Macromolecules

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Synthesis of 1-Vinyl-3-ethylimidazolium-Based Ionic Liquid (Co)polymers by Cobalt-Mediated Radical Polymerization

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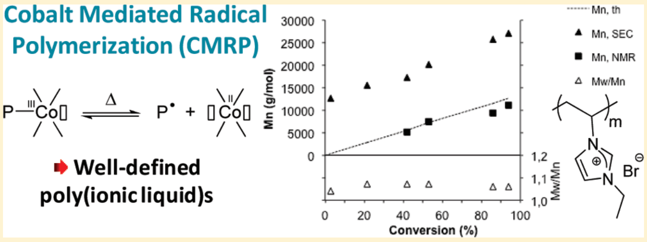
ABSTRACT: The cobalt-mediated radical polymerization (CMRP) of 1-vinyl-3-ethylimidazolium bromide (VEtImBr) is described. Polymerizations were performed at 30 °C in solution either in dimethylformamide (DMF) or in methanol (MeOH) or in a mixture of both solvents, using a preformed alkyl−cobalt(III) adduct, $CH_3OC(CH_3)_2CH_2-C(CH_3)(CN)-(CH_2-CHOAc)_{<4}-Co(acac)_2$, as the mediating agent. Excellent control over molecular weights and dispersities ($M_w/M_n \sim 1.05-1.06$) was achieved in MeOH, with a linear increase of experimental molecular weights with the monomer conversion. Substituting methanol for DMF induced much faster polymerization process, even under quite high diluted conditions: for instance, about 80% monomer conversion was reached in 30 min in DMF, compared to 10 h in MeOH. However, size exclusion chromatography (SEC) traces of PVEtImBr samples synthesized in DMF revealed a side population in the high molecular weight region, presumably due to the occurrence of irreversible coupling reactions of a small proportion of growing chains. Well-defined diblock copolymers featuring both a poly(vinyl acetate) (PVAc) block and a PVEtImBr-based poly(ionic liquid) block, PVAc-*b*-PVEtImBr, were next obtained by sequential CMRP of VAc and VEtImBr. To this end, a PVAc-Co(acac)$_2$ was first prepared by CMRP and employed as a macroinitiator for the polymerization of VEtImBr either in methanol or in a mixture of DMF and MeOH (2/1: v/v) at 30 °C. Finally, cobalt-mediated radical coupling (CMRC) of the aforementioned PVAc-*b*-PVEtImBr diblock copolymers, using isoprene as a simple coupling agent, led to unprecedented and structurally well-defined PVAc-*b*-PVEtImBr-*b*-PVAc triblock copolymers.



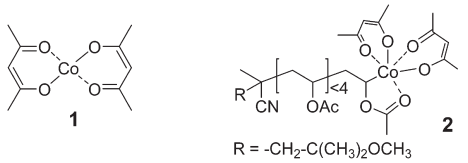
INTRODUCTION

Polymeric ionic liquids, also called poly(ionic liquid)s (PILs), have emerged in the past 10 years as a new class of polyelectrolytes. PILs combine the physicochemical qualities of molecular ionic liquids (ILs), such as chemical and thermal stability, high ionic conductivity, and adjustable solubility, and viscosity, with the specific properties of polymers, such as film formation and processability just to cite a few.[1−5] PILs find potential applications as polymer-supported catalysts,[6,7] polymeric surfactants for the design of porous materials,[8,9] polymeric stabilizers or templates for organic dispersions of conducting polymers,[10,11] CO$_2$-absorbing membranes,[12,13] polymer electrolytes in electrochemical devices,[14−16] microwave-absorbing materials,[17] etc. Applications of ILs in polymer science, including the design of PILs, have been recently reviewed by Texter et al.,[3] Firestone et al.,[2] Long et al.,[1,4] and Yuan and Antonietti,[5] while the synthesis and structural properties of cationic polyelectrolytes in general have been reviewed by Laschewsky et al.[18]

Among ILs and PILs, those based on imidazolium moieties have been the most investigated. The solubility of such cationic (P)ILs is mostly governed by the type of the counteranion, ranging from a high solubility (e.g., with Br$^-$ as anion) to immiscibility in water (with $N^-(SO_2CF_3)_2 = Tf_2N^-$).[1−5] The nature of the substituents on the nitrogen atoms of the imidazole backbone also influences the solubility of PILs but to a lesser extent. Of particular interest, the solubility of PILs can be tuned by a simple and reversible exchange of their counterion, which refers to as the ionic sensitivity.[1−5,19] Such PILs are most often generated by conventional free-radical polymerization of *N*-vinyl-3-alkylimidazolium halides, though methacrylic monomers have also been polymerized.[1−6] A few recent investigations have yet demonstrated that structurally well-defined PILs can be synthesized by controlled radical polymerization (CRP). In particular, atom transfer radical polymerization (ATRP)[20] and reversible addition−fragmentation chain transfer (RAFT)[21−24] polymerization of IL monomers have allowed the preparation

Received: May 6, 2011
Revised: July 10, 2011
Published: July 21, 2011

Scheme 1. Structure of Bis(acetylacetonato)cobalt(II) (Co(acac)$_2$), 1, and Alkyl−Cobalt(III) Adduct, 2 (R−(CH$_2$−CHOAc)$_{<4}$−Co(acac)$_2$; R = Primary Radical from the Decomposition of V-70) Used for CMRP



not only of homopolymers but also of IL-based block copolymers. Interestingly, self-assembly in solution of such copolymers can be triggered by simple anion exchange, giving rise to micelle-like nanostructures.[21−25] It should be mentioned that the arrangement of IL segments in a block copolymer architecture was first reported by Waymouth and Gast et al., who developed a postmodification strategy of a block copolymer based on polystyrene grown by nitroxide-mediated polymerization (NMP).[26,27]

