

IUPAC Subcommittee on Modeling of Polymerization Kinetics and Processes

**Minutes of the meeting held at the Sheraton Downtown (Court St) in Denver CO,
at 5:30 pm on August 29, 2011 (during ACS 2011 Annual Meeting)**

Attendees:

Christopher Barner-Kowollik, Johannes Barth (PhD student at U Göttingen), Denis Bertin, Sabine Beuermann, Michael Buback, Michelle Coote, Atsushi Goto, Hans Heuts, Robin Hutchinson, Atsushi Kajiwara, Bert Klumperman, Patrick Lacroix-Desmazes, Kris Matyjaszewski, Graeme Moad, Michael Monteiro, Devon Shipp, Philipp Vana

Apologies were received from Markus Busch, Patrice Castignolles, Bernadette Charleux, Mathias Destarac, Marion Gaborieau, Bob Gilbert, Klaus-Dieter Hungenberg, Thomas Junkers, Tatsuki Kitayama, Igor Lacík, Pete Lovell, Anatoly Nikitin, Sébastien Perrier, Greg Russell, Ron Sanderson, Eriko Sato, Marek Stach, Manfred Stickler, Alex van Herk, Per Zetterlund and Shiping Zhu.

Minutes (prepared by Sabine Beuermann and Robin Hutchinson):

Sabine Beuermann chaired the meeting in the absence of Greg Russell. The status of the working party projects was reviewed using the slides presented by Greg at the IUPAC general assembly, held in San Juan, Puerto Rico in July 2011.

1. Termination kinetics in radical polymerizations,

(Project 2000-028-1-400, chair Greg Russell)

This long-standing project should be brought to a close. There was a lively discussion on the value of publishing "benchmark" low-conversion averaged k_t values without explicit treatment of chain-length dependent termination.

ACTION: Heuts to send data and analysis (from 2006) for bulk MMA and styrene to Beuermann and Junkers. The data will be reviewed and a recommendation will be made whether to proceed with publication, and how best to present the results ($\langle k_t \rangle$ as a function of DP_n at low conversions with or without reference to the surface functions recently published by Monteiro and Barner-Kowollik.) This review will be completed over the next few months.

2. Critical evaluation of methacrylic acid propagation rate coefficients,

(Project 2004-034-1-400, chair Igor Lacík)

The report on the round-robin test for SEC analysis of poly(methacrylic acid) and poly(acrylic acid) samples has been prepared and distributed to the project members.

ACTION: Stach and Lacík will make final revisions after receiving comments and submit for publication (journal not yet chosen).

3. **Critical evaluation of methyl acrylate propagation rate coefficients,**

(New project just submitted, chairs Christopher Barner-Kowollik and Thomas Junkers)

Data collection and analysis for this project is already well underway. It is important to stress (as was done for butyl acrylate) that the k_p results reported (in the temperature range -28 to 70 °C) are for monomer addition to an MA chain-end radical.

ACTION: Barner-Kowollik and Junkers will circulate the data and manuscript draft to project members when completed in the next few months.

4. **Mechanistic details of RAFT polymerization,**

(Project 2004-040-1-400, chair Philipp Vana)

Since the publication of the first article in *J. Polym. Sci., Polym. Chem. Ed.* in 2006, no agreement has been reached on the remaining open questions regarding the RAFT mechanism, despite 20 papers devoted to the issue. Once again, it was discussed whether the project should be prolonged until consensus is reached or whether it should be immediately terminated. Buback reminded everyone that the original terms of the project were to work towards a consensus on RAFT mechanism, and that it creates no good impression with the scientific community to abandon the project in its current state.

ACTION: Moad to write a short review of the progress made in this area since 2006, and circulate to project members. A decision will then be made whether or not to publish a short "dilemma update", and whether to continue the project until consensus is reached.

5. **Critically evaluated rate coefficients associated with initiation of radical polymerization,**

(Project 2010-050-1-400, chair Graeme Moad)

This new project is to critically evaluate kinetic data published for the initiation rate. The initial focus will be on azo initiators AIBN and AIBME. Data on the initiator decomposition rate coefficients are in good agreement (with minor solvent effects), but the situation is not so clear for AIBN initiator efficiency values (better for AIBME). Selection of a peroxide initiator for benchmark treatment will be more difficult.

ACTION: Data collection for AIBN and AIBME to be finalized by the end of the year.

6. **Critically evaluated dissociation rate coefficients for alkoxyamines used in nitroxide-mediated polymerization** (Project 2010-027-2-400, chair Denis Bertin)

The aim of this new project is to provide critically evaluated kinetic data for alkoxyamine dissociation and recombination in nitroxide-mediated polymerization. For TEMPO and SG1, data from different experimental techniques are available.

ACTION: Bertin will contact project members and collect data by the end of the year.

Other matters discussed at the meeting include:

- Industrial members of the working party are needed. Stickler has recently retired and is recommending a replacement, Dr. Johannes Vorholz, from Evonik. Moad suggested that Ernie Wysong from DuPont (member of initiator project) be invited to join. It was also

suggested that recent PhD students familiar with the working party who have accepted positions in industry be invited to join.

Note: after the conference Johannes Vorholz was invited to join the subcommittee and he accepted this invitation.

- Graeme Moad is chair of a project on Terminology for Chain Polymerization, and will keep the working party informed of findings and recommendations.
- The list of new project ideas prepared by Russell was reviewed at the end of the meeting. It was suggested that butyl acrylate backbiting/MCR propagation be added as a good follow-up project to MA k_p . It was also suggested that a project establishing a set of benchmark parameters for MMA is worth pursuing, especially if Manfred Stickler could be convinced to participate.
- The next meeting of the Subcommittee will be held June 2012 at the IUPAC Polymer Congress in Virginia.