

**Polymer Division Subcommittee on “Modeling of Polymerization Kinetics and Processes”
Combined minutes of two meetings held in summer of 2014**

Tuesday, July 8, 2014 at “Macro2014” IUPAC World Polymer Congress, (Chiang Mai, Thailand)

Attendees: Robin Hutchinson (RH) – committee co-chair, Michael Buback (MB), Igor Lacík (IL), Thomas Junkers (TJ), Atsushi Kajiwara (AK), Kris Matyjaszewski (KM), Graeme Moad (GM), Calista Preusser (Hutchinson group), Greg Russell (GR), Adam Sutton (Castignolles group)

Monday, Aug 11, 2014 at 248th American Chemical Society National Meeting (San Francisco, USA)

Attendees: Sabine Beuermann (SB) – committee co-chair, Robin Hutchinson (RH) – committee co-chair, Michael Buback (MB), Mathias Destarac (MD), Atsushi Goto (AG), Simon Harrisson (SH), Atsushi Kajiwari (AK), Bert Klumperman (BK), Patrick Lacroix-Desmazes (PLD), Kris Matyjaszewski (KM), Graeme Moad (GM), Philipp Vana (PV)

Initials are used as shorthand to refer to members in the minutes below.

For both meetings, the discussions were based upon the set of slides (Attached) used to summarize subcommittee activities at the Polymer Division meeting held in Thailand.

1. Subcommittee Membership.

Dagmar d’hooge (Ghent University, Ghent, Belgium), Jose Ramon Leiza (University of the Basque Country, San Sebastian, Spain), and Davide Moscatelli (Milano Politecnico, Milan, Italy) were welcomed as new members joining the group over the past year. In addition, we were pleased to invite and have Simon Harrisson (Toulouse University, Toulouse, France) join the subcommittee at the August ACS meeting. For further details on subcommittee membership (changes in affiliation, resignation of Marek Stach due to career change), please see Slide 2 of the Attachment. RH mentioned that there remains a need for increased participation from China; the potential members suggested at the 2012 Blacksburg meeting were not interested in joining the activities. GR stressed the need to renew membership, and to remind younger scientists (potential subcommittee members) of the positive impact of participating in projects on their citation record.

2. Completed Projects.

- a. *Critically evaluated propagation rate coefficients for free-radical polymerization of water-soluble monomers polymerized in the aqueous phase* (Project 2004-034-1-400)

At the Thailand meeting, IL provided the update that the project team had finalized and submitted a manuscript to *Macromol. Chem. Phys.* that summarized the precision of size-exclusion chromatography as applied to esterified and non-esterified methacrylic acid (MAA) and acrylic acid (AA) polymers. The article highlighted the important message that esterification of AA leads to a shift in the measured molar-mass distribution (and thus estimated rate coefficients from the PLP technique), and thus made the recommendation to the polymer community that aqueous SEC should be used for accurate analysis. The paper has since been accepted for publication, and will appear in print later this year.

- b. *Critically evaluated rate coefficients for (methyl) acrylate propagation* (Project 2011-034-2-400)
This 2011 project has drawn to a close with the 2014 publication in *Polym. Chem.* of the benchmark data set and resultant k_p estimate for chain-end propagation of methyl acrylate. A discussion led to the consensus that there is insufficient data to extend the project to consider longer-chain alkyl acrylates.
- c. *Towards a holistic mechanistic model for reversible addition-fragmentation chain transfer (RAFT) polymerizations: Dithiobenzoates as mediating agents* (Project 2004-040-1-400)
RH and SB expressed their appreciation to GM, who wrote a summary of the situation as published this year in *Macromol. Chem. Phys.*

ACTIONS: RH to ensure that these three projects are designated as completed in the IUPAC database.

