IUPAC Subcommittee on Modeling of Polymerization Kinetics and Processes

Minutes of the meeting held in room Randolph 316 at Virginia Tech, Blacksburg at 12.30 pm on June 25, 2012 (during Macro2012)

Attendees: Greg Russell (GR) - chair, Michael Buback (MB), Bernadette Charleux (BC), Michelle Coote (MC), Atsushi Goto (AG), Atsushi Kaijiwara, Tatsuki Kitayama, Igor Lacik (IL), Graeme Moad (GM), Devon Shipp (DS).

Apologies (in order received by email)**:** Per Zetterlund, Chris Barner-Kowollik (CBK), Michael Monteiro, Bert Klumperman, Thomas Junkers (TJ), Sabine Beuermann (SB), Hans Heuts, Marion Gaborieau, Philipp Vana, Patrick Lacroix-Desmazes, Kris Matyjaszewski, Marek Stach, Patrice Castignolles, Pete Lovell, Klaus-Dieter Hungenberg, Johannes Vorholz, Markus Busch, Manfred Stickler, Mathias Destarac, Shiping Zhu, Sebastien Perrier, Bob Gilbert, Pascal Hesse, Anatoly Nikitin, Ernie Wysong, Ron Sanderson, Takeshi Fukuda, Alex van Herk (AvH), Yohann Guillaneuf (YG), Eriko Sato, Robin Hutchinson (RH).

Note: If (bracketed) initials are included after a name above, then it means that that person is explicitly mentioned in the minutes below.

Minutes (prepared by GR from notes taken by MC during the meeting):

Opening:

GR welcomed the attendees. He then proceeded to go through the report (in ppt format) that he had delivered a few days previous to the IUPAC Polymer Division (PD) meeting at nearby Roanoke, using this report as a framework for the present meeting.

Next Subcommittee meetings:

- Contrary to usual, **there is no obvious occasion to meet in 2013**. GR asked attendees if they had any ideas in this regard, but no suggestions were forthcoming, or have been subsequently.
- On the other hand, **Macro2014 in Thailand is an obvious occasion to meet in 2014**.

ACTION: SB and RH to try to find an opportunity to meet in 2013.

New Subcommittee leadership:

GR became Vice-President of the IUPAC PD at the beginning of 2012. Therefore he should now step down as Chair of this Subcommittee. This was his last meeting in charge. He wishes to record that it has been a privilege to serve.

The following new leadership arrangement has been approved by the IUPAC Polymer Division:

- **Sabine Beuermann and Robin Hutchinson will co-share both the Chairperson and Secretary positions**. This is with a view to one or other of them being present to chair every meeting.

(Indeed, RH was to have been present at this meeting, but unfortunately had to cancel at the last minute with good cause.)

The members present all concurred with this new leadership arrangement.

New members:

With a view to increasing the presence of industry on the Subcommittee, Pascal Hesse (BASF, Ludwigshafen), Johannes Vorholz (Röhm, Darmstadt) and Ernie Wysong (DuPont, Wilmington) are **new members** acquired over the last year.

GR paid tribute to **Manfred Stickler**, who, after over two decades of valuable and humble service, has formally retired from the Subcommittee (due to having retired from Röhm), but will remain involved in the initiation project and wishes to remain informed of Subcommittee events, in case he can participate.

Jung-Il Jin pointed out to GR and MB at the IUPAC PD meeting that there are no **Subcommittee members from Korea, China or Taiwan**. Indeed this should be addressed.

ACTION: IL to seek suggestions of possible Taiwanese members from contacts he has there.

ACTION: SB/RH to investigate inviting Junpo He (Shanghai) and Yingwu Luo (Hangzhou; http://www.fe.zju.edu.cn/english/redir.php?catalog_id=6586&object_id=7050) as new members (GM can provide further details if desired).

Project on critically evaluated termination rate coefficients:

GR reported: the final output, on **benchmark termination rate coefficients for styrene and MMA in bulk at low conversion**, is still "in preparation". Help from SB and TJ has now been enlisted.

ACTIONS: GR to complete a draft paper on styrene data by the end of September 2012. If he fails to deliver then the matter will be thrown over to SB and TJ. In any event they will be writing up the MMA work.

