IUPAC Polymer Division Meeting, Cairns 2018

"Subcommittee on Modeling of Polymerization Kinetics and Processes"

Co-Chairs	Prof. R. A. Hutchinson	(Kingston, Canada)
	Prof. S. Beuermann	(Clausthal, Germany)

Membership (44 from 16 countries – no recent changes)

Prof. C. Barner-Kowollik (Brisbane, AUS)
Prof. D. Bertin (Marseille, FR)
Prof. S. Beuermann (Clausthal, D)
Prof. M. Buback (Göttingen, D)
Prof. M. Busch (Darmstadt TU, D)
Prof. P. Castignolles (Western Sydney, AUS)
Prof. B. Charleux (Paris, FR)
Prof. M. Coote (Canberra, AUS)
Prof. M. Destarac (Toulouse, FR)
Prof. D. D'hooge (Ghent, BE)
Prof. T. Fukuda (Kyoto, JPN)
Dr. M. Gaborieau (Western Sydney, AUS)
Prof. R. G. Gilbert (Brisbane, AUS)
Prof. A. Goto (Singapore)
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Prof. A. M. van Herk (Singapore)
Dr. P. Hesse (Ludwigshafen, D)
Dr. J. P. A. Heuts (Eindhoven, NL)
Dr. K. Hungenberg (Ludwigshafen, D)
Prof. R. A. Hutchinson (Kingston, CAN)
Prof. T. Junkers (Melbourne, AUS)
Prof. A. Kajiwara (Nara, JPN)
Prof. T. Kitayama (Osaka, JPN)
Prof. B. Klumperman (Stellenbosch, ZA)
Prof. I. Lacík (Bratislava, SK)
Dr. P. Lacroix-Desmazes (Montpellier, FR)
Prof. J. R. Leiza (San Sebastián, ES)
Prof. P. Lovell (Manchester, UK)
Prof. K. Matyjaszewski (Pittsburgh, USA)
Dr. G. Moad (Melbourne, AUS)
Prof. M. Monteiro (Brisbane, AUS)
Prof D. Moscatelli (Milan, IT)
Dr. A. N. Nikitin (Moscow, RUS)
Prof. S. Perrier (Sydney, AUS)
Prof. G. T. Russell (Christchurch, NZ)
Dr. E. Sato (Osaka City, JPN)
Prof. D. A. Shipp (Potsdam, USA)
Prof. J.-P. Vairon (Paris, FR)
Prof. P. Vana (Göttingen, D)
Dr. J. Vorholz (Darmstadt, D)
Dr. E. B. Wysong (Wilmington, USA)
Prof. S. Yamago (Kyoto, JPN)
Prof. P. B. Zetterlund (NSW, Sydney, AUS)
Prof. S. Zhu (Hamilton, CAN)

Subcommittee Mandate

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 have been extended to termination rate coefficients, initiation rate parameters, and reversible-deactivation radical polymerization kinetics.

Origins of the subcommittee: the “dilemma” papers

“Consistent values of rate parameters in free radical polymerization systems”
162 citations
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” **217 citations**

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

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

Critically Evaluated Rate Coefficients in Radical Polymerization: Propagation

Monomer	Journal	Year	Web of Science Citations (Jun18)	Google Scholar Citations (May18)
Styrene	*Macromol. Chem. Phys.*	1995	595	714
Methyl Methacrylate	*Macromol. Chem. Phys.*	1997	473	553
Alkyl Methacrylates	*Macromol. Chem. Phys.*	2000	217	259
Functional Methacrylates	*Macromol. Chem. Phys.*	2003	89	107
n-Butyl Acrylate	*Macromol. Chem. Phys.*	2004	273	319
Methacrylic Acid	*Pure Appl. Chem.*	2007	53	65
Methyl Acrylate	*Polym. Chem.*	2014	45	49
Vinyl Acetate	*Macromol. Chem. Phys.*	2017	3	7

A very successful series: PLP-SEC now widely referred to as "the IUPAC recommended technique"

A New IUPAC Initiative

An “Interdivisional Discussion of Critical Evaluation of Chemical Data” has been started to bring a ‘whole-of-IUPAC’ approach to critical evaluation of data, addressing the following questions:

- How can IUPAC produce critical evaluations that are more useful to chemists and non-chemist users of chemical data?
- How can IUPAC adjust presentation formats and dissemination channels to make critically evaluated data more accessible to potential users?
- How can groups of critical evaluators within IUPAC better learn from one another’s experience?
- How can IUPAC identify overlooked data categories of high societal value for critical evaluation and organize efforts in response?

