



Contents lists available at ScienceDirect

## European Polymer Journal

journal homepage: [www.elsevier.com/locate/europolj](http://www.elsevier.com/locate/europolj)

## *In situ* bidentate to tetradentate ligand exchange reaction in cobalt-mediated radical polymerization

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## ARTICLE INFO

## Article history:

Received 28 May 2014

Received in revised form 21 July 2014

Accepted 1 August 2014

Available online xxx

## Keywords:

Organometallic-mediated radical polymerization (OMRP)

Cobalt-mediated radical polymerization (CMRP)

Vinyl acetate

Acrylate

Block copolymers

## ABSTRACT

Organometallic-mediated radical polymerization (OMRP) has seen a significant growth in the last years notably due to the development of new metal complexes, especially cobalt derivatives. Despite of this, none of the reported complexes offers optimal control for monomers with very different reactivity, which somewhat limits the synthesis of copolymers. In order to expand the scope of cobalt-mediated radical polymerization (CMRP), we investigated an *in situ* ligand exchange reaction for modulating the properties of the cobalt complex at the polymer chain-end and adjusting the C–Co bond strength involved in the control process. With the aim of improving the synthesis of poly(vinyl acetate)-*b*-poly(*n*-butyl acrylate) copolymers, bidentate acetylacetonate ligands, which impart high level of control to the polymerization of vinyl acetate (VAc), were replaced *in situ* at the PVAc–cobalt chain-end by tetradentate Salen type ligands that are more suited to acrylates.

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### 1. Introduction

Controlled radical polymerization CRP has become an important tool for the preparation of well-defined polymer materials [1–9]. The use of organometallic complexes was a significant step towards the development of CRP of various vinylic monomers [1,9–12]. CRP mediated by transition metal complexes can be classified in two families [13], i.e., atom transfer radical polymerization (ATRP) [14–16] and organometallic mediated radical polymerization (OMRP) [11,12,17,18]. The role of the metal center consists in the transformation of the radical species into dormant species through a halogen exchange between the metal center and the radical for the ATRP mechanism (Eq. (1), Scheme 1) [19–21], and in the reversible formation of a metal–carbon covalent bond for the OMRP mechanism (Eq. (2), Scheme 1). In the two cases, the CRP is directed by

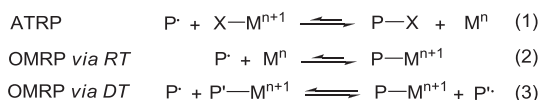
the redox  $M^{n+1}/M^n$  properties of the metallic center (Scheme 1) which are highly affected by the coordination sphere [18,22].

Numerous transition metals including nickel [23], titanium [24,25], molybdenum [26,27], osmium [28,29] cobalt [30] and rhenium [31] are effective for ATRP [32]. This family is however dominated by ruthenium [33–35], iron [36–39] and copper complexes [10,21,28,40–44].

Until now cobalt complexes remain the most versatile and efficient controlling agents for OMRP process [11,17]. Cobalt mediated radical polymerization (CMRP) [45,46] is extensively studied especially for its high ability to control the polymerization of a large range of monomers including acrylic monomers [47–50] and vinyl esters [12,17,46,51,52]. Depending on the reaction conditions, the CMRP process follows a reversible termination (RT) mechanism (Eq. (2), Scheme 1) [51] or a degenerative transfer (DT) one (Eq. (3), Scheme 1) [53,54]. The latter is observed when the amount of radicals exceeds the amount of cobalt complex. The role of the ligand is crucial and determines the ability of the cobalt complex to control

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**Scheme 1.** Radical polymerization controlled via an ATRP or OMRP process.

