Supported cobalt mediated radical polymerization (SCMRP) of vinyl acetate and recycling of the cobalt complex†

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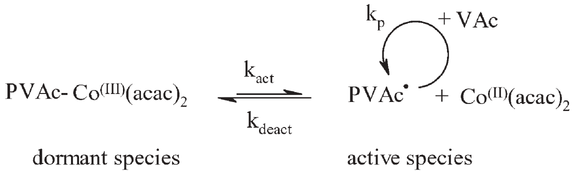
Cobalt complexes supported on silica and Merrifield resin are effective mediators for the controlled radical polymerization of vinyl acetate.

Controlled radical polymerization (CRP) of vinyl acetate (VAc) is a rewarding process because of the key position of poly(vinyl acetate) and related copolymers in the market place. A good control of the radical polymerization of VAc was first achieved by Reversible Addition Fragmentation chain Transfer (RAFT) and Macromolecular Design *via* Interchange of Xanthates (MADIX).[1–4] Very recently, cobalt(II) acetylacetonate ($Co(acac)_2$) proved its effectiveness in CRP of VAc in bulk,[5] suspension[6] and miniemulsion,[7] but also in copolymerization of VAc with n-butyl acrylate,[8] chlorovinyl acetate and *N*-vinylpyrrolidone.[9] This cobalt-mediated radical polymerization (CMRP) is based on the reversible formation of a C–Co bond at the ω-chain-end of PVAc by reaction of the $Co(acac)_2$ with the growing PVAc chains (Scheme 1).

In contrast to the metallic complexes used in Atom Transfer Radical Polymerization (ATRP), the cobalt complex in CMRP is not a catalyst but the mediator reversibly attached at the ω-chain-end of the PVAc chains. For this reason, PVAc prepared by CMRP has the green color typical of an alkyl cobalt(III) complex, even after repeated precipitation in a non-solvent of PVAc and after elution through alumina oxide and silica gel. Although the metal can be eliminated by treatment of PVAc with appropriate chemicals, such as TEMPO and thiols,[10] it is quite a problem to recover and recycle the cobalt complex. A way to tackle this problem consists of supporting the metal complex.

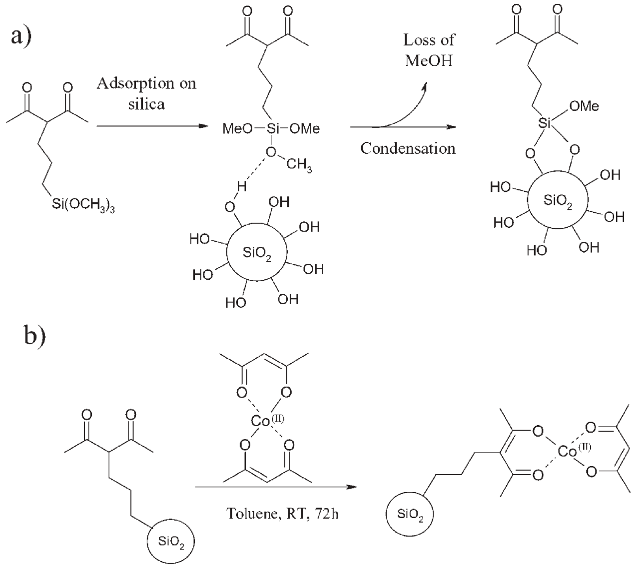
This communication aims at reporting for the first time on the preparation, use and recycling of supported cobalt complexes for the controlled radical polymerization of vinyl acetate.

Two strategies were prepared and tested in order to immobilize the cobalt complex on a support. In a first approach, acetylacetone substituted by a trimethoxysilyl group, the 3-[3-(trimethoxysilyl)-propyl]-2,4-pentanedione (MS-acac-H), was prepared according to the literature,[11] and condensed at the surface of non porous silica (Cab-O-Sil EH5; specific surface: 380 $m^2 g^{-1}$; ∼4.5 Si–OH nm^{-2}) in toluene at 100 °C for 24 h (Scheme 2). Silica was then purified by repeated centrifugation/dispersion cycles in toluene before being analyzed by TGA in order to ascertain the average number of ligands per nm^2 of silica. The actual weight loss was 5.8 wt%, consistent with 0.65 ligand nm^{-2}. 45% of the silanols (Si–OH) on average thus reacted with MS-acac-H. Cobalt was then immobilized by reaction of the modified silica with an excess of $Co(acac)_2$ (3 equivalents per ligand) under stirring for 72 h at room temperature. Cycles of centrifugation/dispersion in toluene were again repeated for elimination of the excess of $Co(acac)_2$ from silica, which was then analyzed by IR. The characteristic absorption of the carbonyl group of the acetylacetonate type ligand was observed at 1591 cm^{-1} and the C–H stretching at 2800–3000 cm^{-1}, as well (see supporting information). In order to quantify the Co complex immobilized at the surface, silica (SiO_2–$Co(acac)_2$) was also analyzed by Inductively Coupled Plasma (ICP). According to this analysis, 5.33 10^{-4} mol of Co was attached per g of silica.



