COBALT MEDIATED RADICAL POLYMERIZATION (CMRP) USING BIS(ACETYLACETONATO)COBALT(II): A UNIQUE TOOL FOR CONTROLLING THE RADICAL POLYMERIZATION OF CONJUGATED AND UNCONJUGATED VINYL MONOMERS

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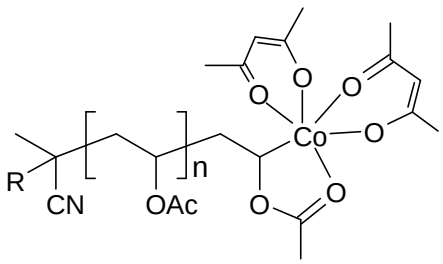
Cobalt-Mediated Radical Polymerization (CMRP) imparts a high level of control on the polymerization of acrylic and vinylic esters, acrylic acid and acrylonitrile. However, each class of monomers appears to be controlled by one class of cobalt complexes.[1] For example, the polymerization of acrylates and acrylic acid is mediated by cobalt porphyrin complexes while vinyl acetate (VAc) and acrylonitrile are efficiently controlled by bis(acetylacetonato)cobalt(II) ($Co(acac)_2$). Therefore, a challenging issue in CMRP remains to broaden the range of monomers that can be controlled by the same cobalt complex. Recently, the controlled random copolymerization of butyl acrylate (BuA) with VAc was performed using the conventional V-70/$Co(acac)_2$ CMRP system, but the homopolymerization of BuA remained uncontrolled.[2]

In this work, we used a new alkylcobalt(III) adduct [3] (see figure) to initiate and control the copolymerization of BuA with VAc. This achievement resulted in a significant improvement over the V-70/$Co(acac)_2$ pair regarding the molecular weight control and the polydispersity indexes. Moreover, for the first time, the alkylcobalt(III) adduct was also efficient in controlling the homopolymerization of BuA and yielded low polydispersity PBuA even in the absence of VAc. These results indicate that $Co(acac)_2$ is a versatile mediator for the CMRP of both unconjugated vinyl monomers (VAc, N-vinylpyrrolidone) and conjugated monomers such as acrylates. It gives access to copolymers that cannot be prepared by other controlled radical polymerization techniques.



n~3
R = $-CH_2-C(CH_3)_2OCH_3$

References

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[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.