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

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Controlled Radical Polymerization techniques have been developed to obtain well-defined architectures and to control polymer parameters. Among these systems is Cobalt-Mediated Radical Polymerization (CMRP), which is based on the reversible deactivation of the growing radical chains with a cobalt complex, the cobalt (II) bis(acetylacetonate) ¹. The interest of this system is not only due to its ability to control the polymerization of very reactive monomers such as vinyl acetate (VAc) and N-vinylpyrrolidone (NVP), but also its peculiar mechanism which exhibits two pathways depending on the polymerization conditions; a reversible termination process and a degenerative chain transfer mechanism. Furthermore, it has been showed that the Co-C bond strength and thus the polymerization

are strongly influenced by the use of some additives, such as water, dimethylformamide,

dimethylsulfoxide and pyridine, which coordinate the cobalt free site.

In this presentation we report the use of a preformed alkylcobalt(III) adduct as initiator ² for the polymerization of various vinyl monomers of different reactivity (VAc, acrylonitrile,...) and on the effect of several ligands on their polymerization control. ⁴⁻⁵

Cobalt (III) adduct
$$n = 3$$

$$OOOO$$

$$R \longrightarrow OOCO$$

$$R \longrightarrow OOOO$$

$$R \longrightarrow OOOOO$$

$$R \longrightarrow OOOO$$

$$R \longrightarrow OOOOO$$

$$R \longrightarrow OOOO$$

$$R \longrightarrow OOOOO$$

$$R \longrightarrow OOOO$$

$$R \longrightarrow OOOOO$$

$$R \longrightarrow OOOO$$

$$R \longrightarrow$$

The preparation of novel block copolymers by CMRP will finally be presented.

As a conclusion, cobalt-coordination appears today as a unique opportunity to adjust the Co-C bond strength and to push back the bounds of possibilities in terms of macromolecular engineering assisted by CMRP.

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