

Well-defined block copolymers by cobalt-mediated radical polymerisation: preparation and mechanism insight.

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Introduction

The radical polymerisation of vinyl acetate (VAc) can be controlled in the presence of cobalt(II) acetylacetonate ($\text{Co}(\text{acac})_2$) as controlling agent. This Cobalt-Mediated Radical Polymerization (CMRP) of VAc can be carried out in bulk,⁽¹⁾ aqueous suspension⁽²⁾ and miniemulsion⁽³⁾ until high monomer conversion and molecular weight. From a mechanistic point of view, it was recently reported that VAc polymerization conducted in the bulk in the presence of $\text{Co}(\text{acac})_2$ and an excess of V-70 follows a degenerative chain transfer process while addition of amino compounds, able to coordinate the cobalt complex, turns the mechanism into a reversible-termination process by cleavage of the Co-C bond.⁽⁴⁾

Efforts are now devoted to the preparation of well-defined PVAc and PVOH based block copolymers by CMRP. For such a purpose, activated bromides (α -bromo ester and α -bromo ketone)⁽⁵⁻⁶⁾ were successfully attached as ω -end groups to PVAc and used to initiate the ATRP of styrene, *n*-butyl acrylate and methyl methacrylate, so making very-well defined block copolymers. Although efficient, this combination of CMRP and ATRP was a multistep approach, including the end-functionalization of the PVAc chains and the time consuming synthesis of an activated halide containing nitroxide. Well-defined poly(vinyl acetate) (PVAc) macroinitiators, thus chains end-capped by a cobalt complex, were then synthesized by CMRP and used to initiate the styrene polymerization at 30°C. Although poly(vinyl acetate)-*b*-poly(styrene) (PVAc-*b*-PS) copolymers were successfully prepared by this technique, the polymerisation of the second monomer (styrene) was not controlled, leading to copolymers with a broad polydispersity and a limited conversion.⁽⁷⁾ Methanolysis of PVAc-*b*-PS led to the amphiphilic poly(vinyl alcohol)-*b*-poly(styrene) (PVOH-*b*-PS) copolymer. The direct preparation of well-defined PVAc based block copolymers by CMRP, while controlling both sequences, was until now very challenging.

This presentation deals with the preparation of well-defined PVAc and PVOH based block copolymers using the CMRP technique. The conditions required for the synthesis of poly(vinyl acetate)-*b*-poly(*N*-vinyl pyrrolidone) (PVAc-*b*-PNVP) and poly(vinyl acetate)-*b*-poly(acrylonitrile) (PVAc-*b*-PAN), and the related PVOH based copolymers, will be reported. The mechanism, i.e. degenerative chain transfer or reversible-termination process, involved during the preparation of the copolymers will be discussed.

Results and discussions

The polymerization of *N*-vinyl pyrrolidone (NVP) was effectively initiated by PVAc macroinitiators in an anisole/toluene mixture (9/1, v/v) at a temperature ranging from 20 to 6°C, and controlled as assessed by a first order kinetics in NVP and the increase of the molar mass of the PNVP with the monomer conversion.⁽⁸⁾ Therefore, the length of the two blocks could be merely tuned by the $[\text{VAc}]/[\text{Co}(\text{acac})_2]$ and the $[\text{NVP}]/[\text{PVAc}]$ ratios for the synthesis of the macroinitiator and the polymerization of the second monomer, respectively. The reverse experiment that consists in initiating the polymerization of VAc by a PNVP macroinitiator was disregarded because CMRP of NVP is not under a control good enough for yielding very effective macroinitiators. The amphiphilicity of the PVAc-*b*-PNVP copolymers, was confirmed by micellization in water. Upon hydrolysis of the PVAc block of these copolymers, double hydrophilic PVOH-*b*-PNVP copolymers of well-defined structure and composition were collected.

As it will be discussed in the presentation, the preparation of PVAc-*b*-PAN block copolymers by CMRP requires specific conditions of solvents and temperatures. When those conditions were

carefully chosen, the polymerization of acrylonitrile initiated by PVAc-Co(acac)₂ was perfectly controlled and novel well-defined PVAc-b-PAN block copolymers with a narrow polydispersity ($M_w/M_n \leq 1.20$) were obtained. Although the preparation of the first PVAc sequence follows a degenerative chain transfer process, the polymerisation of the second block proceeds through a reversible-termination process by cleavage of the Co-C bond at the ω -chain end. This mechanism proposal will be discussed. Complete hydrolysis of both the PVAc and PAN sequences by potassium hydroxide at 75°C in ethanol/water mixture leads to the novel poly(vinyl alcohol)-b-poly(acrylic acid)

Conclusions

Well-defined block copolymers of poly(vinyl acetate) (PVAc) and poly(*N*-vinyl pyrrolidone) (PNVP) or poly(acrylonitrile) (PAN) were synthesized by Cobalt Mediated Radical Polymerization (CMRP). The NVP and AN polymerizations initiated by poly(vinyl acetate) end-capped by the cobalt(II)acetylacetonate complex met the criteria of controlled polymerization, i.e., first order kinetic in NVP, increase of the molar mass with the NVP conversion and narrow molar mass distribution. Although the polymerization of VAc in the bulk by CMRP follows a degenerative chain transfer process, the polymerisation of the second monomer (NVP or AN) proceeds through a reversible-termination process by cleavage of the Co-C bond at the ω -chain end.

Methanolysis of the PVAc sequence of PVAc-b-PNVP led to double hydrophilic PVOH-b-PNVP, while the hydrolysis of both sequences of PVAc-b-PAN led to the novel pH responsive hydrophilic PVOH-b-PAA block copolymer. From these studies, CMRP seems to be a powerful tool for the preparation of well-defined PVAc and PVOH based block copolymers, as far as the polymerisation conditions are well-chosen.

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