Synthetic and Mechanistic Advances in the Cobalt-Mediated Radical Polymerization of *N*-vinyl amides

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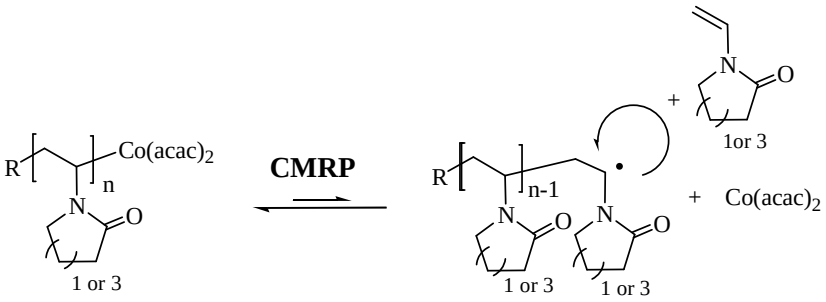
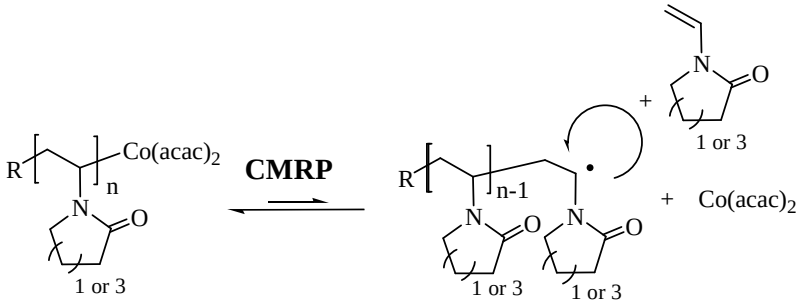
Organometallic-Mediated Radical Polymerization (OMRP) is an emerging class of controlled radical polymerization which permits the synthesis of precise macromolecular architectures with predictable molecular weights.This technique is based on the reversible deactivation of the growing radical chains by a transition metal species, which strongly decreases the probability of irreversible termination reactions, abundant in a free radical polymerization.The OMRP based on cobalt, namely the cobalt-mediated radical polymerization (CMRP), is very efficient for important classes of non-conjugated and reactive monomers like vinyl esters and vinyl amides.This communication will focus on recent synthetic achievements and mechanistic progress in the synthesis of well-defined poly(*N*-vinyl amide)s by CMRP. The synthesis of well-defined amphiphilic block copolymers containing a biocompatible and hydrosoluble segment of poly(*N*-vinylpyrrolidone) (PNVP)or a thermoresponsiveblock of poly(*N*-vinylcaprolactam) (PNVCL) will notably be described. Moreover, the potential of a new radical coupling reaction (CMRC) applied to poly(vinyl amides) and the benefit of the photochemical initiation of the vinyl amides polymerization will be presented. Finally, novel block copolymers containing P*N*VP and poly(caprolactone) segments have been prepared recently by combination of CMRP with ring-opening polymerization.


R
Co(acac)2
n
N
O
1 or 3
CMRP
R
n-1
N
O
1 or 3
1 or 3
+
N
O
1or 3
+
Co(acac)2


R
Co(acac)2
n
N
O
1 or 3
CMRP
R
n-1
N
O
1 or 3
1 or 3
+
N
O
1 or 3
+
Co(acac)2