

## IUPAC Subcommittee on “Modeling of Polymerization Kinetics and Processes”

Minutes of the meeting during SML06, Il Ciocco, September 5, 2006

### Attendees

|                             |                     |
|-----------------------------|---------------------|
| Christopher Barner-Kowollik | James McLeary       |
| Sabine Beuermann            | Graeme Moad         |
| Michael Buback              | Greg Russell        |
| Markus Busch                | Ron Sanderson       |
| Patrice Castignolles        | Irene Schnöll-Bitai |
| Bob Gilbert                 | Marek Stach         |
| Atsushi Goto                | Matthew Tonge       |
| Hans Heuts                  | Nikolay Tsarevsky   |
| Klaus-Dieter Hungenberg     | Philipp Vana        |
| Robin Hutchinson            | Alex van Herk       |
| Atsushi Kajiwara            | Bunichiro Yamada    |
| Bert Klumperman             | Per Zetterlund      |
| Igor Lacík                  |                     |
| Kris Matyjaszewski          |                     |

Minutes prepared by Sabine Beuermann.

1. Michael Buback presented the report to IUPAC Polymer Division of the activities within our Subcommittee. The report was prepared for the IUPAC meeting held the weekend before MACRO 2006.
  - Task group 2000 – 028 – 1 – 400 on “Critically evaluated termination rate coefficients for free-radical polymerization. 1. Current status, evaluation of experimental methods, data for styrene and methyl methacrylate“, chaired by Greg Russell
  - Task group 2002 – 053 – 1 – 400 on “Establishment of quantitative reliability of electron spin resonance techniques for polymerization kinetics“, chaired by Bunichiro Yamada
  - Task group 2004 – 034 – 1 – 400 on “Critically evaluated propagation rate coefficients for free-radical polymerization of water-soluble monomers polymerized in the aqueous phase“, chaired by Igor Lacík
  - Task group 2004 – 040 – 1 – 400 on “Towards a holistic mechanistic model for reversible addition fragmentation chain transfer (RAFT) polymerizations: Dithiobenzoates as mediating agents“, chaired by Philipp Vana
2. An update on the projects was given by the chairpersons.
  - Greg Russell:  
As an outcome of the efforts from his task group two manuscripts were published. Currently, Hans Heuts and Greg Russell are compiling a benchmark data set for MMA and styrene bulk polymerization  $k_t$  at low conversion. A long report on this difficult task was given by Hans Heuts, reflecting the large amount of work he has put into this:

Hans Heuts:

Has analyzed the data in nearly 30 publications, many of them quite old, using the  $k_p$  data recommended in the IUPAC benchmark publications. The factor of two according to the IUPAC definition of the termination rate law has been considered. The data selection and treatment is discussed by the attendees. There are no objections against Greg's suggestion to publish benchmark  $k_t$  values together with a detailed warning about the difficulties encountered. Attendees interested in contributing to the manuscript are asked to contact Greg or Hans soon.

- Igor Lacík:

In phase 1 of the project, propagation rate coefficients for aqueous phase polymerizations of methacrylic acid were collected and a manuscript on benchmark value data was prepared for PAC, which is currently under review. In phase 2 of the project "general" aspects of studies into the propagation rate coefficients for monomers polymerized in the aqueous phase are considered, e.g., such as monomer selection, PLP conditions, SEC strategies. With respect to SEC strategies a round robin test on PLP generated poly(acrylic acid) and poly(methacrylic acid) is currently underway. As an outcome of phase 2, a publication on recommendations for PLP and SEC in aqueous phase will be prepared. While  $k_p$  data are available for acrylic acid, acrylamide, and NIPAM, everybody is invited to carry out additional experiments to enable benchmark value data sets.

- Bunichiro Yamada:

The objective of the project was to obtain consistent values for  $k_p$  from EPR and PLP-SEC. The monomer vinyl pivalate was chosen, which has not been studied so far. At the meeting it was indicated that problems may have occurred in the SEC analysis. Thus, it was suggested to write up the EPR results first.

- Philipp Vana:

As a first milestone of the project a paper on the "dilemmas" with RAFT mechanism and kinetics has been published in J. Polym. Sci, Part A, Polym. Chem. 44 (2006) 5809-5831 as a highlight article. The work on the project initiated new co-operations among the members of the task group. The focus is on mechanisms and will include both pre-equilibrium and main-equilibrium conditions.

Considering these two reaction schemes separately has been identified of key importance for further studies.

3. Everybody was asked to inform the secretary about changes in affiliation or position.
4. Greg Russell will take over as subcommittee chair after the IUPAC meeting in Turin in 2007. Sabine Beuermann has agreed to Greg's request to continue as secretary. Robin Hutchinson and Michael Buback will also assist as deputy-chair and past-chair, respectively.
5. Marek Stach (Polymer Institute of the Slovak Academy of Science) will be a new member of the Subcommittee.

In response to a comment by Greg Russell about a lack of Americans on this subcommittee (Matyjaszewski and Shipp are the only two), Kris Matyjaszewski subsequently suggested Shiping Zhu as a new member. Actually, he works in Canada (McMaster University to be precise). But certainly Zhu would be a welcome addition (Robin to approach him?).

6. The following topics are considered as candidates for new projects:
  - ionic polymerizations
  - chain transfer coefficients
  - ratio of disproportionation to combination in termination reactions
  - ATRP: differences on rate constants and equilibrium data by principal investigators (Kris Matyjaszewski was asked to organize a task group)
  - NMP: ((After the meeting Denis Bertin (Montpellier) made the offer to organize a task group on rate coefficients associated with NMP))
  - Copolymerization: determination of reactivity ratios (Robin Hutchinson to lead?)
  - Modeling: effect of rate coefficient precision on output quantities (Hungenberg to lead?)
  - Database of IUPAC recommended rate coefficients (suggested by both Gilbert and Matyjaszewski; Russell to lead?)
  - Termination: extension of current project (which actually officially ended several years ago), e.g. to look at benchmark values for monomers other than Sty/MMA and/or benchmark values for conversion dependence (suggested by Buback; Russell or Heuts or Buback to lead?)
7. Next Meetings: 29<sup>th</sup> Australasian Polymer Symposium, Hobart, February 2007; Macro 2008 in Taiwan, ACS Meeting Philadelphia in August 2008