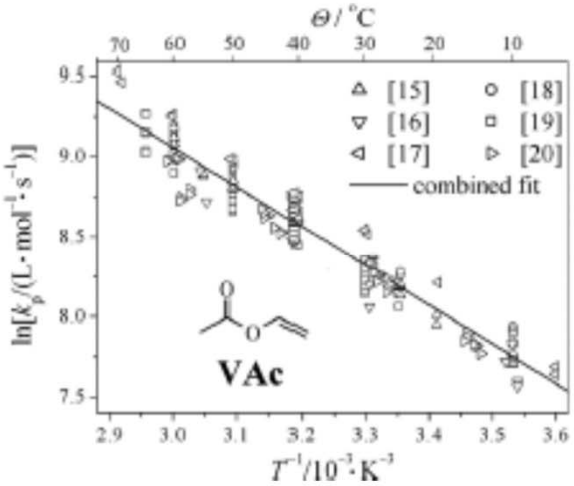
"Determination of the Propagation Rate Coefficient of Vinyl Pivalate based on EPR Quantification of Propagating Radical Concentration" **10 citations (5 since 01/16)**
N. Kubota, A. Kajiwara, P. B. Zetterlund, M. Kamachi, J. Treurnicht, M. P. Tonge, R. G. Gilbert, B. Yamada, *Macromol. Chem. Phys.* **208**, 1403-1411 (2007).

"Critically evaluated rate coefficients for free-radical polymerization, 7. Secondary-radical propagation rate coefficient for methyl acrylate in bulk"
37 citations (21 since 01/16)
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, A. M. van Herk, *Polym. Chem.* **4**, 204-212 (2014).

Critically Evaluated Rate Coefficients in Radical Polymerization – 8. Propagation Rate Coefficients for Vinyl Acetate in Bulk

Christopher Barner-Kowollik, Sabine Beuermann, Michael Buback, Robin A. Hutchinson,* Thomas Junkers, Hendrik Kattner, Bart Manders, Anatoly N. Nikitin, Gregory T. Russell, Alex M. van Herk

Propagation rate coefficient values, k_p, reported by several groups for radical polymerization of bulk vinyl acetate are critically evaluated. All data are obtained by the combination of pulsed-laser polymerization and subsequent polymer analysis by size exclusion chromatography, as recommended by the IUPAC Working Party on Modeling of Polymerization Kinetics and Processes. Although a small (≈15%) increase in k_p is observed as laser pulse repetition rate is increased from low (25–100 Hz) to high (300–500 Hz) values, all of the data fulfill the required consistency criteria and thus are combined into a benchmark set covering the temperature range of 5–70 °C. The data are fitted well by an Arrhenius relation resulting in a pre-exponential factor of 1.35×10^7 L mol^{-1} s^{-1} and an activation energy of 20.4 kJ mol^{-1}, with 95% confidence ellipsoids for the parameters also presented.



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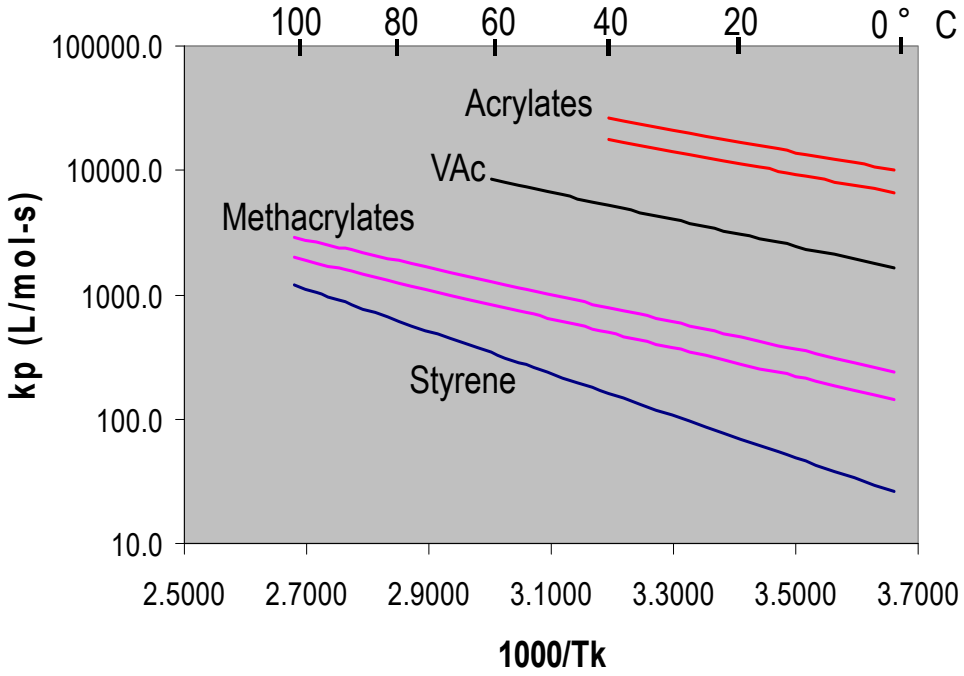
DOI: 10.1002/macp.201600357