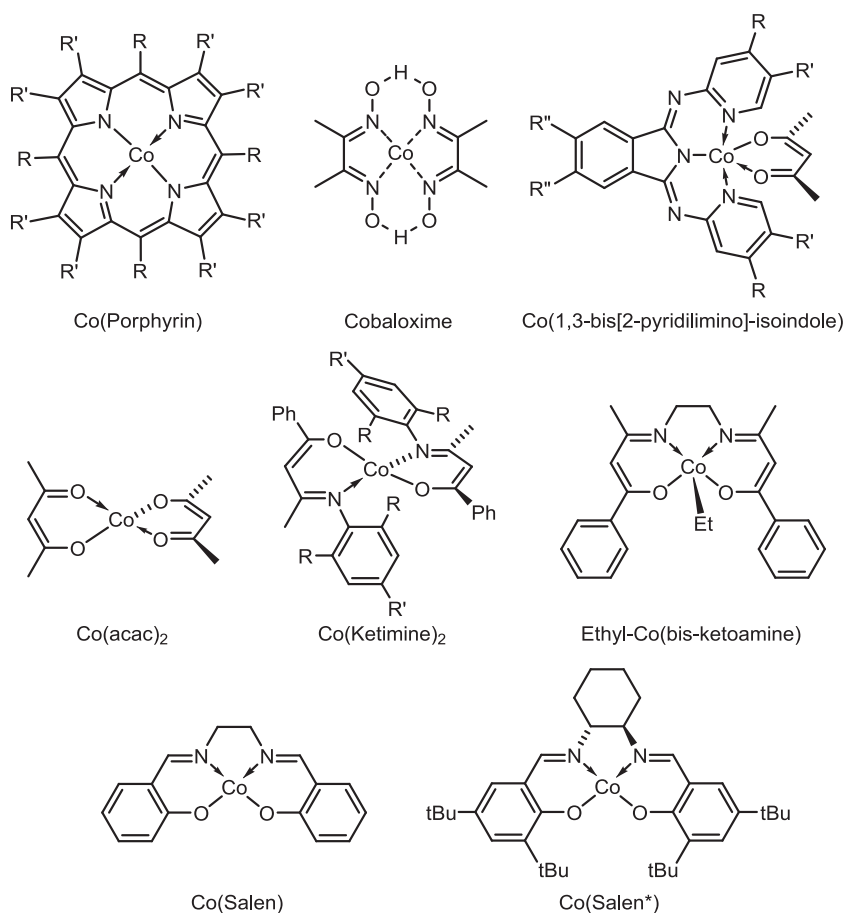
the polymerization by affecting the stability of the cobalt–carbon bond of the dormant species, and therefore the active/dormant species equilibrium [12]. Cobalt complexes bearing high electron donating ligands such as porphyrin derivatives [49,55], cobaloximes [56] or 1,3-bis(2-pyridilimino)isoinolate ligands [57] (Fig. 1) present high ability to control the radical polymerization of conjugated vinyl monomers such as acrylates. In contrast, low electron donating ligands such as bis(acetylacetonate) (Fig. 1), impart to cobalt an exceptional activity for controlling the radical polymerization of unconjugated vinyl monomers such as vinyl ester, [46,58–60] N-vinyl imidazolium [61], N-vinyl pyrrolidone [62], N-vinyl amides [63–65], and well-defined copolymers of ethylene with vinyl esters and vinyl amides are now accessible [66].

Complex  $\text{Co}(\text{acac})_2$  presents high abilities to generate reversible dormant species with unconjugated radicals. In

the case of vinyl esters and some vinyl amides, DFT modeling showed that an extra-stabilization of the C–Co bond occurred via an intramolecular chelation of the cobalt atom with the carbonyl function of the last monomer unit and is responsible for the good control observed (Scheme 2) [51,64].

This intramolecular chelation is made possible by the flexible geometry of  $\text{Co}(\text{acac})_2$  [67,68] that is not possible for cobalt complexes bearing tetradentate ligands with a rigid square-pyramidal geometry (such as cobalt porphyrins) [55,69,70].  $\text{Co}(\text{acac})_2$  is however less efficient for acrylates polymerization as the result of the low stability of the C–Co bond of the dormant species [71]. Controlling the radical polymerization of acrylates by  $\text{Co}(\text{acac})_2$  is feasible but requires specific conditions that allow to shift the active/dormant species equilibrium towards the dormant ones. It can for instance be achieved by decreasing the polymerization temperature to 0 °C and by using an excess of  $\text{Co}(\text{acac})_2$  to force the reversible deactivation of the chain-end [71]. Using more electron donating bis(chelates) ligands such as ketiminato ligands (Fig. 1) instead of acac ligands led to less efficient control over the VAc polymerization [72].

The effect of the type of ligand on the C–Co bond stability was studied by computational calculations of the bond



**Fig. 1.** Cobalt complexes used as controlling agent in CMRP.

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