Scheme 1 Equilibrium between dormant and active species in CMRP of VAc.

The second strategy for the cobalt immobilization consisted of grafting acetylacetone onto a non porous Merrifield resin (chloromethylated polystyrene crosslinked by divinylbenzene; 2 mmol Cl g^{-1} resin; 95–210 μm; Fluka). The nucleophilic



Scheme 2 Immobilization of cobalt at the surface of silica: a) condensation of 3-[3-(trimethoxysilyl)propyl]-2,4-pentanedione (MS-acac-H) onto silica, b) complexation of cobalt at the silica surface.

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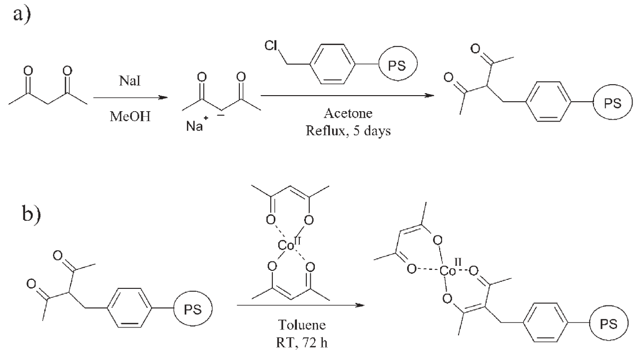


Scheme 3 Immobilization of cobalt at the surface of the Merrifield resin: a) grafting of acetylacetone onto the resin, b) complexation of cobalt at the resin surface.

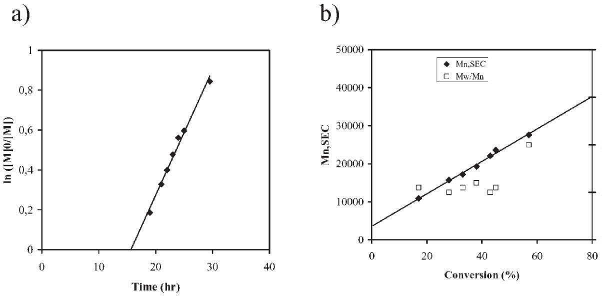


Fig. 1 (a) Time dependence of ln($[M]_0/[M]$) and (b) dependence of M_n on the monomer conversion for the bulk polymerization of VAc initiated by V70 at 30 °C in the presence of the cobalt complex supported on silica [VAc/V70/Co = 203/1.4/1].

substitution of the chloromethyl groups by sodium acetylacetonate (Na(acac)) (3 equivalents Na(acac) per chloride) was catalyzed by NaI in acetone under reflux for 5 days (Scheme 3a). The excess of ligand was eliminated by repeated centrifugation/dispersion cycles and the modified Merrifield was reacted with a 3 fold excess of $Co(acac)_2$ in toluene at room temperature for 72 h. After purification (centrifugation/dispersion in toluene), the Merrifield resin was analyzed by IR. The successful functionalization of the surface was confirmed by the characteristic IR absorptions of the complex at 1587, 1517, 1384 and 2800–3000 cm^{-1}, respectively (see supporting information). According to the ICP analysis of the resin, 7.94 10^{-4} mol of Co was immobilized per gram of resin, which corresponds to approximately 40% functionalization yield.