3. *Ongoing and Newly Approved Projects.*

- a. *Critically evaluated rate coefficients associated with initiation of radical polymerization* (Project 2009-050-1-400)

GM reported that the data collection and analysis for AIBN initiator decomposition kinetics has been completed as part of a larger effort he undertook for the azo initiator family. He is finalizing (expected Sept 2014) a manuscript for submission to *Macromol. Chem. Phys.* containing the benchmark data for AIBN, and is also writing a larger (single author) review for publication in *Prog. Polym. Sci.*

Some discussion was held whether to move onto the second part of the planned project, rate coefficients of peroxide initiators. GM expressed the opinion that this would be difficult, as (i) peroxide decomposition rates are more solvent dependent, and (ii) much of the available, reliable data come from a single research group. The consensus reached was that the project would be terminated with the submission of the AIBN benchmark set.

ACTION: GM to finalize manuscript, circulate it to project members for comments, and submit for publication (hopefully all before the end of 2014).

- b. *Critically evaluated dissociation rate coefficients for alkoxyamines* (Project 2010-027-2-400)

RH reported that Yohann Guillaneuf has taken over project leadership from Denis Bertin. Yohann met with some project members in August 2013 and has reported (by email) that data sets have been collected and were in the process of being compiled and evaluated. However, progress has since stalled due to family medical issues. However, members of the project team at the Thailand and San Francisco meetings (MB, TJ, GM, PLD) reported that they have not received any updates or seen any data circulated.

ACTION: RH to contact Yohann for clarification of his previous update.

- c. *Critically evaluated rate coefficients for vinyl ester propagation* (Project 2013-045-1-400)

RH reported that activities have commenced with collection of published data for vinyl acetate (from student theses) from SB and MB groups, and that additional experiments have also been conducted at Queen's University, with modeling support from Anatoly Nikitin. Published data

from TJ were received after the Thailand meeting. BK has no data set to contribute, although there may be some older data collected at Eindhoven.

ACTION: RH to consolidate data sets (including contacting Alex van Herk) for evaluation.

- d. *Critically evaluated rate coefficients for radical polymerization of styrene* (Project 2013-047-1-400)

SB reported that activity on this project (approved Nov 2013) has not started. There was some discussion as whether to include CLD-termination (tie in to the project discussed below; can CLD-termination be used to calculate a chain-length averaged $\langle k_t \rangle$ value and compared to data compiled several years ago by Hans Heuts?), conversion-dependence of termination, and monomer thermal initiation.

ACTION: SB to contact Klaus Hungenberg and others on project team to better define scope of planned work.

- e. *Critically evaluated rate coefficients for chain-length dependent termination in radical polymerization* (Project 2013-051-1-400)

GR reported that activity will commence on this new project (approved Nov 2013) after the publication of CLD-termination data for styrene by MB and his group at Göttingen.

4. Future Projects.

The long-standing list of future project topics (slide 24 of attachment) was used as a basis of discussion. MB suggested that some of these topics might be assigned to individuals to evaluate their suitability as future projects. RH expressed the opinion that many of the ideas were too broad in scope and that two key criteria for a successful project are (i) sufficient data on the same system collected by multiple research groups, and (ii) a project leader who is willing to do the majority of the work compiling and analyzing the data for publication as a benchmark data set. MB, from his role as President of the Polymer Division, mentioned that there is only limited funding for new projects during the next two years.

The following ideas emerged out of the general discussion as solid contenders for new projects:

- a. Critically evaluated rate coefficients for butyl acrylate mid-chain radical formation and reaction. TJ agreed to write up a proposal draft.
- b. Critically evaluated rate coefficients for reversible addition-fragmentation chain transfer (RAFT) polymerization with trithiocarbonates as mediating agents. SH and MD agreed to survey the literature to determine whether sufficient data exists for a specific monomer/RAFT agent combination.
- c. KM suggested that we evaluate the potential for starting a project on cationic polymerization rate coefficients, with Rudolf Faust (University of Massachusetts-Lovell) as a key contributor. RH discussed the possibility with Faust at Thailand, who was interested in the group's activities.
- d. PV suggested that we compile and publish benchmark Mark-Houwink Sakurada parameters for common polymers in THF. Many of these data are already available, and were considered as part of the PLP-SEC k_p studies; thus the effort should be minimal.

