The influence of cobalt-coordination on Cobalt Mediated Radical Polymerization of vinyl monomers

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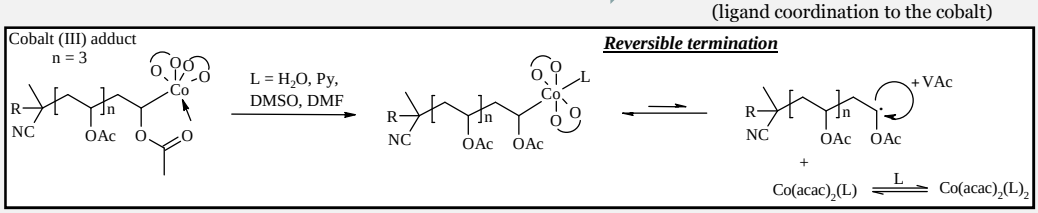
Introduction

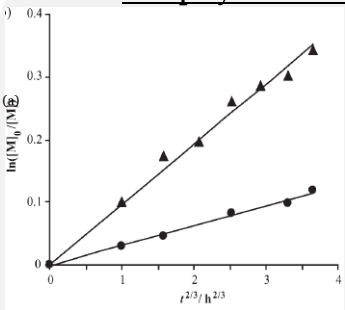
Cobalt-Mediated Radical Polymerization (CMRP) is a CRP technique based on the reversible deactivation of the growing radical chains with the cobalt (II) bis-acetylacetonate complex [1]. The establishment of an equilibrium between polymer chains end-capped by the cobalt complex and the polymer radical chains allows the control of molecular parameters and leads to polymers with controlled architectures.
This system has been able to control the polymerization of very reactive monomers such as vinyl acetate (VAc) and N-vinylpyrrolidone (*N*VP).

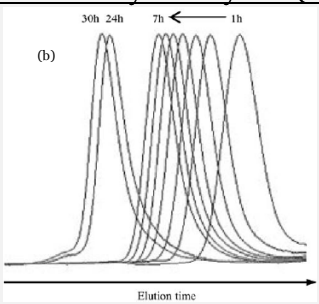
The CMRP mechanism

Polymerization initiated by the alkyl-Co (III) compound : very slow ⟹ Addition of ligands to accelerate the polymerization (ligand coordination to the cobalt)



VAc polymerization initiated by an alkyl-Co (III) adduct in the presence of ligands [2]:





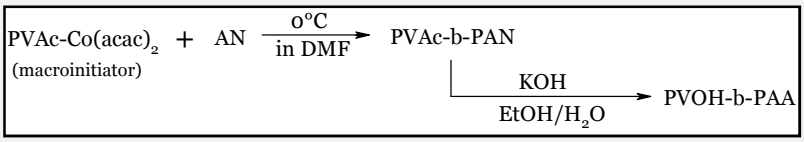
(a) 2/3-order dependence of ln ($[M]_0/[M]$) on time for VAc polymerization initiated by the alkyl-Co (III) adduct **in the presence (▲)and in the absence (•) of PYRIDINE**

(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**

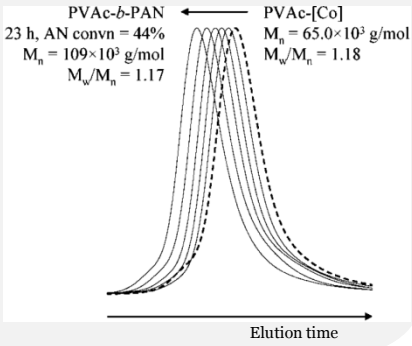
Without any ligand, very slow polymerization

Faster in the presence of pyridine as well as with DMF, DMSO or water

PVAc-*b*-PAN and PVOH-*b*-PAA copolymers [3,4] :



$PVAc_{241}$-*b*-PAN_{185} ⟶ $PVOH_{241}$-*b*-PAA_{150}
$PVAc_{224}$-*b*-PAN_{430} ⟶ $PVOH_{224}$-*b*-PAA_{454}
$PVAc_{308}$-*b*-PAN_{918} ⟶ $PVOH_{308}$-*b*-PAA_{843}



(1) Debuigne, A.; Caille, J.-R.; Jerome, R. *Angewandte Chemie, International Edition* **2005**, *44*, 1101-1104.
(2) Debuigne, A.; Champouret, Y.; Jerome, R.; Poli, R.; Detrembleur, C. *Chemistry--A European Journal* **2008**, *14*, 4046-4059.
(3) Debuigne, A.; Michaux, C.; Jerome, C.; Jerome, R.; Poli, R.; Detrembleur, C. *Chemistry--A European Journal* **2008**, *14*, 7623-7637.
(4) Debuigne, A.; Warnant, J.; Jerome, R.; Voets, I.; de Keizer, A.; Cohen Stuart, M. A.; Detrembleur, C. *Macromolecules* **2008**, *41*, 2353-2360.