First meeting held in São Paulo (General Assembly, July 2017), as summarized in *Chemistry International* (2Q 2018, https://doi.org/10.1515/ci-2018-0214)

Critical Evaluation of Chemical Data (New Initiative)

Two outcomes have emerged:

1. Interdivisional Project "Guidance for the Compilation, Critical Evaluation and Dissemination of Chemical Data" started:
   - "This project will work with all Divisions, and CPCDS, and any other interested parties within IUPAC towards providing a framework to developing the IUPAC guidance for the production and use of high-visibility product evaluated data recognized widely as "Evaluated by IUPAC".
   - Robin Hutchinson is Div IV representative

2. Benchmark data sets to be presented directly on IUPAC website
   - Prototype developed (Stuart Chalk, Committee on Publications and Cheminformatics Data Standards)

Prototype: https://sds.coas.unf.edu/poly/

Polymer Chemistry

PAPER

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Cite this: Polym. Chem. 2014, 5, 204

Criticaly evaluated rate coefficients in radical polymerization – 7. Secondary-radical propagation rate coefficients for methyl acrylate in the bulk†

Christopher Barner-Kowollik,[*ab] Sabine Beuermann,[c] Michael Buback,[d] Patrice Castignolles,[e] Bernadette Charleux,[f] Michelle L. Coote,[g] Robin A. Hutchinson,[h] Thomas Junkers,[*i] Igor Lacík,[j] Gregory T. Russell,[k] Marek Stach[j] and Alex M. van Herk[lm]

Propagation rate coefficient (k_p) data for radical polymerization of methyl acrylate (MA) in the bulk are critically evaluated and a benchmark dataset is put forward by a task-group of the IUPAC Subcommittee on *Modeling of Polymerization Kinetics and Processes*. This dataset comprises previously published results from three laboratories as well as new data from a fourth laboratory. Not only do all these values of k_p fulfill the recommended consistency checks for reliability, they are also all in excellent agreement with each other. Data have been obtained employing the technique of pulsed-laser polymerization (PLP) coupled with molar-mass determination by size-exclusion chromatography (SEC), where PLP has been carried out at pulse-repetition rates of up to 500 Hz, enabling reliable k_p to be obtained through to 60 °C. The best-fit – and therefore recommended – Arrhenius parameters are activation energy E_A = 17.3 kJ mol^{-1} and pre-exponential (frequency) factor A = 1.41 × 10^7 L mol^{-1} s^{-1}. These hold for secondary-radical propagation of MA, and may be used to calculate effective propagation rate coefficients for MA in situations where there is a significant population of mid-chain radicals resulting from backbiting, as will be the case at technically relevant temperatures. The benchmark dataset reveals that k_p values for MA obtained using PLP in conjunction with MALDI-ToF mass spectrometry are accurate. They also confirm, through comparison with previously obtained benchmark k_p values for *n*-butyl acrylate, methyl methacrylate and *n*-butyl methacrylate, that there seems to be identical family-type behavior in *n*-alkyl acrylates as in *n*-alkyl methacrylates. Specifically, k_p for the *n*-butyl member of each family is about 20% higher than for the corresponding methyl member, an effect that appears to be entropic in origin. Furthermore, each family is characterized by an approximately constant E_A, where the value is 5 kJ mol^{-1} lower for acrylates.

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www.rsc.org/polymers

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3py00774j

Welcome to PolyData Online! Demo

This website is demo version of a website for critically evaluated data from Division IV of the International Union of Pure and Applied Chemistry.

View the example data that is available

How this site was built

Data from the paper on the right was extracted using the latest version of PDFtoText (part of the Poppler package) and loaded into Excel. Data in Excel were separated by original reference and Excel functions used to generate SQL statements. The SQL statements were then used to load the data into MySQL v5.6 in a database design based off the SciData Framework.

This website was then scripted using PHP v5.6 using the CakePHP Framework v2 that implements the Mode-View-Controller (MVC) architecture. Styling is done using Twiter Bootstrap v3 with graphs presented using Google Chart. Data from individual papers can be downloaded in JavaScript Object Notation for Linked Data (JSON-LD) in the SciData format.

This demo is a collaboration between Robin Hutchinson (Division IV) and Stuart Chalk (Committee on Publications and Chemical Data Standards - CPCDS).