Very recently, xanthates have been successfully employed as RAFT agents to control the polymerization of *N*-vinylimidazolium-type IL monomers.[22−24] Xanthates, indeed, are well-suited for controlling highly reactive (nonconjugated) propagating radical species, such as those deriving from poly(vinyl acetate) (PVAc), poly(*N*-vinylpyrrolidone) (P*N*VP), and poly(*N*-vinylimidazolium) (PVIm) chains.[28] The so-called organometallic-mediated radical polymerization (OMRP)[29] and particularly cobalt-mediated radical polymerization (CMRP)[30] using bis(acetylacetonato)cobalt(II) (Co(acac)$_2$; species **1**, Scheme 1) is the other method that demonstrated good control over the radical polymerization of nonconjugated vinyl monomers such as vinyl acetate (VAc)[30−33] and *N*-vinylpyrrolidone (NVP).[34,35] A proper selection of the polymerization conditions, especially the temperature and the use of coordinating solvents, allows fine-tuning the CMRP reactivity without changing the controlling agent and extending it to conjugated vinyl monomers such as acrylonitrile[36] and acrylates[37] and to the preparation of unprecedented copolymers.[38,39] Recently, cobalt(II) porphyrins, very active for the CMRP of acrylates,[40] also demonstrated some activity for the CMRP of vinyl acetate.[41,42]

In this contribution, we describe for the first time the controlled CMRP of a *N*-vinyl-3-alkylimidazolium IL monomer, namely, 1-vinyl-3-ethylimidazolium bromide (VEtImBr), under very mild conditions. The polymerizations were carried out either in dimethylformamide or in methanol solution, using a preformed alkyl−cobalt(III) adduct **2** (Scheme 1) as both the polymerization initiator and controlling agent upon dissociation. A remarkable control could be achieved at 30 °C in methanol while the polymerization was extremely fast in dimethylformamide. Diblock copolymers featuring both a PVAc block and a PIL block (PVAc-*b*-PVEtImBr) could also be readily obtained by sequential CMRP of VAc and PVEtImBr. Finally, cobalt-mediated radical coupling (CMRC) of such diblock copolymers, in the presence of isoprene, led to unprecedented PVAc-*b*-PVEtImBr-*b*-PVAc symmetrical triblock copolymers.

■ EXPERIMENTAL SECTION

Materials. Vinyl acetate (>99%, Aldrich) was dried over calcium hydride, degassed by several freeze−thawing cycles before being distilled under reduced pressure and stored under argon. 2,2′-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) (Wako), cobalt(II) acetylacetonate (Co(acac)$_2$) (>98%, Merck), and 2,2,6,6-tetramethylpiperidine-1-oxy (TEMPO) (98%, Aldrich) were used as received. Dimethylformamide (DMF) and methanol (MeOH) were dried over molecular sieves and degassed by bubbling argon for 15 min. Membrane Spectra/Pore (cutoff: 3500 Da) was used for dialysis. 1-Vinyl-3-ethylimidazolium bromide (VEtImBr) was synthesized following the procedure described in the literature.[19] Under vigorous stirring, 22 g (0.202 mol, 15.1 mL) of 2-bromoethane was added dropwise to 10 g (0.106 mol, 9.6 mL) of 1-vinylimidazole in a 100 mL, one-necked, round-bottom flask. The mixture was refluxed for 20 h (80 °C). The resulting white-yellow powder was allowed to cool to room temperature, and then it was washed several times with ethyl acetate. The product was dried prior to use under dynamic vacuum until constant weight (20.4 g, 95% yield). ^{1}H NMR (CDCl$_3$): δ 10.85 (s, N−C*H*−N, 1H), 7.88 (s, N−C*H*═CH−N, 1H), 7.70 (s, N−CH═C*H*−N, 1H), 7.43 (dd, CH$_2$═C*H*−N, 1H), 5.99 (dd, *H*CH═CH−N, 1H), 5.36 (dd, HC*H*═CH−N, 1H), 4.47 (q, N−C*H*$_2$−CH$_3$ 2H), 1.60 (t, N−CH$_2$−C*H*$_3$, H). The synthesis and the complete characterization of the low molecular weight alkyl−cobalt(III) adduct **2** have been described elsewhere.[33] The cobalt complex was stored as a CH$_2$Cl$_2$ solution at −20 °C under argon. The cobalt concentration of the stock solution was determined by ICP-MS ([alkyl−cobalt(III)] = 0.148 M).

Characterization. Size exclusion chromatography (SEC) of poly(vinyl acetate) was carried out in tetrahydrofuran (THF) (flow rate: 1 mL min^{-1}) at 40 °C with a Waters 600 liquid chromatograph equipped with a 410 refractive index detector and styragel HR columns (four columns HP PL gel 5 μm 10^5, 10^4, 10^3, and 10^2 Å). The molar mass of PVAc determined by SEC with polystyrene (PS) calibration was in good agreement with that determined by ^{1}H NMR whenever the α-end group of the initiator (−OCH$_3$ at δ = 3.13 ppm) could be observed and compared to the −C*H*OCOCH$_3$ proton at δ = 4.8 ppm of the monomer unit, as reported elsewhere.[31,32] SEC of PVAc, poly(1-vinyl-3-ethylimidazolium bromide) (PVEtImBr), and poly(vinyl acetate)-*b*-poly(1-vinyl-3-ethylimidazolium bromide) (PVAc-*b*-PVEtImBr) was performed in dimethylformamide (DMF) containing some LiBr (0.025 M) at 55 °C (flow rate: 1 mL min^{-1}), with a Waters 600 liquid chromatograph equipped with a 410 refractive index detector and styragel HR columns (HR1, 100−5000; HR3, 500−30 000; HR4, 5000−500 000; HR5, 2000−40 000 000). In all cases, polystyrene standards ranging from 580 to 225 × 10^4 g/mol were used for calibration. For PVEtImBr and PVAc-*b*-PVEtImBr, a few drops of methanol were added to fully solubilize the (co)polymers before injection.

^{1}H NMR spectra of the PVAc macroinitiators were recorded at 298 K with a Bruker spectrometer (400 MHz) in CDCl$_3$ (D_1 = 2 s, 16 scans, 5 wt % of polymer). ^{1}H NMR spectra of PVEtImBr and PVAc-*b*-PVEtImBr were recorded with a Bruker spectrometer (400 MHz) at 298 K in deuterated dimethyl sulfoxide (DMSO-d_6) (D_1 = 5 s, 32 scans, 5 wt % of polymer).