Project on critically evaluated propagation rate coefficients of water-soluble monomers:

IL reported: the final output, on **precision of SEC for poly(acrylic acid) and poly(methacrylic acid)**, after being tantalizing close to completion, has not moved forward over the last year since BC exposed some serious shortcomings. IL still needs to address these issues.

ACTION: IL to meet with BC and MB during the course of the conference to discuss what further work needs to be done and to formulate a plan for doing it. (Meeting duly held – GR can report that they each ate a medium-cooked sirloin steak as this discussion took place!)

ACTION: IL to orchestrate this work and have the manuscript completed by the end of 2012.

Project on the mechanism of dithiobenzoate-mediated RAFT polymerization:

GM reported: he has been invited to write an article for *Mac. Rapid Commun.* that attempts to draw together the 30-or-so papers there have been on RAFT retardation over the last few years, a veritable flurry of activity. This could possibly double as the long-desired final output of this project.

Intense discussion followed as to the best course of action to take. As befitting this topic, there was no consensus. At one end of the spectrum, MB opined that Graeme should independently write his own article, and if enough people agree with it, then either their names could be added as co-authors, or the contents could be summarized in a separate article for *Pure Appl. Chem.* AG concurred with this view. At the other end of the spectrum, MC believes that GM should lead a genuinely co-authored effort, her feeling being that "90% agreement" could be found on mechanistic issues. It is unclear what GM himself thinks. GR is frustrated by this situation, and simply wants there to be some sort of output to close out the project. Herding cats, anyone?

ACTION: GM to do something.

Project on benchmark rate coefficients for initiation:

GM reported: There has not been a lot of forward progress. There are massive amounts of data for k_d for AIBN, but not a lot for f, in fact really only the two studies in which it has been directly measured (Moad et al. from the 1980s, Buback et al. from the 1990s). Of course it is the product fk_d that is important, not k_d alone (GR comments: true, but k_d varies by orders of magnitude, whereas low-conversion f is usually 0.5–0.8, i.e., to reasonable approximation it can be guessed). For AIBME there is really only Stickler data.

GR observed that with this project there is nothing controversial for the members to thrash out, so it's just a case of getting in there and doing the work.

ACTION: GM to start writing manuscript on rates of azo initiation by the end of the year.

Project on critically evaluated dissociation rate coefficients for alkoxyamines:

Neither BC nor GR are aware of any activity on this project over the last year. Given Denis Bertin's elevation into the political stratosphere of Marseilles, YG will have to assume full leadership of this project.

ACTION: BC and GR each to contact YG to get this project moving again. (Already done by both.)

Project on critically evaluated rate coefficients for acrylate propagation:

Formal approval for this project was (at last) sent to CBK in April 2012.

In the nick of time, TJ emailed GR a first draft of a paper on benchmark (secondary-radical) k_p for MA, for the purposes of discussion at this meeting (well done TJ!). The following feedback is provided:

- The proposed list of authors seems appropriate.
- (Comment added post-meeting by MB and GR) In particular RH should take a leading role in carefully critiquing the tabulated data, given his extensive experience with acrylate k_p.
- The (unpublished) Manders data cannot be included unless the accompanying experimental details are tracked down (from his thesis?), at a bare minimum so that entries in Table 1 can be completed.
- In any event a version of Figure 1 *without* the Manders data should be prepared, in order to see whether these data are even needed.