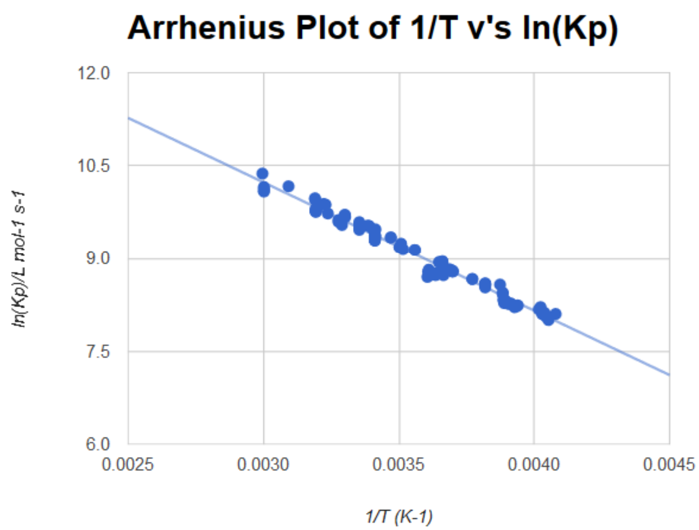
I U P A C INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

IUPAC Division IV - Critically Evaluated Rate Coefficients for Methyl Acrylate

Critically evaluated rate coefficients in radical polymerization - 7. Secondary-radical propagation rate coefficients for methyl acrylate in the bulk, Christopher Barner-Kowollik, Sabine Beuermann, Michael Buback, Patrice Castignolles, Bernadette Charleux, Michelle L. Coote, Robin A. Hutchinson, Thomas Junkers, Igor Lacík, Gregory T. Russell, Marek Stach, Alex M. van Herk *Polym. Chem.* **2013**, 5, 204 - 212

Critically Evaluated Data (110 Points) Reported From:

1. 'Critically evaluated rate coefficients in radical polymerization - 7. Secondary-radical propagation rate coefficients for methyl acrylate in the bulk' Christopher Barner-Kowollik, Sabine Beuermann, Michael Buback, Patrice Castignolles, Bernadette Charleux, Michelle L. Coote, Robin A. Hutchinson, Thomas Junkers, Igor Lacík, Gregory T. Russell, Marek Stach, Alex M. van Herk, Polym. Chem. 2013 5(1) 204-212
2. 'Determination of Propagation Rate Coefficients for Methyl and 2-Ethylhexyl Acrylate via High Frequency PLP-SEC under Consideration of the Impact of Chain Branching' T. Junkers, M. Schneider-Baumann, S. P. S. Koo, P. Castignolles and C. Barner-Kowollik, Macromolecules 2010 43(24) 10427-10434
3. 'Pressure dependence of propagation rate coefficients in free-radical homopolymerizations of methyl acrylate and dodecyl acrylate' Michael Buback, Caroline H. Kurz, Claudia Schmaltz, Macromol. Chem. Phys. 1998 199(8) 1721-1727
4. 'Determination of Propagation Rate Coefficients of a Family of Acrylates with PLP-MALDI-ToF-MS' R.X.E. Willemse, A. M. van Herk, Macromol. Chem. Phys. 2010 211(5) 539-545
5. Dissertation, 'Pulsed initiation polymerization: applications in homogeneous and heterogeneous radical systems' L.G. Manders (1997)



$\ln(k_p/\text{L mol}^{-1}\ \text{s}^{-1}) = 16.46\ (\pm 0.11) - 2080\ (\pm 30)\ K/T$

Activation Energy: 17.27 kJ mol^{-1}

Pre-exponential Factor: 1.41e+7 L mol^{-1} s^{-1}

Motivation for the effort:

- To better link our widely-cited benchmark papers with IUPAC and its goals
- To demonstrate the consensus we have reached on these important rate coefficients
- To make the data more easily accessible to a wider audience (those without access to the papers)
- ???

Publications (non-propagation)

"Critically evaluated termination rate coefficients for free-radical polymerization – 1. The current situation" **143 citations**

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" **96 citations**

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" **332 citations**

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)" **18 citations**

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

Project 2009 – 050 – 1 – 400 (closing)

Critically evaluated rate coefficients associated with initiation of radical polymerization

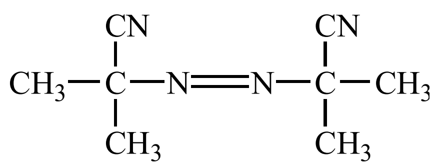
Leader Graeme Moad

Task Group Mathieu Ahr, Sabine Beuermann, Michael Buback, Michelle Coote, Klaus-Dieter Hungenberg, Greg Russell, Manfred Stickler, Ernie Wysong

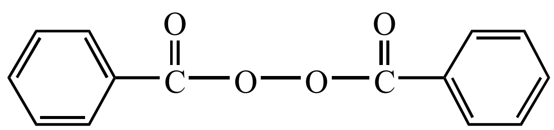
Approval Date 6 April 2010

Objective Provide critically evaluated ("benchmark") data for rates of initiation in radical polymerization.

