IUPAC Subcommittee on Modeling of Polymerization Kinetics and Processes

Minutes of the meeting held in Liberty Ballroom A, Sheraton Hotel, Philadelphia at 5.30 pm on August 18, 2008 (during the 236th ACS National Meeting)

Attendees:

Denis Bertin
Sabine Beuermann
Michael Buback
Bernadette Charleux
Bob Gilbert
Atsushi Goto
Yohann Guillaneuf (invited guest)
Pascal Hesse (invited guest)
Robin Hutchinson
Atsushi Kajiwara
Bert Klumperman
Patrick Lacroix-Desmazes
Graeme Moad
Michael Monteiro
Chris Ober (invited guest, see below)
Sébastien Perrier
Greg Russell
Philipp Vana
Shiping Zhu

Appologies were received from Patrice Castignolles, Michelle Coote, Klaus-Dieter Hungenberg, Aubrey Jenkins, Manfred Stickler, Igor Lacík, Anatoly Nikitin, Christopher Barner-Kowollik (all by prior email), Jean-Pierre Vairon, Kris Matyjaszewski (in person at the ACS Meeting) and Devon Shipp (by subsequent email).

Minutes (prepared by Sabine Beuermann and Greg Russell):

1. Greg Russell expresses his thanks to Michael Buback for leading the Subcommittee for a decade and congratulates him on his election as Vice President of the Polymer Division of IUPAC.

2. Chris Ober, President of the Polymer Division of IUPAC, congratulates the Subcommittee on its work. He indicates that IUPAC will provide around 50 000 US$ for the Polymer Division over the next two years for funding of projects. It is expected that this will include at least 2 new projects from the Subcommittee.

3. Greg Russell starts to go over the presentation on the Subcommittee that he prepared for the meeting of the IUPAC Polymer Division in Taipei prior to MACRO 2008 (where this report was presented by Michael Buback in Greg Russell's absence). This presentation was used as a template for the rest of this meeting.

4. Greg Russell proposes that Michael Monteiro and Sébastien Perrier become **new members** of the Subcommittee. The attendees accept the proposal.
   ACTION: Sabine Beuermann to add these new members to appropriate listings (email, website, etc.).

5. **Short reports on the projects of the Subcommittee** are given:

- *Project on termination, chair Greg Russell, report by Greg Russell*
  The project is almost complete. A final publication on critically evaluated termination rate coefficients is underway. Progress by Hans Heuts has been slow.
  ACTION: Greg Russell to instigate resumption of work on this final publication.

- *Project on the evaluation of vinyl pivalate propagation rate coefficients by EPR, chair Bunichiro Yamada, report by Bob Gilbert*
  A publication was put out in 2007 and the project is completed. As an aside, Greg Russell reports that Robin Hutchinson is now carrying out PLP measurements of vinyl pivalate k_p, which will be an interesting test of the EPR work (it is stressed that this is Robin's own research, not IUPAC work).

- *Project on critical evaluation of methacrylic acid propagation rate coefficients, chair Igor Lacík, report by Bernadette Charleux*
  Last year a publication on critically evaluated propagation rate coefficients was published in *Pure & Applied Chemistry*. A round-robin test for SEC analysis of poly(methacrylic acid) samples was carried out. The experiments in different laboratories have been completed; Igor Lacík has advised that he is still in the process of analyzing the data. Once this is done the project will be complete.
  ACTION: Igor to complete analysis and publish results in an appropriate way if warranted.

- *Project on mechanistic details of RAFT polymerization, chair Philipp Vana, report by Philipp Vana*
  In 2006 the task group published a highlight article in *J. Polym. Sci., Polym. Chem. Ed.*; this has been highly cited (79 citations as of 28 August 2008). Since then worldwide work on rate retardation has largely ceased, and so it is not clear where to take the project from here. One suggestion is to switch the focus to determination of rate coefficients. At a meeting of the taskgroup later in the evening it was suggested that Philipp prepare a publication for *Pure & Applied Chemistry* that ties up loose ends from the previous publication by summarizing work since then on the mechanism of (retarded) RAFT polymerizations, and in so doing presents the scientific community with a consensus view of what is happening in these systems. Any remaining dissenters from this view may elect not to be coauthors. This will complete the taskgroup's activities. A new RAFT project may then be commenced (see below).
  ACTION: Philipp to prepare final publication for *Pure & Applied Chemistry*.

- *Project on terminology for radical polymerizations with minimal termination, chair Aubrey Jenkins, report by Graeme Moad*
  Although this is a project of the Subcommittee on Terminology, it is being carried out with major input from this Subcommittee, for whom it is of high importance. The project is basically complete, with the report being subjected to final scrutiny

by the members of the Terminology Subcommittee (according to their required practices). The proper name of what has hitherto been called living and/or controlled radical polymerization will be "reversible deactivation polymerization". ACTION: Graeme Moad to provide report for circulation when it is finished.

