

COBALT MEDIATED RADICAL POLYMERIZATION (CMRP) : PROGRESS IN TECHNOLOGY AND MACROMOLECULAR ENGINEERING.

Debuigne A.*, Detrembleur Ch., Bryaskova R., Sciannamea, V., Piette Y., Jérôme R.

Center for Education and Research on Macromolecules (CERM), University of Liège (ULG), Sart-Tilman, B6a, 4000 Liège, Belgium. A.D. is "Chargé de Recherche F.N.R.S". e-mail : adebuigne@ulg.ac.be .

During the last few years, an increasing attention has been paid to the Organometallic Mediated Radical Polymerization (OMRP), with emphasis on cobalt complexes as reversible end-cappers of growing radical polymer chains (Figure 1).^{1,2}

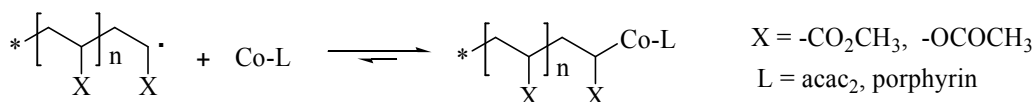


Figure 1 – Equilibrium between dormant and active species in Cobalt Mediated Radical Polymerization (CMRP).

Recently, cobalt(II) acetylacetonate proved efficiency in the controlled radical polymerization of vinyl acetate and in the successful functionalization of poly(vinyl acetate) (PVAc) and derivatized poly(vinyl alcohol) (PVOH) (co)polymers.²⁻⁴ In spite of substantial progress in Cobalt Mediated Radical Polymerization (CMRP), including extension to other monomers by Matyjaszewski et al.,⁵ and extension of CMRP to aqueous dispersions,⁶ several questions remained pending, such as the implementation of the initiating system, the recovery and recycling of the metal. These issues will be discussed in this communication, together with recent progress in macromolecular engineering of PVAc and PVOH.

Because CMRP of vinyl acetate is better controlled at low temperature (30°C), 2,2'-azo-bis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) was used until now as an initiator. However, transportation and supplying of this initiator is quite an issue because of poor thermal stability. This problem has been overcome by initiating CMRP of vinyl acetate by a redox system consisting of ascorbic acid and either lauroyl peroxide or benzoyl peroxide. Under these optimized conditions, the VAc polymerization is fast and controlled (Figure 2), which is a key step forward to the scale-up of the process.⁷

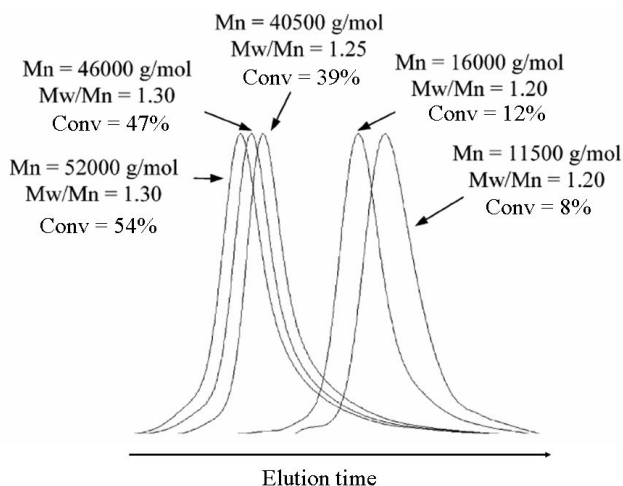


Figure 2 – Evolution of SEC chromatograms with the time for the bulk CMRP of VAc at 30°C initiated by lauroyl peroxide and ascorbic acid in the presence of Co(acac)₂.

In contrast to Atom Transfer Radical Polymerization (ATRP), the metallic species is reversibly attached to the end of the polymer chains in CMRP. Therefore, the cobalt complex is not a catalyst, and stoichiometric amount of cobalt with respect to polymer chains is needed. This is a severe requirement, except whether the metal can be recovered and recycled. In order to tackle this problem, the cobalt complex has been supported onto silica and Merrifield resin.⁸ (Figure 3)

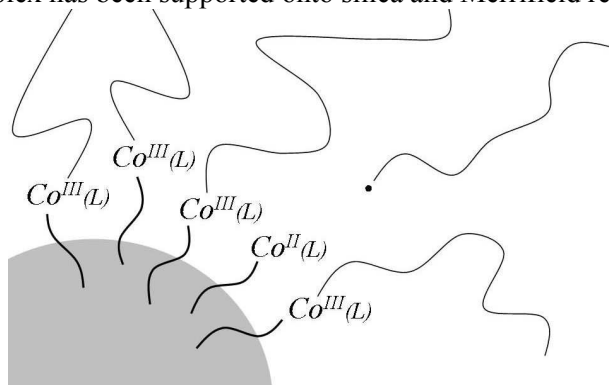


Figure 3 - Schematic representation of CMRP using a supported cobalt complex (SCMRP).

The Supported Cobalt Mediated Radical Polymerization (SCMRP) of vinyl acetate was also effective in the control of the PVAc molecular parameters. At the end of the VAc polymerization, the chains were released from the cobalt complex, and thus from the support, by exchange with a permanent radical (2,2,6,6-tetramethylpiperidine-1-oxyl, TEMPO). The recycling of the recovered metal is quite encouraging, although the process needs further optimization. Nevertheless, the preliminary results pave the way to the preparation of well-defined cobalt free PVAc (co)polymers and the recovery and recycling of the cobalt.

In an effort to make headway in the macromolecular engineering of PVAc and PVOH by CMRP, the dormant PVAc chains collected at the end of the polymerization, were used as macroinitiators for the polymerization of other monomers, i.e., styrene (Sty),⁹ N-vinylpyrrolidone (NVP) and acrylonitrile (AN), with formation of the corresponding block copolymers (Figure 4).

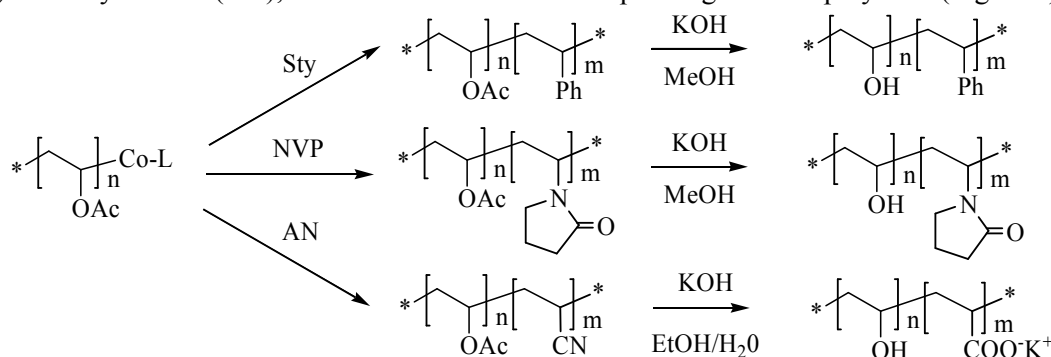


Figure 4 - Synthesis of poly(vinyl acetate) and poly(vinyl alcohol) containing block copolymers by CMRP.

Further treatment of the resulting PVAc containing block copolymers by potassium hydroxide is a straightforward way to PVOH-*b*-PS, PVOH-*b*-PNVP and PVOH-*b*-PAA, thus diblocks not easily accessible by other techniques.

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