IUPAC Subcommittee on Modeling of Polymerization Kinetics and Processes

Minutes of the meeting held in the Crowne Plaza Hotel, Glasgow at 5 pm on August 3 2009 (during the 42nd IUPAC Congress)

Attendees:

Sabine Beuermann
Michael Buback
Bob Gilbert
Robin Hutchinson
Igor Lacík
Pete Lovell (invited guest/incipient member)
Graeme Moad
Sébastien Perrier
Greg Russell

Appologies were received from Anatoly Nikitin, Patrice Castignolles, Bernadette Charleux, Michelle Coote, Klaus-Dieter Hungenberg, Manfred Stickler, Christopher Barner-Kowollik, Patrick Lacroix-Desmazes, James McLeary, Hans Heuts, Marek Stach, Takeshi Fukuda, Atsushi Goto, Per Zetterlund, Michael Monteiro, Bert Klumperman, Alex van Herk, Shipping Zhu and Devon Shipp.

Minutes (prepared by Sabine Beuermann and Greg Russell):

The meeting was based around the report that Greg Russell had earlier delivered to the General Assembly.

1. **Membership**

- Aubrey Jenkins has recently retired from the Committee due to ill health. In recent times he has made an enormous contribution on radical polymerization terminology (see below). He is thanked for this. Sadly, Irene Schnöll-Bitai died in December 2008 after a three-year battle with cancer. She too made invaluable IUPAC contributions, especially in the area of size exclusion chromatography.

- A number of members have changed their affiliations in recent times, including: Chris Barner-Kowollik from Sydney to Karlsruhe, Patrice Castignolles from Sydney to Brisbane to Mainz, Bob Gilbert from Sydney to Brisbane, Per Zetterlund from Kobe to Sydney (what is it about Sydney?).

- As a result of the above, the geographic spread of membership has changed. In particular, these changes leave no members in either Austria or the UK, both countries with fine traditions in radical polymerization.

- **New members:** It was proposed that Thomas Junkers (who enthusiastically approached GR about 6 months ago) and Pete Lovell become new members. Both were approved. In the case of PL this addresses the issue of having a UK member (see above). However TJ is not quite Austrian!

ACTION: Sabine Beuermann to add these new members to appropriate listings (email, website, etc.).

2. It was discussed where **publications** coming out of the work of the Subcommittee and the associated projects should be published. Michael Buback noted that any publication containing new data or new material and any publication that is expected to have an impact should not be published in *Pure and Applied Chemistry* (PAC). However short reports summarizing the results are appropriate for PAC. Although it has a low impact factor, there is some responsibility on IUPAC committees to support the flagship journal of IUPAC. The policy outlined here would seem to be a good compromise that should be reasonably satisfactory to all parties.

3. **Short reports on the projects of the Subcommittee** were given:

   - *Project on critical evaluation of methacrylic acid propagation rate coefficients, chair Igor Lacík, report by Igor Lacík*
     A round-robin test for SEC analysis of poly(methacrylic acid) samples was carried out. The polymers were provided by the group of Michael Buback in Göttingen and by CAMD in Sydney (Chris Barner-Kowollik and Zachary Szablan). These polymers were characterized in Bratislava (group of IL), Paris (Bernadette Charleux), KCPC Sydney (Bob Gilbert and Patrice Castignolles, before their moves elsewhere – see above) and PSS Mainz (G. Reinhold). At CAMD difficulties occurred in obtaining a PLP structure of the molecular weight distributions. The SEC analyses showed very good reproducibility of aqueous phase SEC and that the esterification of poly(methacrylic acid) works very well. In contrast, some discrepancies occurred in using aqueous phase SEC for poly(acrylic acid). Moreover, esterification of poly(acrylic acid) is problematic, most likely due to side reactions of the α-H atoms that result in changes in the molecular weight distributions. In particular the latter finding for poly(acrylic acid) is important and may be worth publication in a higher impact journal than PAC.
     ACTION: Igor Lacík will distribute the existing data. On the basis of these data it will be decided in which journal the material should be published.