AIBN



BPO



Current Status A review by Graeme on azo initiation to be published in *Prog. Polym. Sci.* (under revision), followed by summary document on AIBN for *Pure Appl. Chem.*

No further activities planned

Project 2013 – 045 – 1 – 400 (closing)

Critically evaluated rate coefficients for vinyl ester propagation

Leader	**Robin Hutchinson**
Task Group	Christopher Barner-Kowollik, Sabine Beuermann, Michael Buback, Thomas Junkers, Bert Klumpermann, Igor Lacík, Anatoly Nikitin
Approval Date	01-Nov-2013 (close date 01-Nov-2016)
Objective	To provide benchmark values for the propagation rate coefficient in vinyl ester systems. The particular challenges associated with measuring k_p for vinyl acetate (degradative chain transfer; difficult initiation) will be addressed. The related system vinyl pivalate will also be examined.
Current Status	Benchmark paper published in January 2017. Writing summary paper (including acrylates) for *Pure Appl.Chem.*

Project 2013 – 047 – 1 – 400 (in progress)

Critically evaluated rate coefficients for radical polymerization of styrene

Leader Sabine Beuermann

Task Group Michael Buback, Hans Heuts, Klaus-Dieter Hungenberg, Robin Hutchinson, Graeme Moad, Greg Russell, Johannes Vorholz, Per Zetterlund, Shiping Zhu

Approval Date 01-Nov-2013

Objective To provide a complete set of rate coefficients of all elementary reactions that are relevant for modeling of polymerization processes of a well-studied monomer of high industrial importance.

Planned Collection and critical review of published data for all relevant elementary reactions

Current Status Relevant elemental reactions and associated rate coefficients were identified in the group of the project leader, which will be sent to all task group members after MACRO2018 for critical evaluation (identification of missing reactions and/or data); after consensus on content is reached the manuscript will be prepared until spring 2019

Project 2013 – 051 – 1 – 400 (in progress)

Critically evaluated rate coefficients for chain-length-dependent termination in radical polymerization

Leader	**Greg Russell**
Task Group	Christopher Barner-Kowollik, Sabine Beuermann, Michael Buback, Dagmar d'Hooge, Klaus-Dieter Hungenberg, Thomas Junkers, Anatoly Nikitin, Gerhard Zifferer
Approval Date	01-Nov-2013
Objective	Critical evaluation of rate parameters for chain-length-dependent termination of styrene and *n*-alkyl methacrylates, leading to the provision of benchmark data for such; and guidelines on the correct employment of these parameters for evaluation of (steady-state) rate and average degree of polymerization.
Current Status	To be updated

Project 2015 – 034 – 1 – 400 (in progress)

Critically evaluated ESR (EPR) spectra of important polymerization-related radicals

Leader	**Atsushi Kajiwara**
Task Group	M. Buback, E. Chernikova, P. Hoefer, H. Kattner, Y. Mizuta, G. Russell, P. Vana, S.-I. Yamabe
Approval Date	01-Dec-2015
Objective	The objective is to provide the ESR spectra and the complete set of the associated hyperfine splitting constants of radicals from various monomers that are relevant for both modeling of technical polymerization processes and for fundamental studies in academia and in industry. In addition, ESR spectra of radicals occurring in reversible deactivation polymerization will be collated.
Update	Preliminary discussions have occurred among task group at several locations. First report in preparation.

