

IUPAC Subcommittee on Modeling of Polymerization Kinetics and Processes

**Minutes of the meeting held in Room Boisdale 1 of the Scottish Exhibition and Conference Centre,
Glasgow at 6 pm on July 12, 2010 (during MACRO2010)**

Attendees:

Johannes Barth (PhD student at U Göttingen)
Denis Bertin
Sabine Beuermann
Michael Buback
Bernadette Charleux
Mathias Destarac
Bob Gilbert
Thomas Junkers
Atsushi Kajiwara
Bert Klumperman
Igor Lacík
Kris Matyjaszewski
Graeme Moad
Anatoly Nikitin
Sébastien Perrier
Greg Russell
Eriko Sato (from Matsumoto group at Osaka City U)
Alex van Herk
Jean-Pierre Vairon
Philipp Vana
Alex Wu (PhD student at U Queensland)

Apologies were received from Christopher Barner-Kowollik, Patrice Castignolles, Michelle Coote, Takeshi Fukuda, Atsushi Goto, Yohann Guillaneuf, Hans Heuts, Klaus-Dieter Hungenberg, Robin Hutchinson, Patrick Lacroix-Desmazes, Pete Lovell, James McLeary, Michael Monteiro, Devon Shipp, Marek Stach, Manfred Stickler, Per Zetterlund and Shipping Zhu.

Minutes (prepared by Sabine Beuermann and Greg Russell):

1. Greg Russell notified the attendees about his report to the IUPAC Polymer Division on Saturday 10 July. The citations of the publications are still developing well. He pointed out that the geographic spread has altered slightly because some members have new affiliations while Thomas Junkers and Pete Lovell are new members.

The status of the projects associated with the Subcommittee were provided by the chairmen, as follows:

2. **Project on termination kinetics in radical polymerizations**, chair Greg Russell
The third publication from the project is still in preparation. It is hoped that the manuscript will be finalized during a visit of Hans Heuts to Göttingen in October.

ACTION: Russell to prepare paper on benchmark k_t for bulk styrene, and then terminate (no pun intended!) the project.

3. **Project on mechanistic details of RAFT polymerization**, chair Philipp Vana

Since the publication of the first article in *J. Polym. Sci., Polym. Chem. Ed.* in 2006, no consensus has been reached on the remaining open questions regarding the RAFT mechanism. Due to retardation in RAFT polymerizations with dithiobenzoates, these RAFT agents are now used only rarely, and hence the mechanistic issues that they raise have ceased to be of such intense interest. However, there has still been some new work in this area, most notably by the groups of Perrier, Klumperman and Buback/Vana. It was discussed how the project may continue or whether it should be immediately terminated. Michael 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. Therefore it was agreed to write a short paper that summarizes the very latest situation and tries to find a level of agreement between the major players in the area.

ACTION: Klumperman and Vana to write a first draft of a final paper by the end of September (drawing on Klumperman's recent paper on this topic). This will then be distributed to taskgroup members for discussion and finalization. After that the project will be terminated.

4. Greg Russell informs the attendees that a new **project on terminology for chain polymerizations** has recently been started. Involved are Graeme Moad (taskgroup leader), Kris Matyjaszewski, and Greg Russell.

5. **Project on Critically evaluated rate coefficients associated with initiation of radical polymerization**, chair Graeme Moad

The aim of this new project is to critically evaluate kinetic data published for the initiation rate. The focus will be on AIBN and a yet-to-be determined peroxide (probably BPO). Within the project the following aspects may be addressed: mechanism of decomposition, addition rates to monomer, and the solvent influence on initiation rate. It was discussed that it may be advantageous to add a representative to the taskgroup from a Japanese company producing initiators to the task group. The first meeting of the task group was scheduled to take place during MACRO2010 (and it duly did!).

ACTION: Moad to seek a representative from a Japanese company.

6. **Project on Critically evaluated dissociation rate coefficients for alkoxyamines used in nitroxide-mediated polymerization**, 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. The first meeting of the task group was scheduled to take place during MACRO2010 (and it duly did!).