   - *Project on mechanistic details of RAFT polymerization, chair Philipp Vana*
     It was Philipp's intention to attend this meeting, but unfortunately he had to cancel at the last minute. Due to this there could only be brief discussion of the project he chairs. Since the publication of the first article in *J. Polym. Sci., Polym. Chem. Ed.* in 2006, no consensus has been reached on remaining open questions. Thus it was suggested to write up what has happened since the previous publication (e.g. the missing-step model, the Perrier model, new experimental information) and at the same time to see if a 'minimum consensus' may be reported. Michael Buback correctly argues that at the very least the scientific community should be left with a final summary on an issue that has generated hundreds of publications and has taken up hours and hours of conference sessions.
     ACTION: The decision on whether an additional manuscript is to be written should

be made by Philipp Vana. In case he does not write the paper, Graeme Moad and Sebastien Perrier may do so.

- *Project on the terminology for radical polymerizations with minimal termination – the so-called "living" and/or "controlled" radical polymerization from the Subcommittee on polymer terminology, chaired by Aubrey Jenkins, Richard Jones, and Graeme Moad, report by Graeme Moad*
  The project members agreed that the appropriate name is "reversible-deactivation radical polymerization". This recommendation will soon be published in *Pure and Applied Chemistry*. The draft is available at http://old.iupac.org/reports/provisional/abstract08/jenkins_prs.pdf

4. **Future projects**

Proposals for the following two **new projects** are currently being prepared:

- *Critically evaluated rate coefficients associated with **initiation** of radical polymerization, designated taskgroup chair Graeme Moad*
  Having devoted several taskgroups to the determination of reliable rate coefficients for propagation and termination, it seems to be a matter of priority to devote a taskgroup to evaluate the rate of initiation. These data are important to accurately model rates of polymerization and molecular weight distributions.

- *Critically evaluated dissociation rate coefficients for **alkoxyamines** used in **nitroxide mediated polymerization**, designated taskgroup chair Denis Bertin*
  Reversible-deactivation radical polymerizations, including nitroxide mediated polymerizations, are becoming increasingly important. Thus, the evaluation of dissociation and association rate coefficients, which are important for modeling and optimization of reactions, is of high importance.

Chris Ober (Polymer Division chair) advised at the General Assembly that all project funds for the two years 2008-9 have been allocated. It therefore should be good timing to submit the above proposals in the final months of 2009, so that hopefully they can be supported in the new funding cycle beginning January 2010.

Beyond the above two proposals, the following projects were identified as strong candidates for 2010:

- *Critically evaluated rate coefficients for **chain-length-dependent termination,** suggested taskgroup chairs Michael Buback and Greg Russell*
  As a logical continuation of previous work on termination, CLDT should be addressed. Specifically, it would seem that benchmark CLDT rate coefficients can now be identified. This project should be started once the current project on termination is (finally) finished.

- *Critically evaluated rate coefficients for **RAFT polymerization,** suggested taskgroup chairs Philipp Vana and/or Chris Barner-Kowollik and/or Sebastien Perrier and/or Graeme Moad and/or …*
  As a logical continuation of previous work on RAFT polymerization, an attempt should be made to identify benchmark rate coefficients for RAFT polymerization, for the same reasons as given above in association with NMP. PV has suggested trithiocarbonate systems as most appropriate for this work.

- *Project on mechanistic details of ATRP, suggested taskgroup chair Kris Matyjaszewski*
  As another important potential project, the mechanism of ATRP was identified. The chemistry community at large is aware of the tremendous potential of ATRP, but to some extent this appreciation is being held back by an awareness of ongoing debate about the mechanism of ATRP. If the major players in this debate could find some level of agreement, this could only add to their own standing, not to mention that of the radical polymerization community in general. Bob Gilbert asked: is it possible to define a measurable mechanistic quantity on which ATRP experts disagree, and then measure it? Another option would be to write a dilemma paper on the problems with ATRP, as was done with RAFT in 2006 (see above).
  ACTION: GR to bring all this to Kris Matyjaszewski's attention.

It is stressed that the above is neither an exhaustive list – many other possible project ideas have arisen – nor an exclusive list. The preeminent requirement for a project is for someone to have the enthusiasm to lead it. If someone has a strong desire for there to be a particular project, they are welcome to assemble a taskgroup and write a proposal.

5. Next Meetings

Suggestions for upcoming meetings of the Subcommittee are:

- *Possible*: December 2009, Cairns: 11th Pacific Polymer Conference
- *Definite:* July 2010, Glasgow: 43rd IUPAC World Polymer Congress (MACRO 2010)
- *Possible:* August 2010, ACS National Meeting in Washington DC
- *Definite:* December 2010, Honolulu: PACIFICHEM 2010 (www.pacifichem.org)