When the bulk polymerization of vinyl acetate was initiated by 2-2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V70) in the presence of the cobalt complex immobilized onto silica (SiO_2–$Co(acac)_2$) at 30 °C ([VAc]/[V70]/[Co] = 203/1.4/1), an induction period of 16 h was observed (Fig. 1a), as was the case whenever $Co(acac)_2$ was not supported. After this period of time, the molecular weight increased linearly with the monomer conversion (Fig. 1b); the time dependence of ln($[M]_0/[M]$) was linear (Fig. 1a) and the polydispersity was rather narrow ($1.3 \leqslant M_w/M_n \leqslant 1.4$) (Fig. 1b). All these observations are consistent with a controlled process. The M_n,th/M_n,exp ratio (initiator efficiency) was 0.37, which indicates that 37% of the immobilized cobalt contributed to the controlled process.

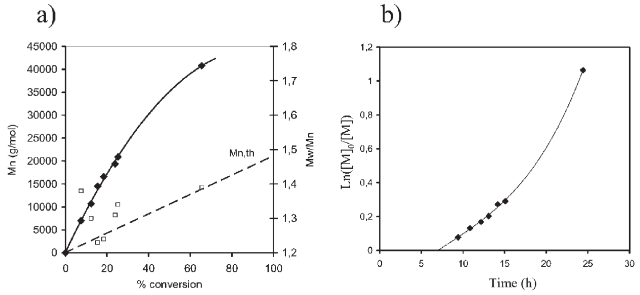
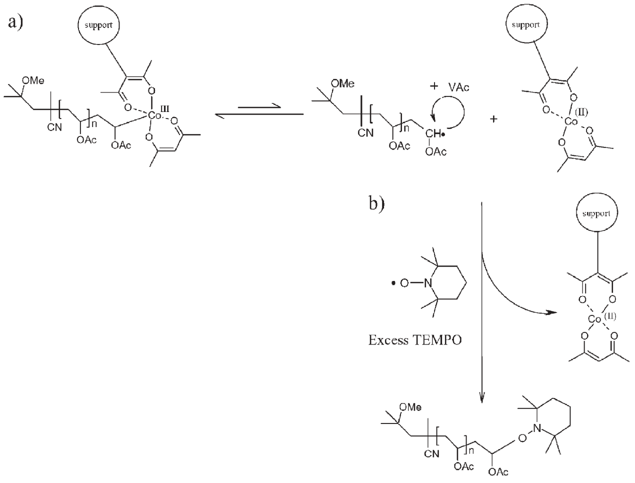


Fig. 2 (a) Dependence of M_n on the monomer conversion and (b) time dependence of ln($[M]_0/[M]$), for the bulk polymerization of VAc initiated by V70 at 30 °C in the presence of the cobalt complex supported on the Merrifield resin [VAc/V70/Co = 247/1.5/1].



Scheme 4 a) Mechanism proposed for the supported CMRP, and b) possible recycling of the supported cobalt.

At constant Co/V70 molar ratio, the molecular weight changed with the VAc/Co molar ratio and the initiator efficiency remained unmodified (Table 1). PVAc of quite a high molecular weight (M_n = 81500 g mol^{-1}) could be prepared with a narrow polydispersity (M_w/M_n = 1.25) at 30 °C within 16 h, which emphasized the efficiency of the system.

When the cobalt was supported on the Merrifield resin rather than on silica, the molecular weight also increased with the

Table 1 Polymerization of VAc initiated by V70 in the presence of cobalt supported on silica using different VAc/Co molar ratios at 30 °C

[VAc]/[Co]	Time (h)	Conv. %	$M_{n,SEC}$ (g mol^{-1})[a]	$M_{n,th}$ (g mol^{-1})[b]	M_w/M_n	f
203/1	29	51	24000	8900	1.35	0.37
305/1	19	49	33200	12900	1.40	0.39
407/1	21	48	42600	16800	1.35	0.39
814/1	16	45	81400	31900	1.25	0.39

[a] $M_{n,SEC}$: M_n determined by SEC with a PS calibration. [b] $M_{n,th}$ = ($[VAc]_0/[Co]_0$) × M_w(VAc) × conversion. [c] f = initiator efficiency (M_n,th/M_n,exp).