ACTIONS: (i) TJ to write draft proposal and contact potential project members. (ii) RH to follow up with Rudolf Faust and other subcommittee members (Klaus Hungenberg, ???) to assess feasibility of a project on cationic polymerization. (iii) RH and SB to follow up with Destarac and Harrisson regarding the trithiocarbonate RAFT suggestion. (iv) RH and SB to summarize project ideas and circulate to the entire subcommittee by email to solicit input and participation.

5. Upcoming Meetings.

As usual, most of the project activities will proceed via email. Upcoming conferences that should have a critical mass of subcommittee members to warrant a meeting are *Polymer Reaction Engineering IX* (Cancun, Mexico, 10-15 May 2015) and *Pacifichem 2015* (Hawaii, United States, 15-20 December 2015).

IUPAC Polymer Division Meeting, Chiang Mai 2014

Report on the “Subcommittee on Modeling of Polymerization Kinetics and Processes”

Co-Chairs	Prof. R. A. Hutchinson	(Kingston, Canada)
	Prof. S. Beuermann	(Clausthal, Germany)
Past Chair I	Prof. G. T. Russell	(Christchurch, NZ)
Past Chair II	Prof. M. Buback	(Göttingen, Germany)

Recent meetings: 25 June 2012, Blacksburg (MACRO2012)
29 August 2011, Denver (242nd ACS meeting)

Next meetings: MACRO2014, Thailand
ACS Annual Meeting, San Francisco

Members (additions/moves since last report)

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

Membership Geography

44 from 16 countries

8	Australia
8	Germany
6	France
5	Japan
3	USA
2	Canada, Belgium, South Africa
1	Netherlands, New Zealand, Russia, U.K., Italy, Singapore, Spain, Slovakia

Targeted areas for expansion remain Asia and U.K.

3

Membership Employment

Industry	5
(Hungenberg, Hesse, Vorholz, Wysong, Charleux)	
Research Institute	3
(Lacík, Moad, Nikitin)	
University	36

4

Activities 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” are 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, and methacrylic acid 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.**

5

Publications and Citations: The early papers

Citations: 22 June 2012 → 22 June 2014

**“Consistent values of rate parameters in free radical polymerization systems”
160 → 161 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” 190 → 200 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”
31 → 36 citations**

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

6

Publications and Citations – Propagation

“Critically evaluated rate coefficients for free-radical polymerization,

1. Propagation rate coefficients for styrene” 487 → 526 citations

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” 364 → 400 citations

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 coefficients in free radical polymerizations.

1. Styrene and methyl methacrylate” 101 → 106 citations

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

Citations: 22 June 2012 → 22 June 2014

7

Publications and Citations – Propagation (cont.)

“Critically evaluated rate coefficients for free-radical polymerization -

3. Propagation rate coefficients for alkyl methacrylates” 138 → 162 citations

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” 52 → 61 citations

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” 145 → 190 citations

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).

Citations: 22 June 2012 → 22 June 2014

8

Publications and Citations – Propagation (cont.)

“Critically evaluated rate coefficients for free-radical polymerization, Part 6. Propagation rate coefficient of methacrylic acid in aqueous solution”

24 → 30 citations

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” **1 → 1 citation**

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”

0 → 2 citations

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).

“

Citations: 22 June 2012 → 22 June 2014

9

Critically Evaluated Rate Coefficients in Radical Polymerization: Propagation *A very successful series*

Monomer	Journal	Year	Web of Science Citations (Jun14)
1. Styrene	<i>Macromol. Chem. Phys.</i>	1995	526
2. Methyl Methacrylate	<i>Macromol. Chem. Phys.</i>	1997	400
3. Alkyl Methacrylates	<i>Macromol. Chem. Phys.</i>	2000	162
4. Functional Methacrylates	<i>Macromol. Chem. Phys.</i>	2003	61
5. <i>n</i> -Butyl Acrylate	<i>Macromol. Chem. Phys.</i>	2004	190
6. Methacrylic Acid	<i>Pure Appl. Chem.</i>	2007	30
7. Methyl Acrylate	<i>Polym. Chem.</i>	2014	2
8. Vinyl Acetate (new)			

Publications – Termination and RDRP

“Critically evaluated termination rate coefficients for free-radical polymerization – 1. The current situation” 102 → 115 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” 66 → 78 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” 224 → 274 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).

