

## IUPAC Subcommittee on Modeling of Polymerization Kinetics and Processes

**Minutes of the meeting held in Room 323A of the Hawaii Convention Center, Honolulu at 4.30 pm on December 17, 2010 (during Pacificchem 2010)**

**Attendees:** Greg Russell (GR) - chair, Christopher Barner-Kowollik (CBK), Denis Bertin (DB), Michael Buback (MB), Patrice Castignolles (PC), Bernadette Charleux (BC), Michelle Coote (MC), Mathias Destarac, Marianne Gaborieau (MG), Atsushi Goto, Yohann Guillaneuf (YG), Robin Hutchinson (RH), Peter Lovell (PL), Kris Matyjaszewski (KM), Graeme Moad (GM), Eriko Sato, Per Zetterlund.

**Apologies:** Sabine Beuermann (SB), Hans Heuts (HH), Klaus-Dieter Hungenberg, Thomas Junkers (TJ), Bert Klumperman (BK), Igor Lacik, Patrick Lacroix-Desmazes, Michael Monteiro, Anatoly Nikitin, Sébastien Perrier, Ron Sanderson, Manfred Stickler, Alex van Herk (AvH), Philipp Vana (PV).

**Minutes** (prepared by PC and GR):

*Opening:*

GR welcome the participants. There is no meeting of the IUPAC Polymer Division at Pacificchem, hence GR does not have a formal presentation for this meeting.

*New members:*

- Eriko Sata is welcomed as a new member, replacing Akikazu Matsumoto, her colleague at Osaka City University.

The following are proposed and subsequently accepted as new members at this meeting:

- Markus Busch (Technische Universität Darmstadt, Germany) (Busch@Chemie.TU-Darmstadt.de)
- Yohann Guillaneuf (Université de Provence, France) (yohann.guillaneuf@gmail.com, yohann.guillaneuf@univ-provence.fr)
- Marianne Gaborieau (University of Western Sydney, Australia) (m.gaborieau@uws.edu.au)

**ACTION:** SB to process membership changes.

*Project on benchmark rate coefficients for nitroxide-mediated polymerization (NMP):*

Due to the IUPAC Polymer Division being in a difficult financial position, there has been a hold-up in this project being approved. MB explains it will receive a token amount of funding, probably something like USD 800. DB is ready to start the project now.

**ACTION:** MB to contact Chris Ober to get project officially approved and started.

A meeting on this project subsequently took place at 11.30 am on Sunday 19 December at Pacificchem (Convention Center Room 323A). DB led the meeting.

*Project on benchmark rate coefficients for acrylates:*

CBK and TJ propose to start a new project on benchmark rate coefficients for acrylates.  $k_p$  is the obvious focus. There are a lot of issues. A first task would be to agree on and publish benchmark  $k_p$  for methyl acrylate (MA). There are different sets of  $k_p$  values available in published work from Karlsruhe (CBK, TJ, PC), Eindhoven (Bart Manders' thesis, Alex van Herk), Göttingen (MB), and maybe Sydney-CAMD (MC, Tom Davis) and Paris (PC, BC). There has also been recent theoretical work on methyl acrylate  $k_p$  in Canberra (MC). It seems sensible for a taskgroup initially to restrict itself to  $k_p$  for chain-end (i.e., secondary) acrylate radicals.

The uncertainty in  $k_p$  (averaged over the mixture of secondary and tertiary radicals) of acrylates mainly comes from long-chain branching (PC, MG). Long-chain branching creates heterogeneity in hydrodynamic volume and this can significantly lower accuracy of determination of molecular weight by SEC. This is especially an issue with 2-ethyl hexyl acrylate (EHA), where error can be very large due to unusually high levels of branching, as quantified by NMR (unpublished work by PL). This difference is not due to hydrogen abstraction on the EH side group: the hydrogen abstraction has been proven by NMR to happen only on the backbone (PL).

MB emphasizes the importance of not limiting ourselves to propagation, otherwise this is useless for industry: we must eventually try to provide a complete set of benchmark rate coefficients for acrylates. BC mentions the increasing use of substituted acrylamides, even though their kinetic coefficients are unknown. PLP studies have not been performed on these monomers but are needed. RH and CBK discuss vinyl acetate as a possible candidate for benchmark values: different sets of consistent data are available, although there are more problems with frequency variation than are encountered in MA.

The group agrees to proceed on collecting  $k_p$  for MA and perhaps other alkyl acrylates. CBK and TJ will lead the project; many others from the Subcommittee are interested in being involved.

ACTION: TJ and CBK to complete application with assistance from GR.

*Degree of branching in conventional vs controlled polymerization of acrylates:*

Studies have shown that the degree of branching is lower in reversible-deactivation radical polymerization (RDRP) than in conventional radical polymerization.<sup>1</sup> This was highly unexpected and the reason is still under debate.

