Cobalt-Mediated Radical Polymerization of vinyl monomers: investigation of cobalt-coordination

Antoine Debuigne\textsuperscript{a}, Yasmine Piette\textsuperscript{a}, Rinaldo Poli\textsuperscript{b}, Christine Jérôme\textsuperscript{a}, Christophe Detrembleur\textsuperscript{a}

\textsuperscript{a} Center for Education and Research on macromolecules (CERM), University of Liège, Sart-Tilman, B6a, B-4000 Liège Yasmine.Piette@ulg.ac.be
\textsuperscript{b} Laboratoire de Chimie de Coordination, UPR CNRS 8241, Toulouse University of Toulouse, 31077 Toulouse, France

Cobalt-Mediated Radical Polymerization (CMRP) is a CRP technique based on the reversible deactivation of the growing radical chains with a cobalt complex, such as cobalt tetramesitylporphyrin (1), cobaloxime (2) or Co(acac)\textsubscript{2} (3). The latest is the most versatile Co complex. Indeed, it has allowed the control of polymerization of very reactive monomers such as vinyl acetate (VAc), N-vinylpyrrolidone (NVP) and acrylonitrile (AN).

Introduction

For the CMRP mechanism, two pathways are possible:
- Degenerative transfer (DT) process in bulk in the presence of continuous supply of radicals;
- Reversible termination (RT) process in the presence of ligands able to coordinate the cobalt and thus prevent the system to polymerize via the DT pathway.

Effect of ligands on VAc polymerization rate

(a) 2/3-order dependence of ln ([M]/[M]_0) on time for VAc polymerization initiated by the alkyl-Co (III) compound in the presence (\(\Delta\)) and in the absence (\(\bullet\)) of PYRIDINE

(b) Evolution of size-exclusion chromatograms with time for VAc polymerization initiated at 30°C by the alkyl-Co (III) adduct in the presence of PYRIDINE

Importance of ligands on macromolecular engineering

Faster in the presence of ligands such as pyridine, DMF, DMSO or water


The authors are grateful to the Fonds National de la Recherche Scientifique (FNRS) and the Belgian Science Policy in the frame of the Interuniversity Attraction Poles Programme (PAI VI/27) for financial support.