7. **Project on critical evaluation of methacrylic acid propagation rate coefficients**, chair Igor Lacík

The report on the round-robin test for SEC analysis of poly(methacrylic acid) samples has been

prepared (by Marek Stach and Igor) and will be distributed to the project members after the conference.

ACTION: Lacík to distribute report on SEC analysis, and members to decide whether it should be published or just kept as an internal report. Then the project will be terminated.

8. Future projects:

- As discussed in previous meetings a task group on critically evaluated rate coefficients for chain-length-dependent termination appears to be a matter of priority. An application will be prepared by Buback and Russell after the current project on termination is finally finished.
- Philipp Vana suggests starting a project on trithiocarbonates as RAFT agents. Due to the absence of any retardation problems these compounds are now frequently used.
- Subsequent to the meeting, Christopher Barner-Kowollik expresses enthusiasm for a project on acrylate k_p that builds on the previous project on BA k_p , perhaps having methyl acrylate as its first focus and including also dodecyl and other alkyl acrylates.
- Greg reports that at the IUPAC Polymer Division meeting it was pointed out that the title of the Subcommittee does not state Radical Polymerization. Thus, other types of polymerization could also be considered. It is discussed that the current Subcommittee members are (with one or two notable exceptions!) no experts on, e.g., ionic polymerizations. In order to run a successful project, however, an excellent and enthusiastic project leader is required. Bernadette Charleux points out that in cationic polymerizations a number of problems occur, for example widely varying literature data based on stationary-state assumptions. An idea for a project is to summarize and critically evaluate current data, which should serve at least to point people in the right direction in terms of benchmark data (which it would probably require more experimentation to acquire). This idea should be pursued at Pacificchem (in December 2010), where experts in ionic polymerization are likely to be present and easily accessible. If no projects on non-radical polymerizations are started in the near future, it should be considered whether the Subcommittee requests to add the word "radical" to its name.

9. Miscellaneous

- Greg Russell points out that members of this Subcommittee should set a good example by using the term *reversible-deactivation radical polymerization* rather than *living/controlled radical polymerization*.¹ Kris Matyjaszewski is so inspired by this exhortation that he uses the IUPAC-recommended term once (but through gritted teeth). Similarly, *dispersity* rather than the tautologous *polydispersity index* should be used.²

¹ "Terminology for reversible-deactivation radical polymerization previously called "controlled" radical or "living" radical polymerization (IUPAC Recommendations 2010)", A.D. Jenkins, R.G. Jones and G. Moad, *Pure Appl. Chem.*, **82**, 483-491 (2010).

² "Dispersity in polymer science (IUPAC Recommendations 2009)", R.F.T. Stepto, *Pure Appl. Chem.*, **81**, 351-353 (2009).

- Greg Russell requests that members having contact with industry, especially in Germany, should take a moment to mention the usefulness of our activities to and for these people, for example benchmark rate coefficients they can use in modeling. The background here is that it has come to Michael Buback's attention that some German companies are becoming reluctant to pay their IUPAC subscriptions. What this reflects is that these companies are not being made aware of the valuable return they are actually getting for a very small investment.
- Kris Matyjaszewski informs the attendees that the next CRP (make that RDRP!) symposium will take place in August 2010 at the fall ACS National Meeting in Denver.

10. Membership

- Mathias Destarac is accepted as a new member.
- Tatsuki Kitayama is proposed as a new member, with a view to broadening our horizons beyond radical polymerization (see point 8).
- Akikazu Matsumoto has asked to cease being a member. At his request he will be replaced by Eriko Sato, a Lecturer at the same University (Osaka City) who has an interest in polymerization kinetics and mechanisms.

ACTIONS: Russell to contact Kitayama and Matsumoto; Beuermann to process membership changes.

11. Next Meeting

The next meeting of the Subcommittee will be in December 2010 at the Pacificchem conference in Honolulu.