6. **Future projects:**

Greg Russell prefaces this discussion with two points:

1. Project proposals are very short and do not require a lot of time. The project proposals should define clear milestones and a completion date. Michael Buback adds that the scope of IUPAC projects is to provide knowledge to the public, e.g. collect and distribute good data, rather than doing original science.

2. All the above projects are either finished or very close to completion. Thus, as emphasized by Chris Ober and Michael Buback, there is an urgent need for the Subcommittee to start new projects, otherwise there is no point in its existence continuing. After discussion of a range of possibilities (see minutes of previous meetings and reports to the IUPAC PD), the following course of action was agreed upon:

Projects for immediate commencement:

- *Benchmark initiator decomposition rate coefficients and efficiencies*

Having already carried out projects on propagation and termination, it is logical to turn now to initiation, because values of k_p and k_t are of no use for rate and molecular weight calculation unless initiation rate data is also available. Graeme Moad agrees to lead this project. Other possible taskgroup members include Michael Buback, Greg Russell, Devon Shipp, Klaus-Dieter Hungenberg, Manfred Stickler and further industry representation from Akzo (with Michael Buback to identify a suitable candidate). An obvious aim would be for the project to recommend benchmark data for an azo initiator (e.g. AIBN) and a peroxide initiator (e.g. BPO or BTMHP) as a function of temperature.
ACTION: Graeme Moad to prepare project proposal.

- *Benchmark rate coefficients for nitroxide mediated polymerizations*

Given the massive academic interest in "reversible deactivation polymerization" and its likely widespread uptake by industry, it is logical for the Subcommittee to turn its attention to this class of radical polymerization. Nitroxide mediated polymerization is the obvious place to start given that its mechanism is not the subject of major disputes (cf. RAFT and ATRP) and there have been many reports of rate coefficients for NMP. Denis Bertin agrees to lead this project. Other possible taskgroup members include Yohann Guillaneuf, Bernadette Charleux, Patrick Lacroix-Desmazes, Takeshi Fukuda, Atsushi Goto, Per Zetterlund, Shiping Zhu, Graeme Moad and Michael Buback. Data

to be evaluated may be provided by the project members and taken from literature, e.g. the work of Paul Tordo, Mike Georges and Mike Cunningham. An obvious aim would be for the project to recommend benchmark data for TEMPO (or similar) and SG1 (or similar) as a function of temperature.
ACTION: Denis Bertin to prepare project proposal.

Projects to be commenced in approximately one year:

- *Critically evaluated chain-length-dependent termination rate coefficients*

This is a logical continuation of work on termination. It should be commenced once the final publication of the current termination taskgroup is completed (see above). Greg Russell and Michael Buback would be logical leaders of this project.

- *Benchmark rate coefficients for RAFT polymerization*

This is a logical continuation of work on RAFT, which has so far been on mechanism. Trithiocarbonates are an obvious candidate for benchmark rate coefficients given the high level of interest in them and that they are not attended by major mechanistic questions. Philipp Vana is the obvious person to lead this new project.

- *Set of benchmark rate coefficients for a particular monomer*

As already mentioned, only if all fundamental rate coefficients are known with accuracy can one calculate important information such as rate and molecular weight with confidence. Thus the suggestion arises to recommend such a data set for a particular monomer, something that not least of all would be useful for educational purposes (e.g. textbooks, student assignments). Obvious candidates are styrene and methyl methacrylate, given previous Subcommittee work on k_p and k_t for them. However, it would be ideal to use a monomer for which depropagation and transfer can be significant. Thus butyl methacrylate is suggested as a good candidate, as its propagation, depropagation, termination and transfer are all either well studied, reasonably well studied, or easily studied as necessary for this project. Robin Hutchinson would be an excellent candidate to lead this project; he seems to agree to do this.

7. Next Meetings

Suggestions for upcoming meetings of the Subcommittee are:

- February 2009, Melbourne: Symposium in honor of Ezio Rizzardo's 65th birthday
- August 2009, Glasgow: IUPAC General Assembly
- December 2009, Cairns: 11th Pacific Polymer Conference
- July 2010, Glasgow: 43rd IUPAC World Polymer Congress (MACRO 2010)

- December 2010, Honolulu: PACIFICHEM 2010 (www.pacifichem.org)

It is not clear that a large number of Subcommittee members will be at the first three of these meetings. Thus the next major meeting of the Subcommittee will probably be nearly two years hence, at MACRO 2010. Until this time, Subcommittee members should try to meet in smaller groups, for example at the first three meetings listed above.
ACTION: Greg Russell, Sabine Beuermann and Michael Buback to facilitate such meetings and to keep members informed of opportunities and occurrences.