2342 total citations (an increase of 257)

11

Report on Activities – Outline

Finished Projects:

- Methyl acrylate propagation – 2014 publication
- Aqueous phase propagation – 2014 submission
- Raft polymerization mechanism

Continuing Projects:

- NMP rate parameters
- Initiation rate parameters

New Projects (initiated late 2013)

- Styrene polymerization rate parameters
- Vinyl ester propagation
- Chain-length dependent termination

12

Completed projects

Project 2004 – 034 – 1 – 400

Critically evaluated propagation rate coefficients for free-radical polymerization of water-soluble monomers polymerized in the aqueous phase

Leader	Igor Lacík
Task Group	Christopher Barner-Kowollik, Sabine Beuermann, Michael Buback, Patrice Castignolles, Bernadette Charleux, Tom Davis, Marion Gaborieau, Robert G. Gilbert, Klaus-Dieter Hungenberg, Robin Hutchinson, Peter Kilz, Christine Wandrey
Start Date	October 2004
Completion	2013
Objective	To critically evaluate propagation rate coefficients for water-soluble monomers polymerized in aqueous phase.
Completion	Finalized second publication , on precision of SEC for poly(acrylic acid) and poly(methacrylic acid), submitted to <i>Macromol. Chem. Phys.</i>

13

Completed projects

Project 2011 – 034 – 2 – 400

Critically evaluated rate coefficients for (methyl) acrylate propagation

Leaders	Christopher Barner-Kowollik and Thomas Junkers
Task Group	Michael Buback, Patrice Castignolles, Bernadette Charleux, Robin Hutchinson, Peter Lovell, Anatoly Nikitin, Greg Russell, Alex van Herk, Sabine Beuermann, Michelle Coote
Approval Date	April 2012
Meetings	August 2011 (ACS Meeting), IUPAC Macro 2012
Objective	To provide benchmark values for the propagation rate coefficient in alkyl acrylate systems, with a particular emphasis on methyl acrylate. The particular challenges associated with measuring k_p for acrylates will be addressed anew. This follows the earlier successful project on <i>n</i> -butyl acrylate k_p .
Completion	Manuscript on k_p of MA published (<i>Polym. Chem.</i> 2014)

14

Critically Evaluated Rate Coefficients in Radical Polymerization - 7. Secondary-Radical Propagation Rate Coefficients for Methyl Acrylate in Bulk

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

15

Completed projects

Project 2004 – 040 – 1 – 400

Towards a holistic mechanistic model for reversible addition-
fragmentation chain transfer (RAFT) polymerizations:
Dithiobenzoates as mediating agents

Leader	Philipp Vana
Task Group	Christopher Barner-Kowollik, Michael Buback, Bernadette Charleux, Michelle Coote, Marco Drache, Takeshi Fukuda, Atsushi Goto, Bert Klumperman, Andrew Lowe, James McLeary, Graeme Moad, Michael Monteiro, Ronald Sanderson, Matthew Tonge
Start Date	February 2005
Completion Year	2013
Objective	To obtain a detailed understanding of the mechanism of reversible addition fragmentation chain transfer (RAFT) polymerization and to determine the corresponding kinetic coefficients.
Completion	G. Moad prepared a paper for <i>Macromol. Chem. Phys.</i> (2014) on the current situation of RAFT retardation, to wrap up the project.

16

Ongoing projects

Project 2009 – 050 – 1 – 400

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
Meetings	July 2010 (at Macro 2010), December 2010 (Pacifichem), July 2011 (IUPAC GA & C), August 2011 (ACS Meeting), June 2012 (MACRO2012)
Objective	To begin the task of providing critically evaluated (“benchmark”) data for rates of initiation in radical polymerization.

17

Project 2009 – 050 – 1 – 400 (cont.)

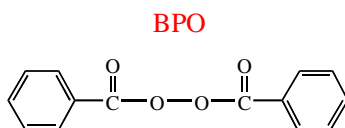
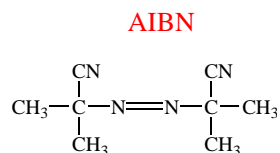
Rationale

Projects so far on propagation and termination.