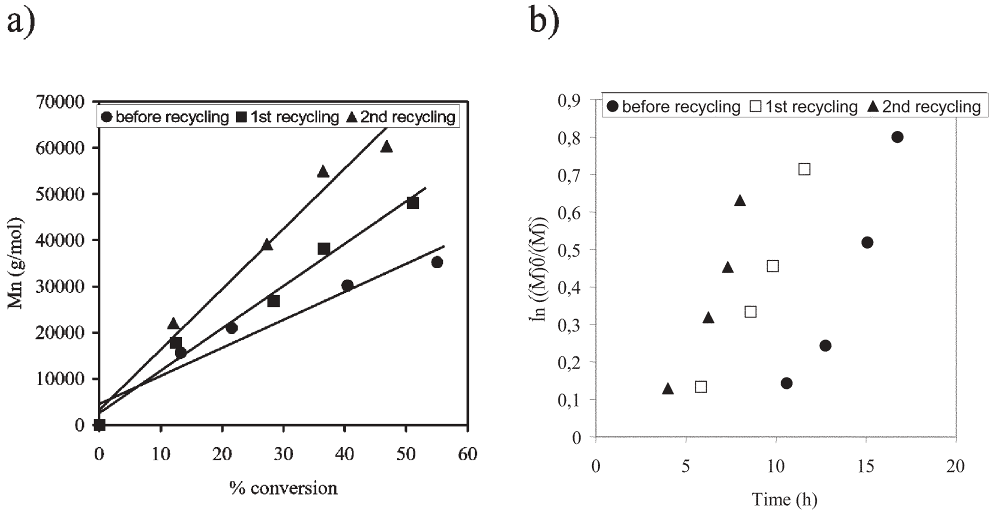


Fig. 3 (a) Dependence of M_n on the monomer conversion and (b) time dependence of $\ln([M]_0/[M])$ for the bulk polymerization of VAc initiated by V70 at 30 °C in the presence of the cobalt complex supported on the Merrifield resin, before and after the first and second recycling [VAc/V70/Co = 247/1.5/1].

monomer conversion and the polydispersity was rather narrow ($1.25 \leqslant M_w/M_n \leqslant 1.40$) (Fig. 2a). Surprisingly enough, the evolution of M_n *vs.* conversion and the time dependence of $\ln([M]_0/[M])$ deviated from linearity after approximately 40% conversion (Fig. 2a and 2b, respectively). Such a behavior might be due to the poor dispersion of cobalt supported on Merrifield compared to the one with the silica. The initiator efficiency was also lower compared to the polymerization mediated by the cobalt complex supported on silica (0.25 *vs.* 0.37, respectively).

The major interest of supporting the Co complex is to have it easily recovered and recycled. According to the mechanism shown in Scheme 4a, most of the PVAc chains are grafted onto the support through a C–Co bond. In order to release these chains from the support, an excess of TEMPO (3 equivalents compared to Co) was added to the polymerization medium containing the cobalt complex supported on the Merrifield resin at a monomer conversion of 55% ($M_n = 35000$ g mol^{-1}). As reported elsewhere,[10] the PVAc macroradicals are trapped irreversibly by TEMPO with release of the cobalt complex (Scheme 4b). As a result, the support is expected to be easily recovered and purified by three centrifugation/dispersion cycles in toluene.

Polymerization of vinyl acetate was mediated by the recycled support under the same conditions as before recycling (VAc/V70/Co = 247/1.5/1; 30 °C). Fig. 3a shows that the experimental molecular weight is higher after recycling than before, at the same conversion, consistent with a decrease in the initiator efficiency (*f*). This loss of activity could result from some cobalt leaching during polymerization and/or from partial cobalt oxidation during recycling. The increase in molecular weight is again observed after a second run of recycling. It must be noted that the polymerization rate is basically independent of the recycling, in contrast to the induction period which decreases (Fig. 3b). This observation supports the loss of "active" cobalt during the recycling procedure.

Briefly, a cobalt(II) acetylacetonate complex was immobilized on silica and Merrifield resin and successfully used for the cobalt-mediated radical polymerization of vinyl acetate. The polymerization was controlled by the cobalt complex supported on silica, whereas some loss of control was observed for conversions higher than 40–50% when the support was the Merrifield resin rather than silica. The poor dispersion might be responsible for this observation. A strategy to recycle the supported cobalt was proposed, and the polymerization of vinyl acetate mediated by the recycled cobalt (supported on Merrifield) was proved to be quite efficient, although some cobalt leaching and/or deactivation is noted. Although the control is not optimum yet, the supported CMRP (SCMRP) opens the way to the production of PVAc and related copolymers free of cobalt and to the recycling of the cobalt mediator. The possible influence of the support on the CMRP of vinyl acetate and the optimization of the support recycling are currently under investigation.

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