- There is a discrepancy between the approx. 0 °C cluster of Manders points in Figure 1, which lie appreciably below the best fit (whereas the rest of the Manders points are close to the best fit), and the same points as presented by AvH in seminars (e.g. see the ppt file of AvH's 60th birthday talk for MB, as provided to TJ by GR), in which there is no such irregularity. This needs to be urgently resolved. It means that these two versions of the same data are inconsistent – which version is correct? (Again, this argues for being very cautious about including the Manders data in any benchmark set.)
- Prepare a version of Figure 1 with only bulk data. Really the manuscript should recommend *bulk* k_p only, including giving Arrhenius parameters for such data; if any solution data should happen to be the same within error, that should be regarded as happenstance, not as scientific necessity.
- The discussion should include a short section on solvent effects, including whether the data indicate any such effect for MA.
- There should also be some brief discussion of the argument related to (ideal) chain-end k_p and actual (SPR and MCR affected) k_p. This is important so as to avoid incorrect use of the reported data.
- How confident can one be of good temperature control for these data points? At the very least there needs to be some discussion of this. Acrylates polymerize rapidly, therefore they are prone to exotherm effects.
- AvH's MALDI data should *not* be included in the benchmark data set, because one cannot yet be totally confident that this technique delivers MMD shape accurately. However, a plot in which the benchmark fit is compared with said MALDI data should be prepared as part of the discussion. Given the indications of expected good agreement, this comparison will probably serve to engender more confidence in MALDI as a method for k_p determination.
- A visual version of Table 2 should be prepared, i.e. the MMA/BMA vs MA/BA comparison. On the basis of MMA/BMA, one expects that (1) MA and BA should have the same $E_a(k_p)$, and (2) $A(k_p)$ should be about a factor of 1.2 higher for BA than for MA. In a sense these may almost be considered "consistency checks", because theory and experiment both suggest they are necessities. Table 2 as it stands shows that (1) is fulfilled but that (2) does not look like it is, because the two *A* values are essentially the same. However the "recommended" values of k_p at 20 °C (see Table 2) do fulfil this "consistency check" nicely: 14 476 L mol^{-1} s^{-1} BA, 12 054 L mol^{-1} s^{-1} MA (incidentally, it is unjustified to quote to so many significant figures – please rectify). GR suggests 3 actions here:
    - First refine the current data set according to the suggestions above, so as to get better estimates of E_a and *A*.
    - Prepare a plot showing the benchmark MA and BA *data* (RH can provide BA numbers in digital form), and then use the **one value of E_a to fit both data sets**, in order to see how *A* varies between the two monomers (this is just the Buback/Lacik approach in analysing methacrylic acid k_p values for different water contents, e.g. see their *Macromoluecules* **2006** paper).
    - Prepare a plot showing all the Arrhenius fits for MMA, BMA, MA and BA, each fit only being presented over the measured range of temperatures.
- (Comment added post-meeting) There was discussion from GR, MC and MB about inclusion of the section on quantum mechanical calculations. Understandably, MC is for this. On the other hand, MB and GR are against it, on the grounds that there is no precedent for including discussion of quantum mechanical calculations in a work of this nature, and nor is any especial reason apparent in this case. A paper like this is about *data*, not theory, which in any event is far less accurate than the data: a factor of 2–4 at best in the case of theory, while experiment is about ±15%. A compromise here would be to have a condensed and cautionary section on QM. The project-leading authors (TJ and CBK) should decide this after further reasoned consultation with the various co-authors.

- The manuscript should be circulated to authors ASAP for detailed discussion.
- (Comment added post-meeting by GR) Figures are good, so try to include more of them, e.g. according to the suggestions above.
- (Comment added post-meeting by IL) If there is any need for further MA k_p data to be generated, IL would like to carry out such experiments in Bratislava, and says he can do so within one month. He is prepared to generate k_p as a function of *T* and pulse repetition rate.

AOB:

MB stressed the importance of **new projects**. GR responded that there are many such ideas that have been floating around for a long time, as listed in the ppt file referred to above. Some of these are of more merit than others. Suggestions mentioned at this meeting:

- MB: critically evaluated rate coefficients for chain-length-dependent termination.
- GR: copolymerization reactivity ratios, especially recommended protocols for their measurement, something that synthetic chemists are often vague about.
- BC (new idea): pH effects on RAFT transfer constants for AA and MAA. (IL would like to participate in such a project.)
- DS (new idea): k_p N-vinyl pyrrolidone.
- MB/BC (new idea): k_p of water-soluble monomers in general, e.g. acrylic acid and acrylamides. (Again, IL would like to participate in such a project.)
- MB/MC (new idea): backbiting and tertiary-radical propagation rate coefficients for BA.

Final word:

IUPAC should be about tangible outputs. This Subcommittee has an extraordinary record of producing high quality, excellently cited outputs. However the last few years have been very lean in this regard, with **no new outputs since 2007** (reasonably excluding the 2010 terminology paper on RDRP). As documented above, currently there are 4 papers in the pipeline, viz. on termination, SEC of water-soluble polymers, RAFT mechanism and MA k_p.

MB and GR would like to set the Subcommmittee the challenge of **completing at least 3 outputs** before the next meeting of the IUPAC PD, which will be in August 2013 in Istanbul.