Homopolymerization of VEtImBr Initiated by the Alkyl−Cobalt(III) Initiator. 1-Vinyl-3-ethylimidazolium bromide (0.5 g; 2.46 × 10^{-3} mol) was introduced in a Schlenk tube and degassed by three vacuum−argon cycles. Dry and degassed methanol (1.5 mL) was added, and the reaction medium was stirred at 30 °C. A solution of alkyl−cobalt(III) initiator (Co(acac)$_2$(−CH(OCOCH$_3$)CH$_2$)$_{<4}$−R$_0$) and 0.25 mL of a 0.148 M stock solution in CH$_2$Cl$_2$ (3.7 × 10^{-5} mol) was then added, and the polymerization occurred at 30 °C. Samples were periodically taken out of the medium via a syringe during the polymerization and added with few milligrams of TEMPO in order to quench the polymerization. Monomer conversions were determined by ^{1}H NMR spectroscopy in DMSO-d_6, and macromolecular parameters (M_n, M_w/M_n) were determined by SEC in DMF/LiBr as eluent. For calculating the experimental molecular weight by ^{1}H NMR ($M_{n,NMR}$), the samples were precipitated three times in diethyl ether and dried at 40 °C under vacuum overnight. (see Table 1, entry 1, and

Table 1. Homopolymerization of 1-Vinyl-3-ethylimidazolium Bromide Initiated by Alkyl−Cobalt(III) Adduct 2 in Different Solvents at 30 °C[a]

entry	solvent	solvent/monomer (v/w)	time (h)	conv (%)[b]	$M_{n,SEC}$[c] (g/mol)	M_w/M_n[d]
1	MeOH	3/1	0.5	3	14 400	1.05
			1	21.5	15 600	1.05
			2	42	17 200	1.06
			6	53	20 200	1.06
			10	86	25 700	1.06
			33	94	27 000	1.06
2	DMF	3/1	0.16	52	24 300	1.10
			0.33	63	24 600	1.09
			0.5	78	26 800	1.09
3	DMF	6/1	0.75	85	24 800	1.07
			1.5	90	25 600	1.07
			2.5	100	23 200	1.07
4	DMF	12/1	0.16	30	15 800	1.05
			0.5	75	17 500	1.05
			4	96	21 200	1.07

[a] Conditions: [VEtImBr]/[alkyl−cobalt(III)] = 66; 30 °C. [b] VEtImBr conversion measured by ^{1}H NMR in DMSO-d_6. [c] Number-average molecular weight determined by SEC analysis in DMF. [d] Molecular weight distribution determined by SEC in DMF.

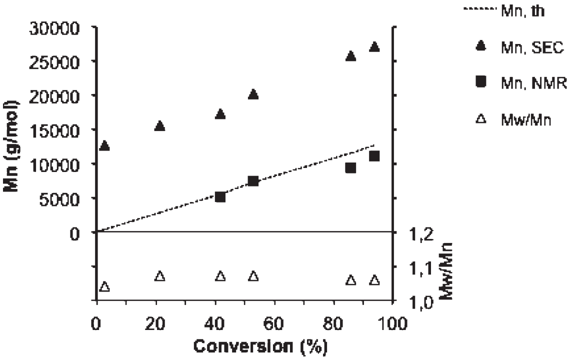


Figure 1. Number-average molecular weight evolution with the monomer conversion for the VEtImBr polymerization initiated by alkyl−cobalt(III) in methanol at 30 °C. Conditions: [alkyl−cobalt(III)]/[VEtImBr] = 1/66, MeOH/VEtImBr = 3/1. $M_{n,th}$ = theoretical number-average molecular weight calculated by the following equation: $M_{n,th}$ = ([VEtImBr]/[alkyl−cobalt(III)]) × $MW_{VEtImBr}$ × conversion, where $MW_{VEtImBr}$ is the molecular weight of VEtImBr.

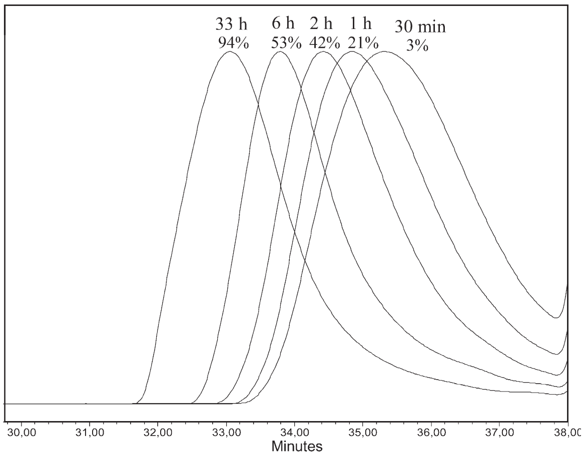


Figure 2. Evolution of SEC traces of PVEtImBr prepared in methanol at 30 °C with conversion (Table 1, entry 1).

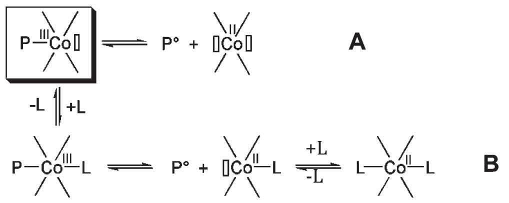
Figures 1 and 2). The same experiment was carried out using dimethylformamide as solvent (see Table 1, entry 2).

Synthesis of PVAc-*b*-PVEtImBr Diblock Copolymers by Sequential CMRP

(a) *Synthesis of the Poly(vinyl acetate) Macroinitiator End-Capped by Co(acac)$_2$.* A solution of the alkyl−cobalt(III) initiator ($Co(acac)_2(-CH(OCOCH_3)CH_2)_{<4}-R_0$) in CH_2Cl_2 was introduced under argon in a Schlenk tube (1.5 mL of a 0.148 M stock solution, 2.2 × 10^{-4} mol) and evaporated to dryness under reduced pressure at room temperature (RT). The residue was then placed under argon at 0 °C and added with dry VAc (2 mL, 0.162 mol). The reaction medium was then stirred for 5.5 h at 40 °C. An aliquot was withdrawn for calculating the conversion by ^{1}H NMR in $CDCl_3$ (50% conversion) and for the determination of the molecular weight parameters by SEC using THF (M_n = 4000 g/mol; M_w/M_n = 1.05) and DMF/LiBr (M_n = 17 500 g/mol; M_w/M_n = 1.04) as solvents. Residual monomer was then removed under vacuum at RT.

