



First controlled radical polymerization of n-butyl acrylate mediated by bis(acetylacetonato)cobalt(II)

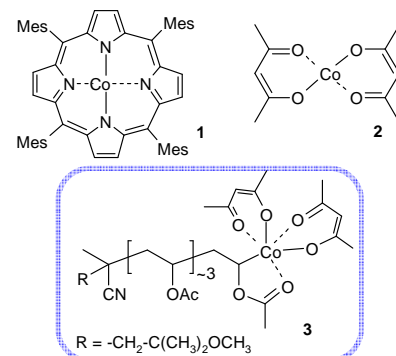
Marie Hurtgen, Antoine Debuigne, Christine Jérôme, Christophe Detrembleur

marie.hurtgen@ulg.ac.be, University of Liège, Sart-Tilman, B6a, B-4000 Liège

Introduction

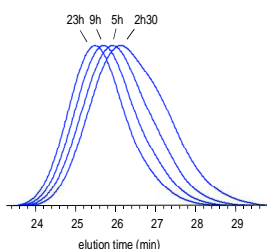
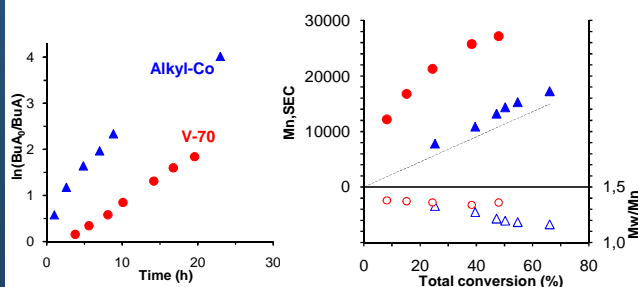
Cobalt-Mediated Radical Polymerization (CMRP) is characterized by the high level of control imparted to the polymerization of acrylates and vinyl esters. As a rule, cobalt porphyrins (**1**) are efficient for the CRP of acrylic monomers while bis(acetylacetonato)cobalt(II) (**2**) can mediate vinyl acetate (VAc), N-vinylpyrrolidone and acrylonitrile.^[1]

A challenge for CMRP still lies in broadening the range of monomers that can be controlled by the same cobalt complex. Recently, the controlled random copolymerization of n-butyl acrylate (nBuA) with VAc was performed using the conventional V-70/Co(acac)₂ CMRP system, but the homopolymerization of nBuA remained uncontrolled.^[2] In this work, we used a new ^[3] preformed alkylcobalt(III) adduct (**3**) to initiate and control the nBuA/VAc copolymerization and, more importantly, the homopolymerization of nBuA.^[4]



Copolymerization of nBuA with VAc

Preliminary results have been obtained previously with V-70/Co(acac)₂.^[2] Here, critical experimental parameters (initiator, temperature, additives) were tuned for optimization. The best results were obtained with the alkylcobalt(III) adduct **3** as initiator in presence of additional Co(acac)₂.

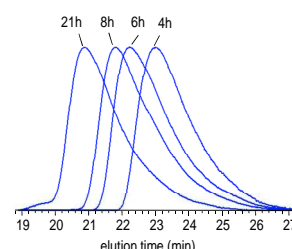
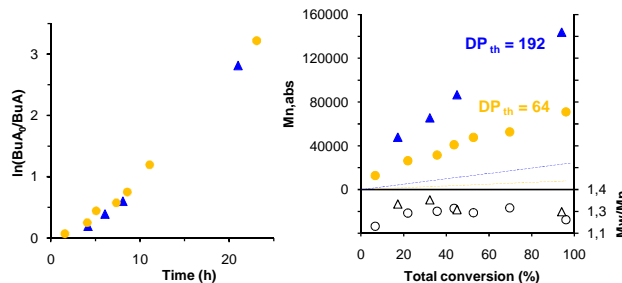


Conditions:
nBuA / VAc / V-70 / Co(acac)₂
96 / 96 / 1 / 1 at 30°C
nBuA / VAc / Alkyl-Co / Co(acac)₂
96 / 96 / 1 / 0.3 at 30°C

⇒ The replacement of V-70 by the alkylcobalt(III) adduct **3** resulted in an improvement of the control of the nBuA/VAc copolymerization.

Homopolymerization of nBuA

The first attempt to polymerize nBuA with V-70/Co(acac)₂ resulted in a rapid gelation because the nBuA-Co(acac)₂ bond is much weaker than the VAc-Co(acac)₂ one.^[2] The alkylcobalt(III) adduct **3**, which improved the control of the nBuA/VAc copolymerization, was therefore tested for the homopolymerization of nBuA and other parameters were tuned for optimization.



Conditions:
nBuA / Alkyl-Co / Co(acac)₂
192 / 1 / 1 at 0°C
nBuA / Alkyl-Co / Co(acac)₂
64 / 1 / 1 at 0°C

⇒ The use of the alkylcobalt(III) adduct **3** enabled to control the radical polymerization of nBuA with Co(acac)₂, which was up to now assumed elusive.

Conclusion

⇒ A current challenge for CRP lies in mediating monomers displaying a wide range of reactivity with the same control agent. In this work,^[4] the homopolymerization of nBuA was controlled using an alkylcobalt(III) adduct. For the first time, Co(acac)₂ revealed as an efficient mediator for the CMRP of nBuA without VAc as a co-monomer, which was up to now assumed elusive. This work, combined with our previous ones, clearly demonstrates that Co(acac)₂ is a versatile mediator for the CMRP of both unconjugated (VAc, NVP) and conjugated (AN, nBuA) vinyl monomers, thus opening the door to copolymers that cannot be prepared by other controlled radical polymerization techniques.

Acknowledgement :The authors are indebted to the Fonds National de la Recherche Scientifique (F.R.S.-FNRS) and to the "Belgian Science Policy" for financial support in the frame of the "Interuniversity Attraction Poles Programme (PAI VI/27) – Functional Supramolecular Systems". M. H. , A. D. and C. D. are respectively research fellow, postdoctoral researcher and senior research associate by the F.R.S.-FNRS. **References**: [1] A. Debuigne, R. Poli, C. Jerome, R. Jerome, C. Detrembleur, *Prog. Polym. Sci.* **2009**, *34*, 211. [2] H. Kaneyoshi, K. Matyjaszewski, *Macromolecules* **2005**, *38*, 8163. [3] A. Debuigne, Y. Champouret, R. Jerome, R. Poli, C. Detrembleur, *Chem.-Eur. J.* **2008**, *14*, 4046. [4] M. Hurtgen, A. Debuigne, C. Jérôme, C. Detrembleur, *Macromolecules*, to be submitted.