Critically Evaluated Rate Coefficients in Radical Polymerization: Propagation

A very successful series

Monomer	Journal	Year	Web of Science Citations (Jun17)
1. Styrene	*Macromol. Chem. Phys.*	1995	584
2. Methyl Methacrylate	*Macromol. Chem. Phys.*	1997	455
3. Alkyl Methacrylates	*Macromol. Chem. Phys.*	2000	201
4. Functional Methacrylates	*Macromol. Chem. Phys.*	2003	84
5. *n*-Butyl Acrylate	*Macromol. Chem. Phys.*	2004	256
6. Methacrylic Acid	*Pure Appl. Chem.*	2007	52
7. Methyl Acrylate	*Polym. Chem.*	2014	37
8. Vinyl Acetate	*Macromol. Chem. Phys.*	2017	1

Widely-recognized Outcome: Generalization of Structure/Reactivity



	Activation Energy (kJ/mol)	k_p at 30 °C (L/mol-s)
Styrene	32-33	110
Methacrylates:	21-23	
Methyl		380
Dodecyl		600
Vinyl Acetate	20-21	4000
Acrylates:	15-18	
Methyl		14000
Dodecyl		21000

- Clear differences seen between monomer families
- Similar behavior within a monomer family (e.g.; acrylates or methacrylates):
  - k_p increases with ester size; very similar activation energies (and activation volumes)
- functional methacrylates (e.g.; glycidyl, hydroxypropyl) have also been studied

Success arose from a confluence of factors

Recognized need in the research committee

+

New experimental technique(s)

+

Multiple academic and industrial groups interested in collecting data (aligned with their own research interests)

+

Consensus on evaluation criteria

+

Reward for researchers (heavily cited papers)

IUPAC offered an umbrella structure for arriving at consensus through face-to-face meetings at sponsored conferences, and for funding projects

Other Publications from Subcommittee

"Critically evaluated termination rate coefficients for free-radical polymerization – 1. The current situation" **136 citations (11 since 01/16)**

M. Buback, M. Egorov, V. Kaminsky, O. F.Olaj, G. T. Russell, P. Vana, G. Zifferer, *Macromol. Chem. Phys*. **203**, 2570-2582 (2002).

"Critically evaluated termination rate coefficients for free-radical polymerization, 2. Experimental methods" **93 citations (7 since 01/16)**

C. Barner-Kowollik, M. Buback, M. Egorov, T. Fukuda, R. G. Gilbert, A. Goto, G. T. Russell, P. Vana, B. Yamada, P. B. Zetterlund, *Prog. Polym. Sci*. **30**, 605-643 (2005).

"Mechanism and Kinetics of Dithiobenzoate-Mediated RAFT Polymerization, 1. The Current Situation" **315 citations (12 since 01/16)**

C. Barner-Kowollik, M. Buback, B. Charleux, M. L. Coote, M. Drache, T. Fukuda, A. Goto, B. Klumperman, A. B. Lowe, J. B. McLeary, G. Moad, M. J. Monteiro, R. D. Sanderson, M. P. Tonge, P. Vana, *J. Polym. Sci. Polym. Chem.* **44**, 5809-5831 (2006).

"SEC Analysis of Poly(Acrylic Acid) and Poly(Methacrylic Acid)"
11 citations (9 since 01/16)

I. Lacík, M. Stach, + 18 others, *Macromol. Chem. Phys.* **216**, 23-37 (2015).

Future Outlook

IUPAC does not perform or sponsor experimental work that produces chemical data. Rather it encourages the formation of international teams of qualified experts to compile and critically evaluate data gathered by others. (Hibbert, Shaw, Magalhães)

We may be approaching the point of diminishing returns.

- Technique is widely recognized and utilized to examine new and difficult systems. (*Role of IUPAC has been realized*.)

However,

- Difficult to get momentum/consensus on topics (low-hanging fruit has been harvested)
- Applications are getting more specialized (difficult to have multiple groups study the same system)