(b) *Synthesis of PVAc-b-PVEtImBr-Co(acac)$_2$ Diblock Copolymer.* The flask containing the PVAc-Co(acac)$_2$ macroinitiator under argon was cooled to 0 °C, and 1 mL of DMF at 0 °C was added to dissolve the macroinitiator. A degassed solution of VEtImBr (1 g, 4.92 × 10^{-3} mol) in a mixture of DMF/MeOH (3/2 v/v; 5 ml) was then added, and the polymerization occurred at 30 °C under stirring. Aliquots were regularly withdrawn for calculating the conversion by ^{1}H NMR in DMSO-d_6 and for the determination of the molecular weight parameters by SEC using DMF/LiBr as solvent. All samples were quenched by adding excess TEMPO. Results are summarized in Figure 8. The final product was precipitated in diethyl ether. After redissolution in methanol, the product was dialyzed against methanol for 48 h and finally dried at 40 °C in vacuum for 24 h. The composition of the copolymer was calculated by ^{1}H NMR in DMSO-d_6: $PVAc_{(4000\ g/mol)}$-*b*-$PVImBr_{(4100\ g/mol)}$.

Scheme 2. Reversible Deactivation (RD) Process for CMRP Mediated by $Co(acac)_2$[a]



[a] Activation was promoted thermally (pathway A) and by adding appropriate ligands (pathway B).

Synthesis of PVAc-*b*-PVEtImBr-*b*-PVAc Triblock Copolymers by CMRC

(a) A poly(vinyl acetate) macroinitiator end-capped by $Co(acac)_2$ was first synthesized as previously described, using 1.5 mL of a 0.148 M CH_2Cl_2 solution of the alkyl–cobalt(III) initiator (2.2×10^{-4} mol) and 2 mL of VAc (0.162 mol), affording a PVAc-$Co(acac)_2$ (t = 6.5 h, 44% conversion; $M_{n,abs}$ = 4000 g/mol; M_w/M_n = 1.05). Relative molecular weight was also determined by SEC in DMF/LiBr ($M_{n,SEC\ DMF}$ = 18 100 g/mol; M_w/M_n = 1.05). The residual monomer was removed under vacuum at RT.

(b) *Synthesis of PVAc-b-PVEtImBr-Co(acac)₂ Diblock Copolymer.* The flask containing the PVAc-$Co(acac)_2$ macroinitiator under argon was cooled to 0 °C, and 1 mL of DMF at 0 °C was added to dissolve the macroinitiator. A degassed solution of VEtImBr (1 g, 4.92×10^{-3} mol) in a DMF/MeOH (3/2 v/v; 5 ml) mixture) was then added, and the polymerization occurs at 30 °C under stirring. After 1.5 h of reaction, an aliquot was withdrawn for calculating the conversion by ^1H NMR in DMSO-d_6 (48% conversion) and for the determination of the molecular weight parameters by SEC using DMF/LiBr as solvent. $M_{n,SEC\ DMF}$ = 22 600 g/mol; M_w/M_n = 1.05.

(c) *Coupling of PVAc-b-PVEtImBr-Co(acac)₂ in the Presence of Isoprene.* Into the DMF solution of the PVAc-*b*-PVEtImBr-Co-$(acac)_2$ diblock copolymer described above was added a solution of isoprene (1 mL, 10^{-2} mol) in methanol (4 mL). The coupling reaction occurred at 30 °C overnight. The mixture was analyzed by ^1H NMR to check that residual VEtImBr was not polymerized during the coupling reaction, and the polymer was analyzed by SEC in DMF/LiBr as solvent. $M_{n,SEC\ DMF}$ = 36 500 g/mol; M_w/M_n = 1.08 (see Figure 9). The polymer was finally precipitated twice in diethyl ether, dissolved in methanol, and dialyzed against methanol for 48 h. The product was finally dried under vacuum at 40 °C and analyzed by ^1H NMR in DMSO-d_6 for determining the composition of the copolymer (Figure 9): $PVAc_{(4000\ g/mol)}$-*b*-$PVEtImBr_{(6700\ g/mol)}$-*b*-$PVAc_{(4000\ g/mol)}$.

■ RESULTS AND DISCUSSION

Homopolymerization of 1-Vinyl-3-ethylimidazolium Bromide by CMRP. The preformed alkyl–cobalt(III) adduct **2** ($R-(CH_2-CHOAc)_{<4}-Co(acac)_2$; R = primary radical from the decomposition of V-70; Scheme 1), which is very efficient to control the CMRP of vinyl acetate,[33] *N*-vinylpyrrolidone,[43] acrylonitrile,[36] and *n*-butyl acrylate,[37] was first investigated as both the initiator and the controlling agent for the homopolymerization of 1-vinyl-3-ethylimidazolium bromide (VEtImBr). Upon thermal treatment and/or by adding suitable coordinating solvents, the carbon–cobalt bond of adduct **2** cleaves to release both the alkyl radical serving as initiator and the cobalt(II) complex. Control of the polymerization is thus ensured according to a reversible deactivation (RD) process, as shown in Scheme 2.[33,36,44]

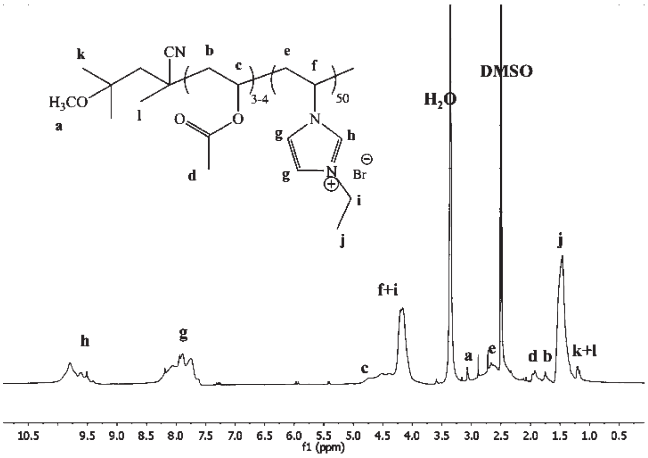


Figure 3. 400 MHz ^1H NMR spectrum in DMSO-d_6 of PVEtImBr prepared from alkyl–cobalt(III) in methanol at 30 °C after 33 h (Table 1, entry 1).