But need k_p , k_t and rate of initiation in rate law for RP:

$$\frac{dx}{dt} = k_p(1-x) \left(\frac{R_{\text{init}}}{2k_t} \right)^{0.5}$$

Initial Targets



Current Status

Preparation of a manuscript with a compilation of published data and a recommendation for AIBN; in addition, a review by Graeme on azo initiation to be published in Prog. Polym. Sci. (both to be completed this summer)

18

Ongoing projects

Project 2010 – 027 – 2 – 400

Critically evaluated dissociation rate coefficients for alkoxyamines

Leader	Denis Bertin-Yohann Guillaeneuf
Task Group	Elena Bagryanskaya, Michael Buback, Bernadette Charleux, Michelle Coote, Didier Gigmes, Atsushi Goto, Barney Grubbs, Yohann Guillaeneuf, Thomas Junkers, Patrick Lacroix-Desmazes, Sylvain Marque, Graeme Moad, Peter Nesvadba, Gudrun Schmidt-Naake, Armido Studer, Per Zetterlund, Shiping Zhu
Approval Date	February 2011
Meetings	July 2010 (Macro 2010), December 2010 (Pacifichem), August 2013 (APME, Durham)
Objective	To provide critically evaluated dissociation rate coefficients for different alkoxyamines used in nitroxide-mediated polymerization. TEMPO and SG1-based compounds will be processed first. Data from different techniques (computational, NMR, ESR, liquid chromatography, etc.) will be considered. The issue of Arrhenius parameters (activation factor A and activation energy E_a) will be particularly emphasized.

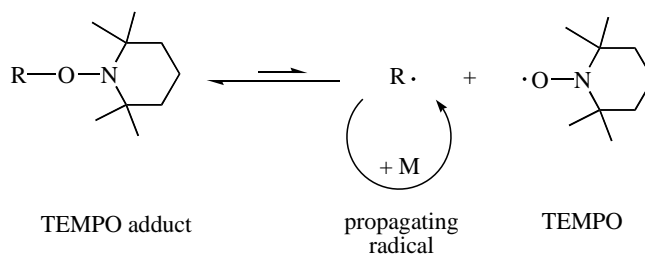
Project 2010 – 027 – 1 – 400 (cont.)

Rationale

Reversible-deactivation radical polymerization, including NMP, is becoming increasingly important. Therefore there is a need to have reliable rate coefficients for these processes.

The Basic Chemistry

Rate coefficients for these reactions
(*dissociation/activation* and *deactivation*)



Current Status

Gathering data for 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO) and *N-tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1).

Data were collected and are currently being processed; manuscript preparation started. Project team met in August 2013.

New project

Project 2013 – 045 – 1 – 400

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, possibly more
Approval Date	01-Nov-2013
Meetings	Project will be started by email; MACRO 2014, Thailand; Pacifichem 2015, Hawaii.
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	New data being collected; data compilation to follow (older 1990's + new data obtained with higher repetition rate lasers) ²¹

New project

Project 2013 – 047 – 1 – 400

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
Meetings	Project will be started by email; ACS 2014, San Francisco; Pacifichem 2015, Hawaii.
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

New project

Project 2013 – 051 – 1 – 400

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
Meetings	Macro2014, Thailand; ACS 2014, San Francisco; Pacifichem 2015, Hawaii.
Objective	Critical evaluation of rate parameters for chain-length-dependent termination of styrene and <i>n</i> -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.
Planned	Data collation to start after imminent publication by Buback of styrene CLDT data measured by SP-PLP-ESR

23

Future Project Ideas (a long standing list)

- Critically evaluated **termination rate coefficients** as a function of **conversion**
- Critically evaluated **chain-transfer** rate coefficients and constants
- Critically evaluated **depropagation** rate coefficients
- Critically evaluated copolymerization **reactivity ratios**
- Critically evaluated **combination/disproportionation** ratios
- Critically evaluated rate coefficients for **ionic polymerizations**
- **ATRP**: current situation on mechanisms; benchmark rate coefficients
- Set of benchmark rate coefficients for a **particular monomer**

24