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

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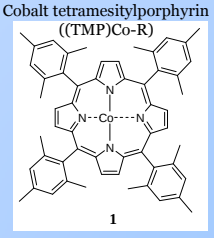
Introduction

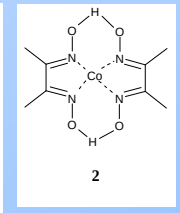
Cobalt-Mediated Radical Polymerization (CMRP) is a CRP technique based on the reversible deactivation of the growing radical chains with a cobalt complex, such as cobaltporphyrin (1), cobaloxime (2) or $Co(acac)_2$ (3). The latest is the most versatile Co complex. Indeed, it has allowed the control of polymerization of very reactive monomers such as vinyl acetate (VAc)[1], N-vinylpyrrolidone (*NVP*) [2] and acrylonitrile (AN) [3].

Cobalt tetramesitylporphyrin ((TMP)Co-R)



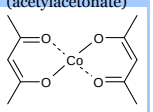
1

Cobaloxime



2

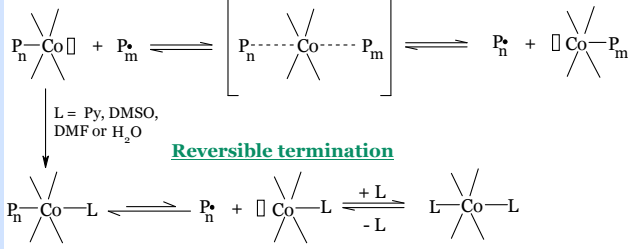
Cobalt bis-(acetylacetonate)



3

CMRP mechanism

Degenerative transfer

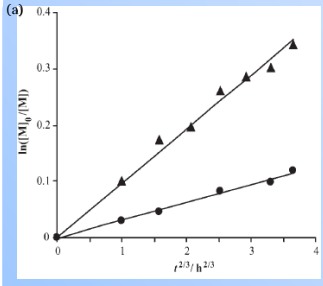


For the CMRP mechanism, two pathways are possible :

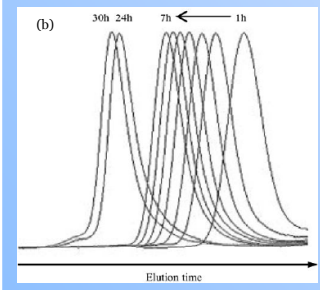
-**Degenerative transfer** (DT) process in bulk in the presence of continuous supply of radicals ;

- **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 [4]



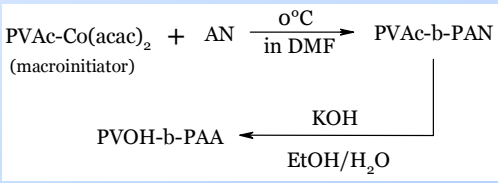
(a) 2/3-order dependence of ln ($[M]_0/[M]$) on time for VAc polymerization initiated by the alkyl-Co (III) compound **in the presence (▲)** and **in the absence (•) of PYRIDINE**

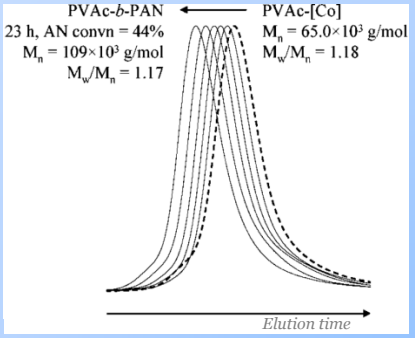


(b) Evolution of size-exclusion chromatograms with time for VAc polymerization initiated at 30°C by the alkyl-Co (III) adduct **in the presence of PYRIDINE**

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

Importance of ligands on macromolecular ingeneering [5]





$PVAc_{241}$-*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.
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(3) Debuigne, A.; Michaux, C.; Jerome, C.; Jerome, R.; Poli, R.; Detrembleur, C. *Chemistry--A European Journal* **2008**, *14*, 7623-7637.
(4) Debuigne, A.; Champouret, Y.; Jerome, R.; Poli, R.; Detrembleur, C. *Chemistry--A European Journal* **2008**, *14*, 4046-4059.
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