Methanol was selected as a good solvent for both the monomer (VEtImBr) and the poly(1-vinyl-3-ethylimidazolium bromide) (PVEtImBr), and the polymerization was carried out at 30 °C. Under these mild experimental conditions, an almost complete conversion was reached after 33 h of reaction (Table 1, entry 1). Figure 1 shows that the molecular weight of PVEtImBr increases linearly with the monomer conversion, while the dispersity remains very low ($M_w/M_n \sim 1.05-1.06$) even at high conversion. SEC traces are monomodal and clearly shift toward the higher molecular weight region with the polymerization time (Figure 2), consistently with a controlled polymerization process. However, weak tailing can be observed in the low molecular weight region of the SEC traces, which is most likely due to polymer adsorption onto the SEC columns. As can be seen from Figure 1, molecular weights of PVEtImBr measured by SEC are higher than theoretical values calculated from the monomer/alkyl–cobalt(III) adduct molar ratio and conversion of the monomer (Figure 1). This discrepancy likely results from the difference in hydrodynamic volume between PVEtImBr and the linear poly(styrene) (PS) standards used for SEC calibration. PVEtImBr samples were thus analyzed by ^1H NMR spectroscopy to determine the initiator efficiency of the alkyl–cobalt(III) **2**. For this purpose, PVEtImBr samples were purified by repeated precipitation in diethyl ether to remove unreacted monomer and any residual alkyl–cobalt(III), before analysis in DMSO-d_6. The comparison of the signal intensity of protons **a** at 3.1 ppm, corresponding to the methoxy group of the initiating fragment of alkyl–cobalt(III), with that of protons **g** at 8.0 ppm characteristic of the imidazolium ring in the PVEtImBr repeating units allowed us to calculate the experimental number-average molecular weight of the polymers (Figure 3). The latter value eventually appears very close to the theoretical prediction, attesting to the high initiation efficiency of these CMRPs of VEtImBr (Figure 1).

When methanol was substituted for dimethylformamide (DMF) as the solvent under otherwise identical reaction conditions, the polymerization was extremely fast, with about 80% conversion being reached after 30 min only. For comparison, a polymerization time of 10 h was necessary to reach

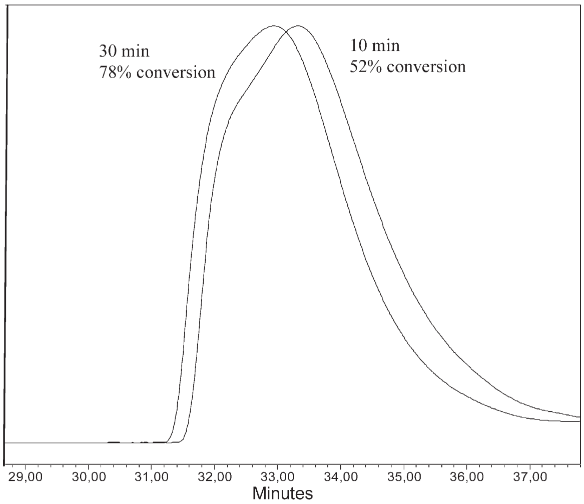


Figure 4. Evolution of SEC traces of PVEtImBr prepared in DMF (DMF/VEtImBr = 3/1 (v/w)) at 30 °C with conversion (Table 1, entry 2).

the same conversion in methanol. Although the dispersity is also very low in DMF, a closer look at the SEC traces clearly shows the appearance of a shoulder at the high molecular weight region (Figure 4). This shoulder might result from some irreversible coupling reactions between polymer chains that are favored with highly reactive propagating radicals. Complexing solvents such as DMF have already been demonstrated to speed up the VAc polymerization by activating the C−Co bond cleavage at the polymer chain end of dormant species and by transforming part of the $Co(acac)_2$ into the inactive bis-ligated $Co(acac)_2L_2$ complex (Scheme 2, pathway B).[44]

To slow down the polymerization and tentatively decrease the extent of side reactions, the polymerization temperature was decreased to 0 °C. However, part of the monomer precipitated out under such conditions, leading to a heterogeneous polymerization medium. Another way to decrease the polymerization rate while avoiding precipitation of the monomer was to further dilute the reaction medium with DMF at 30 °C. Although the quite high dilution of the reaction medium (DMF/monomer v/v = 6 and 12) slowed down the polymerization (Table 1, entries 3 and 4), the latter remained very fast at 30 °C (completion in less than 4 h). However, coupling reactions could not be totally suppressed with DMF, as illustrated in Figure 5. Methanol was therefore preferred as the polymerization solvent in our subsequent investigations.

Block Copolymerization of VEtImBr and VAc by CMRP. PVAc-*b*-PVEtImBr block copolymers were tentatively prepared by sequential CMRP of VAc and VEtImBr in the presence of $Co(acac)_2$. First, a poly(vinyl acetate) end-capped by $Co(acac)_2$ (PVAc-$Co(acac)_2$) was prepared by CMRP of VAc, using the alkyl−cobalt(III) at 40 °C in bulk. After 7 h of reaction, about 50% conversion was reached. After removal of the residual monomer under vacuum, the resulting PVAc-$Co(acac)_2$ ($M_{n,abs}$ = 5200 g/mol; M_w/M_n = 1.06) was employed as a macroinitiator for the polymerization of VEtImBr in methanol at 30 °C. Block copolymerization was found effective, as illustrated by the SEC traces of copolymers collected after 2 and 7 h of reaction, compared with the SEC trace of the PVAc macroinitiator (Figure 6). The elution peak of the macroinitiator is indeed completely shifted toward higher molar masses for the copolymers with no unreacted PVAc chains left. It has to be noted that the copolymers were not precipitated before SEC analysis, in order to avoid any fractionation of the copolymer and elimination of hypothetical unreacted macroinitiator. Only a slight shoulder in the high molecular region is observed, likely resulting from coupling reactions that occurred during sampling. The dispersity remains very low during the whole copolymerization process (M_w/M_n = 1.04−1.06), attesting to an effective crossover reaction.

