

Prediction and Experimental Characterization of the Molecular Architecture of FRP and ATRP Synthesized Polyacrylate Networks

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Abstract:

Following recent research works [1, 2], this work reports additional experimental and modeling studies concerning the conventional (FRP) and atom transfer radical polymerization (ATRP) of acrylate/diacrylate monomers. In the framework of a recently developed general approach [3-5], kinetic models including crosslinking reactions and branching by chain transfer to polymer are discussed for FRP and ATRP polymerization systems. Besides MWD, the prediction of the z -average radius of gyration is shown to be possible for these non-linear polymers.

A set of experiments was performed at 1 L scale in a batch reactor using *n*-butyl acrylate (BA) or methyl acrylate (MA) as monovinyl monomers and 1,4-Butanediol diacrylate (BDDA), 1,6-Hexanediol diacrylate (HDDA) or bisphenol A ethoxylate diacrylate (BEDA) as crosslinkers. In FRP experiments, AIBN was used as initiator and ATRP polymerizations were initiated by ethyl 2-bromopropionate (EBrP) and mediated by CuBr using PMDETA (*N,N,N',N'',N''*-pentamethyldiethylenetriamine) as ligand. Polymerizations were carried out in solution at $T=60\text{ }^{\circ}\text{C}$ at different dilutions (15 to 56% volumetric fraction of monomer) using toluene, anisole and DMF as solvents. Products formed at different polymerization times were analyzed by SEC/RI/MALLS yielding average MW, MWD, z -average radius of gyration and monomer conversion.

Important differences in the molecular architecture of FRP and ATRP polyacrylate networks were identified and it is shown that huge errors can result from the interpretation of chromatograms of these networks using linear calibrations. Comparison of experimental results with predictions put into evidence the important effect of intramolecular cyclizations at all dilutions, even with ATRP polymerizations.

References:

- [1] Gao, H., Min, K., Matyjaszewski, K., 2007, *Macromolecules*, 40, 7763.
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- [3] Costa, M.R.P.F.N., Dias, R.C.S., 2005, *Chem. Eng. Sci.*, 60, 423.
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- [5] Costa, M.R.P.F.N., Dias, R.C.S., 2007, *Polymer*, 48, 1785.

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POLYMER REACTION ENGINEERING 7 (PRE 7)

**May 3-8, 2009
Niagara Falls, Ontario, Canada**

February 17, 2009

I am pleased to inform you that your submission to the Polymer Reaction Engineering VII Conference (PRE 7) website has been accepted as a poster contribution. A committee of three people from academia and industry went through about 170 submissions and made the first selection, which was subsequently revisited by a separate committee of three more people. Please inform your co-authors (if applicable).

The very popular poster sessions during the PRE conferences form an extremely important and integral part of the conference, and are complementary to the conference six lecture sessions. The two long poster sessions (usually held on Monday and Wednesday afternoon) are the forum of great interactions and fruitful (and often animated) discussions and exchange of ideas between academic and industrial people, poster co-authors and conference participants. As per common practice, there will be several poster prizes for posters presented by graduate students.

After we hear from you (**please confirm that you will attend and present your poster via a brief e-mail to penlidis@uwaterloo.ca**), we will finalize the poster list and schedule, which will appear on the conference website. Conference registration is open via the website (www.engconfintl.org/9ab.html). More relevant details will be posted on the website as we move closer to the conference dates in May 2009.

The poster dimensions are 4 feet x 4 feet and push pins will be provided to presenters at the conference.

Once more, congratulations and welcome to the poster sessions of PRE 7. The co-chairs of the poster sessions (Prof. **Mike Cunningham**, Queen's Univ., Canada; Dr. **Daryoosh Beigzadeh**, Dow Chemical Co., USA; and Dr. **Jon Debling**, BASF, USA), and the conference co-chairs, John Richards, Marc Dube and I, are looking forward to greeting you and interacting with you in Niagara Falls in May 2009. Needless to say, we are also looking forward to your poster presentation and ensuing lively discussions!

Best regards,

Alex Penlidis (PRE 7 conference chair)

Polymer Reaction Engineering VII, Niagara Falls, Canada, May 3-8, 2009