A separate meeting on this subsequently took place on Saturday 18 December at 11.30 am in Room 323A. A lower degree of branching than in conventional polymerization is also observed with thiols (CBK, TJ, MG, PC). It seems likely that these phenomena have the same cause. It might also be wondered if the elevated level of branching in EHA (see above) has the same mechanistic cause. The two most highly favoured postulates for explaining the RDRP phenomenon are chain-length-

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<sup>1</sup> Ahmad, N. M.; Charleux, B.; Farcet, C.; Ferguson, C. J.; Gaynor, S. C.; Hawket, B. S.; Heatley, F.; Klumperman, B.; Konkolewicz, D.; Lovell, P. A.; Matyjaszewski, K.; Venkatesh, R. *Macromol. Rapid Commun.* **2009**, *30*, 2002-2021.

dependent backbiting<sup>1</sup> and time-dependent backbiting, as recently published by Asua et al. in *Mac. Rapid Commun.* The idea with the former is that  $k_{bb}$  declines with chain length in a similar way to  $k_p$ , and so the smaller number of short radicals in RDRP results in lower time-averaged occurrence of backbiting. The idea with the latter is that a radical takes a while to become “activated” for backbiting, and so the many ‘power-naps’ taken by a radical in RDRP mean that it may not undergo backbiting for some of the time it is ‘awake’. Someone witty suggested that this is like ‘hot radical theory’ but in reverse (i.e., ‘cold radical theory’). While this suggestion is attractive, it is hard to believe that a radical is inactive for backbiting on the timescale of milliseconds (what is required) given that it is undergoing collisions on the timescale of nanoseconds. Also, this idea would predict that the level of branching should change with the concentration of RDRP-mediating agent (the higher this concentration, the briefer the periods before deactivation). The large study coordinated by PL<sup>1</sup> found no evidence for this. On the other hand, there is also no direct evidence for the chain-length-dependent idea.

The time-dependent idea could be investigated by a really careful look at whether there is variation of branching level with concentration of RDRP agent (see above). Another idea to emerge from this meeting is as follows. BC proposes to measure the degree of branching on a 2<sup>nd</sup> block extension. If branching is chain-length dependent, then this should result in lower levels of branching than in equivalent systems that start with a micro-RDRP agent. This could be done easily from a first ATRP block (KM). Starting with a PMMA first block would make the NMR difficult (overlap of peaks). Having a block of <sup>13</sup>C labelled *n*-butyl acrylate would be best for the NMR (MG), but may be too expensive. BC, KM, PC and MG will keep in touch on this.

*Project on benchmark rate coefficients for initiation:*

The project has started. GM is the leader; others involved include GR, MB and MC. These people had a project meeting at the conclusion of this Subcommittee meeting.

*Project on benchmark rate coefficients for termination:*

Just when it seemed that GR had skilfully avoided this topic being broached, MB cruelly raised it. The final paper from this project remains on standby. Due to a lack of time, HH has been forced to abandon this paper. He has bequeathed to GR all his working material, including some very scary Excel files and some figures generated by an unknown graphics program. CBK volunteers TJ to work further on this paper. Does CBK now have one friend fewer?

ACTION: GR to finish the paper on benchmark  $k_t$  values for styrene (and perhaps methyl methacrylate), seeking assistance from TJ and CBK.

*Project on mechanistic details of RAFT polymerization:*

GR forgot to raise this topic at the meeting but had private discussions with several stakeholders. The situation is not promising. At the Subcommittee meeting in Glasgow in July, it was agreed that PV and BK would write a first draft of a final paper by the end of September. This has not happened. Further, if anything the divide between the opposing schools (slow vs. fast fragmentation) has widened in recent months due to new developments that are interpreted differently by each school. GR wonders whether the best thing is to terminate the project now without any further activity. At some stage in the future after further research has been done it may be possible to publish a final

consensus view on what causes retardation in RAFT polymerization with dithiobenzoates. But right now this goal seems distant.

(POSSIBLE) ACTION: Project to be terminated and taskgroup disbanded?

*Next Il Ciocco meeting:*

MB and AvH are considering holding another Il Ciocco meeting in either 2012 or 2013. GR asked for feedback on this. In 2012 there is already a World Polymer Congress, which should be supported by this Subcommittee, especially MB, who will be IUPAC Polymer Division president by then. It would not look good to organize a "rival" conference around the same time. Also, it is surely too late to start organizing a conference for 2012. So there was general agreement for the date to be in 2013. For a more precise date, September is not good for France or Australia. August is OK for France and Germany, not Australia. July is OK for France and Australia, not Germany. Thus there does not seem to be a time that is ideal for all. Should the themes be kinetics and mechanisms again? Synthesis and characterization were also indeed well-represented in the last meeting (CBK). MB reminds that the Il Ciocco conferences are unique in the sense that they cover all of radical polymerization, not just RDRP or characterization. The idea is to keep an overview of the entire field of radical polymerization. GR suggests it may be good to have a French person on the organizing committee (e.g. BC?), not just Dutch and Germans.

*Next Subcommittee meetings:*

There may be a small Subcommittee meeting at the 32<sup>nd</sup> Australasian Polymer Symposium in Coffs Harbour, Australia in February 2011. This will depend on how many Subcommittee members are there. If held it will be informal and casual.

The next major Subcommittee meeting will be at the 242<sup>nd</sup> ACS National Meeting & Exposition to be held in Denver over August 28 – September 1, 2011. This will include the 6<sup>th</sup> symposium organized by KM in the series *Controlled/Living Radical Polymerization*, started in San Francisco in 1997 and most recently in Philadelphia in 2008. KM invited everyone to attend this symposium.

In 2012 there should be opportunity to have a major Subcommittee meeting at the IUPAC World Polymer Congress to be held June 24 – 29 at Virginia Tech in Blacksburg, USA.

And then in 2013 there will hopefully be an Il Ciocco meeting (see above).