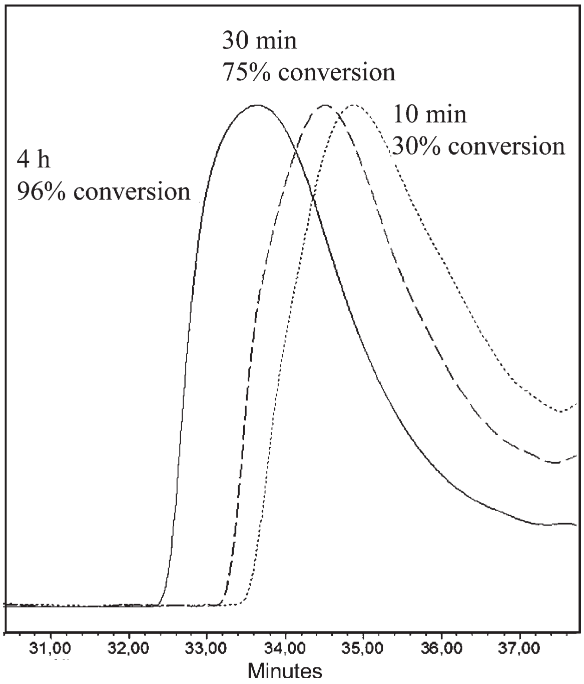


Figure 5. Evolution of SEC traces of PVEtImBr prepared in DMF (DMF/VEtImBr = 12/1 (v/v)) at 30 °C with conversion (Table 1, entry 4).

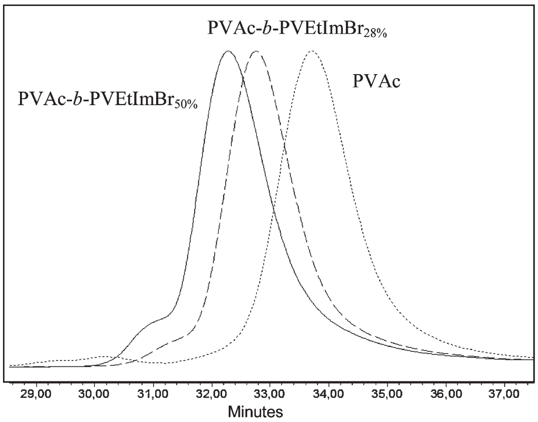


Figure 6. SEC chromatograms of PVAc-$Co(acac)_2$ macroinitiator ($M_{n,abs}$ = 5200 g/mol; $M_{n,SEC\ DMF}$ = 21 900 g/mol, M_w/M_n = 1.06; dotted line), PVAc-*b*-PVEtImBr diblock copolymer formed after 2 h of reaction (28% conversion; $M_{n,SEC\ DMF}$ = 30 000 g/mol; M_w/M_n = 1.04; dashed line) and PVAc-*b*-PVEtImBr diblock copolymer formed after 7 h of reaction (50% conversion; $M_{n,SEC\ DMF}$ = 33 400 g/mol; M_w/M_n = 1.06; solid line) in methanol at 30 °C. Conditions for block copolymerization: methanol/VEtImBr = 3/1 (v/w), [PVAc-$Co(acac)_2$]/[VEtImBr] = 1/22; 30 °C.

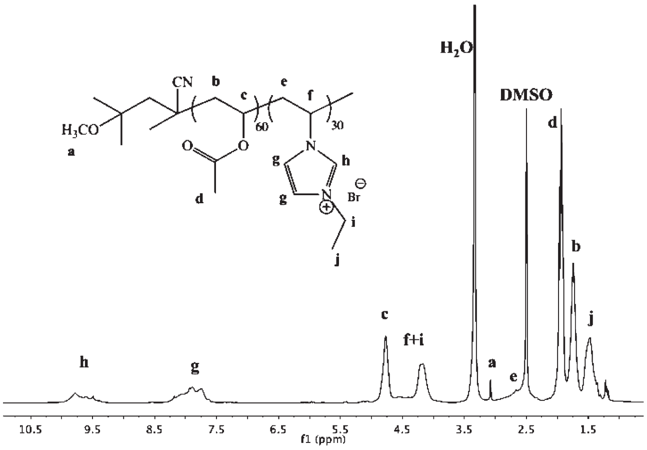


Figure 7. 400 MHz ^{1}H NMR spectrum in DMSO-d_6 of PVAc$_{(5200)}$-*b*-PVEtImBr$_{(5500)}$ diblock copolymer prepared in methanol at 30 °C.

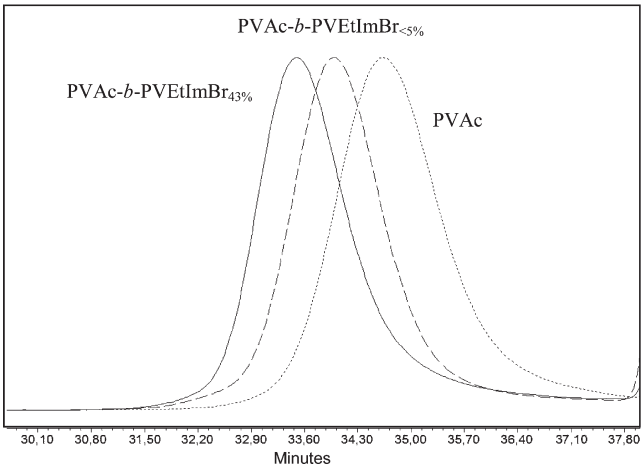
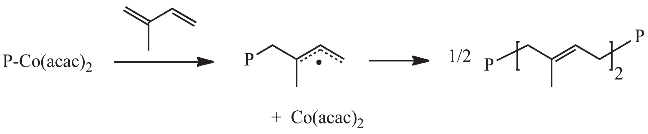


Figure 8. SEC traces of PVAc-Co(acac)$_2$ macroinitiator ($M_{n,abs}$ = 4000 g/mol; $M_{n,SEC\ DMF}$ = 17 500 g/mol, M_w/M_n = 1.04; dotted line), PVAc-*b*-PVEtImBr diblock copolymer formed after 10 min of reaction (<5% conversion; $M_{n,SEC\ DMF}$ = 21 400 g/mol; M_w/M_n = 1.04; dashed line), and PVAc-*b*-PVEtImBr diblock copolymer formed after 1.5 h of reaction (43% conversion; $M_{n,SEC\ DMF}$ = 23 700 g/mol; M_w/M_n = 1.04; solid line) in DMF/methanol (2/1) at 30 °C. Conditions for block copolymerization: DMF/VEtImBr = 4/1 (v/w), DMF/MeOH = 2/1 (v/v), [PVAc-Co(acac)$_2$]/[VEtImBr] = 1/22; 30 °C.