Project 2017 – 028 – 1 – 400 (new)

Critically evaluated rate coefficients for backbiting in acrylate radical polymerization

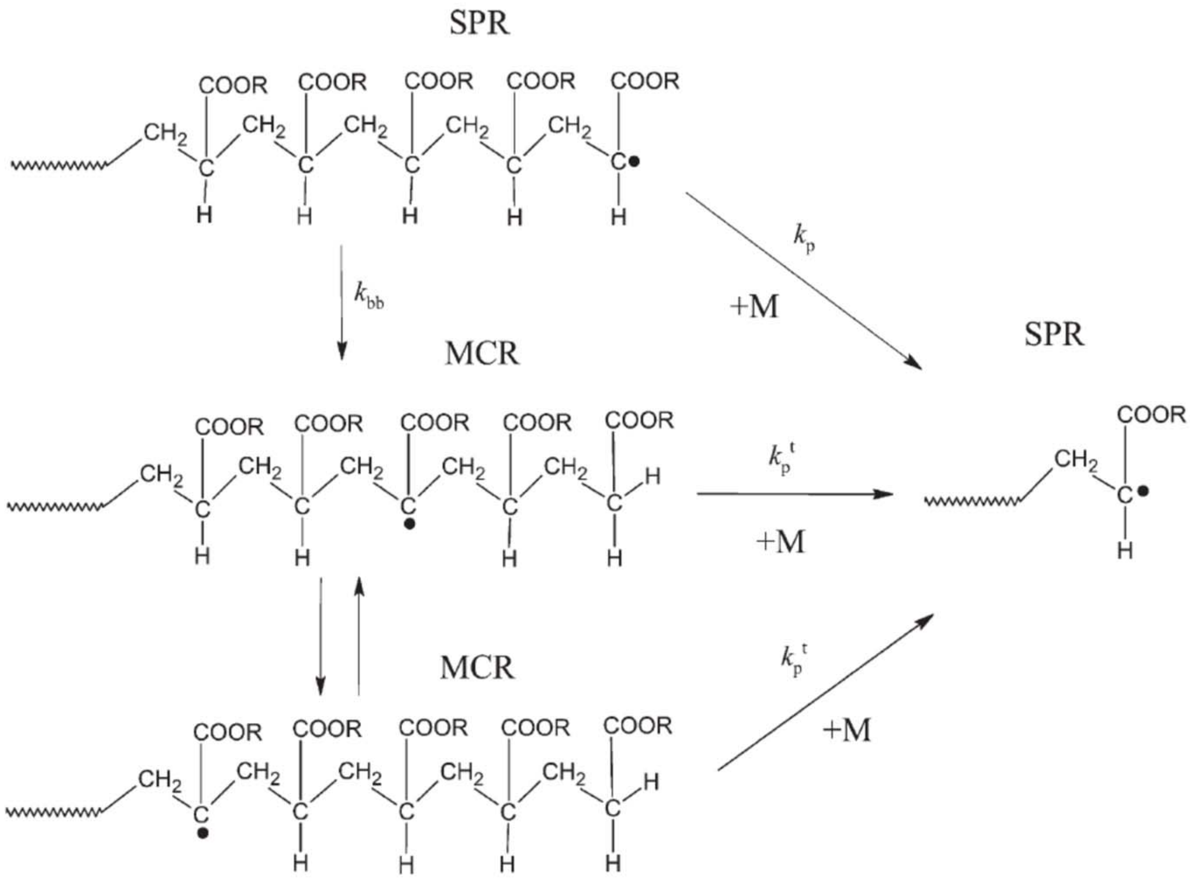
Leader **Tanja Junkers, Robin Hutchinson**

Task Group J. M. Asua, C. Barner-Kowollik, S. Beuermann, M. Buback, P. Castignolles, D. D’hooge, A. Nikitin, G. Russell

Approval Date 01-Dec-2017

Objective The objective is to define criteria for the measurement of transfer to polymer rate coefficients (specifically values for intramolecular transfer, also referred to as “backbiting”), and to provide benchmark values for butyl acrylate and methyl acrylate.

Update First meeting held yesterday



Multiple studies providing estimation of k_{bb} for butyl acrylate;

Many (but not all) estimates in reasonable agreement at T< 60 C

Three main methodologies:

- SP-PLP-EPR (measurement of MCR)
- Modified PLP-SEC studies (e.g., "frequency tuned")
- Measurement of branchpoints by ^{13}C NMR

Survey of techniques to be completed by the end of 2018

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)

Success in k_p series arose from a confluence of factors

Recognized need in the research community

+

New experimental technique(s) [PLP-SEC]

+

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)

Future Outlook on Subcommittee Activities

Is our Subcommittee approaching the point of diminishing returns?

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

Nowadays,

- Few specific conferences held on polymerization kinetics (Therefore, limited opportunities to have open discussions among a "critical mass" of subcommittee members)
- 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)

Ideas on how to add to the subcommittee activities are welcomed!

Plan to organize a symposium at Pacifichem (Hawaii, 15-20Dec 2020)