After purification by dialysis against methanol for 48 h, ^{1}H NMR analysis of the copolymer evidenced the presence of diagnostic signals of both PVAc and PVEtImBr (Figure 7). The composition of the copolymer and the molecular weight of each sequence could be determined in this way by comparing the intensities of signals corresponding to methine protons **c** of PVAc (4.82 ppm) with that of protons **g** in the imidazolium ring (8 ppm) of PVEtImBr. The composition was as follows: PVAc$_{(5200\ g/mol)}$-*b*-PVEtImBr$_{(5500\ g/mol)}$ (Figure 7).

When carrying out the block copolymerization in a mixture of DMF and methanol as solvent (DMF/MeOH = 2/1), the reaction proved faster despite a twice more diluted polymerization medium. 43% monomer conversion was reached after 1.5 h of polymerization in such conditions. Importantly, SEC traces were monomodal and shifted toward the higher molecular weights with the progress of the reaction (Figure 8). Moreover, the dispersity remained very low all along the polymerization process (M_w/M_n = 1.04) with no detectable coupled chains. All these observations are thus consistent with a controlled process and the formation of well-defined PVAc-*b*-PVImBr diblock copolymers. ^{1}H NMR analysis allowed us to calculate the composition of this copolymer after purification by dialysis against methanol for 48 h: PVAc$_{(4000)}$-*b*-PVEtImBr$_{(4100)}$.

Scheme 3. Cobalt-Mediated Radical Coupling (CMRC) Process



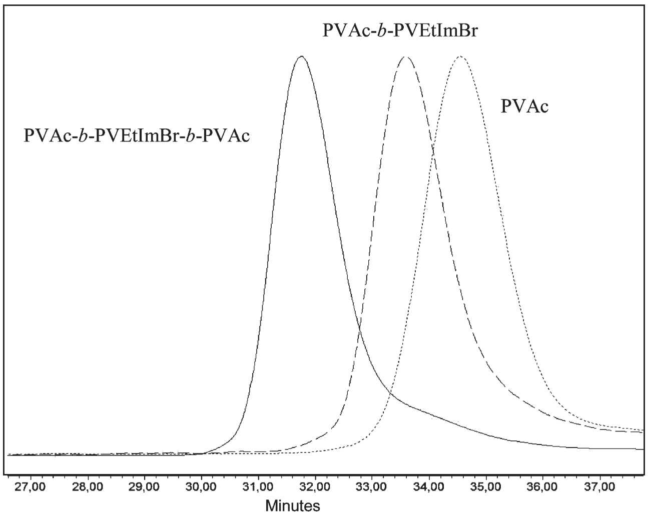


Figure 9. SEC traces of PVAc-Co(acac)$_2$ macroinitiator ($M_{n,abs}$ = 4000 g/mol; $M_{n,SEC\ DMF}$ = 18 100 g/mol, M_w/M_n = 1.05; dotted line), PVAc-*b*-PVEtImBr diblock copolymer ($M_{n,SEC\ DMF}$ = 22 600 g/mol; M_w/M_n = 1.05; dashed line), and PVAc-*b*-PVEtImBr-*b*-PVAc triblock copolymer ($M_{n,SEC\ DMF}$ = 36 500 g/mol; M_w/M_n = 1.08; solid line) in DMF/methanol (2/1) at 30 °C.

Synthesis of PVAc-*b*-PVEtImBr-*b*-PVAc Symmetrical Triblock Copolymers by Cobalt-Mediated Radical Coupling (CMRC). When an excess of isoprene is added to polymer chains end-capped by Co(acac)$_2$ prepared by CMRP, a fast and quantitative radical coupling of the chains is observed.[39] This coupling reaction, named cobalt-mediated radical coupling (CMRC), has been recently reported for PVAc-Co(acac)$_2$,[43] poly(*N*-vinylpyrolidone)-Co(acac)$_2$ (PNVP-Co(acac)$_2$),[43] and poly(acrylonitrile)-Co(acac)$_2$ (PAN-Co(acac)$_2$)[45] homopolymers and for PVAc-*b*-PAN-Co(acac)$_2$ and PVAc-*b*-PNVP-Co(acac)$_2$ diblock copolymers.[39] In the latter case, symmetrical PVAc-*b*-PAN-*b*-PVAc[39] and PVAc-*b*-PNVP-*b*-PVAc[43] triblock copolymers could be readily obtained. During this CMRC process, the radical formed at the polymer chain end by homolytic cleavage of the carbon−cobalt bond rapidly adds onto an isoprene unit, forming the corresponding allyl radical (Scheme 3). The weak propensity of Co(acac)$_2$ to deactivate the allyl radical terminated chains results in the release of a large

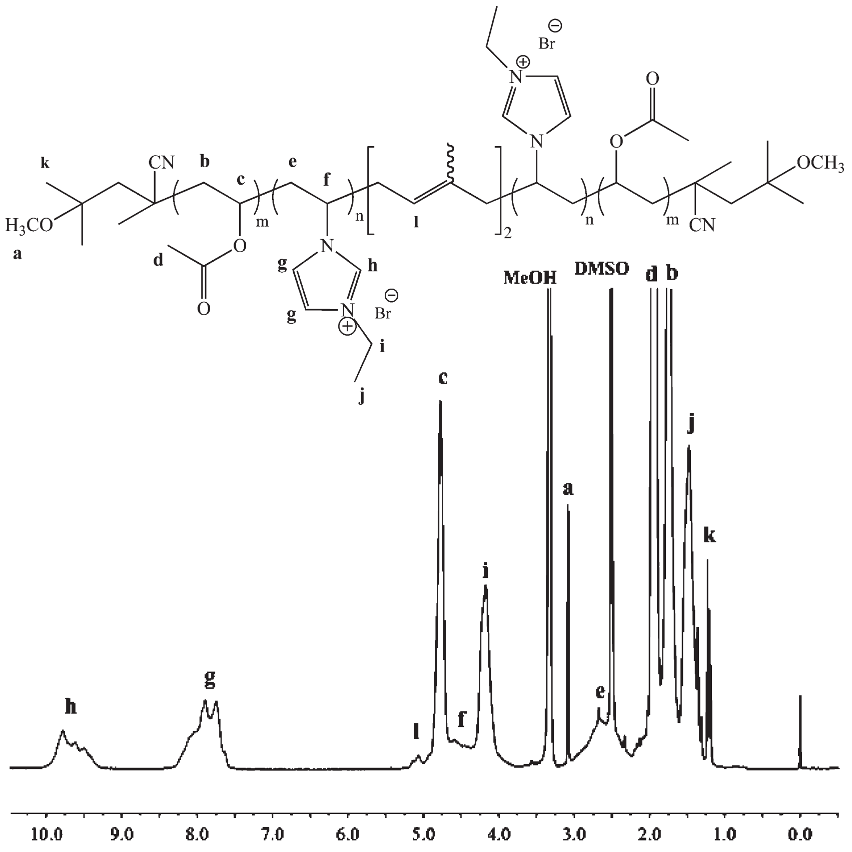


Figure 10. 400 MHz ^{1}H NMR spectrum in DMSO-d_6 for PVAc$_{46}$-*b*-PVEtImBr$_{33}$-*b*-PVAc$_{46}$ triblock copolymer.

amount of radical chains in the medium followed by a fast combination reaction instead of isoprene polymerization. Because of the very low propagating constant (k_p) of isoprene at room temperature, only two isoprene units are thus incorporated at the middle of the polymer chains.[45] The process is so efficient and fast that removing the residual monomer before adding isoprene is not needed. The coupling reaction occurs almost instantaneously after isoprene is just added, and no more polymerization of the vinyl monomer is observed.

On this basis, we investigated the CMRC of PVAc-*b*-PVEtImBr-Co(acac)$_2$ diblock copolymers described above. For this purpose, the PVAc-Co(acac)$_2$ (M_n = 4000 g/mol; M_w/M_n = 1.05) prepared from **2** at 40 °C was employed to initiate the polymerization of VEtImBr at 30 °C in a DMF/MeOH (2/1) mixture. After 1.5 h of polymerization (48% monomer conversion), excess isoprene was added, leading to a rapid buildup of the viscosity of the reaction medium. ^{1}H NMR analysis confirmed that residual VEtImBr was no more polymerized after addition of isoprene. SEC traces clearly show the efficiency of the reaction forming the targeted PVAc-*b*-PVEtImBr-*b*-PVAc triblock copolymer, with a complete shift of the SEC peak of the PVAc-*b*-PVEtImBr diblock copolymer toward the higher molecular weights side (Figure 9). The small tailing at the low molecular weight side (slight increase of the dispersity from 1.04 to 1.08) is likely the result of very limited amount of nonreacted diblock copolymer. The copolymer was finally purified by dialysis against methanol to remove any residual monomer and characterized by ^{1}H NMR spectroscopy; the composition was found as follows: PVAc$_{(4000\ \mathrm{g/mol})}$-*b*-PVEtImBr$_{(6700\ \mathrm{g/mol})}$-*b*-PVAc$_{(4000\ \mathrm{g/mol})}$.

Besides ^{1}H NMR signals that are characteristic of both PVAc and PVEtImBr (Figure 10), small signals are detected in the vinylic region at 5.2 ppm corresponding to the 1,4-trans addition of isoprene in the copolymer during coupling. In agreement with previous CMRC works,[39,43,45] integration of this vinylic signal with that of methoxy protons present at both chain ends, at 3.15 ppm, allowed us to conclude that two isoprene units in average were incorporated during the coupling procedure. CMRC is therefore a convenient and straightforward approach for preparing novel PVAc-*b*-PVEtImBr-*b*-PVAc symmetrical triblock copolymers. This coupling experiment also demonstrates that most of the PVAc-*b*-PVEtImBr-Co(acac)$_2$ chains are active before adding isoprene, attesting to the livingness of growing poly(*N*-vinylimidazolium) chains prepared by CMRP.

■ CONCLUSION

The cobalt-mediated radical polymerization (CMRP) was extended to a *N*-vinyl-3-alkylimidazolium ionic liquid monomer, allowing its "controlled/living" polymerization as well as its block copolymerization with vinyl acetate (VAc). Polymeric ionic liquids (PILs) deriving from 1-vinyl-3-ethylimidazolium bromide (VEtImBr) as well as amphiphilic block copolymers based on both VAc and VEtImBr units could thus be obtained with a good control over molecular weights and dispersities. Use of DMF instead of methanol as solvent was shown to dramatically speed up the VEtImBr polymerization, presumably due to an activating effect on the $C-Co^{III}(acac)_2$ bond cleavage at the polymer chain end by DMF. Such an acceleration of the CMRP of VEtImBr occurred, however, at the expense of the control of the reaction, a small fraction of growing chains undergoing irreversible couplings in DMF. Well-defined PVAc-*b*-PVEtImBr-Co(acac)$_2$ diblock copolymers could be readily obtained by sequential CMRP of VAc and VEtImBr. Finally, addition of isoprene as simple coupling agent onto a solution of these diblock copolymers enabled the direct preparation of symmetrical PVAc-*b*-PVEtImBr-*b*-PVAc triblock copolymers. Investigations into the self-assembly both in bulk and in solution of di- and triblock copolymers described in this work are underway in our groups. It might be expected that many other highly reactive *N*-vinylimidazolium ionic liquid monomers (for instance with different counteranions and/or alkyl chains in 3-position of the imidazolium ring) could be polymerized in a controlled fashion by CMRP.

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ACKNOWLEDGMENT

The authors from Liège are grateful to the "Belgian Science Policy" for financial support in the frame of the Interuniversity Attraction Pole Programme (PAI VI/27) and to the National Funds for Scientific Research (F.R.S.-FNRS). They also thank Grégory Cartigny for his skillful assistance. D.T. thanks the European Commission for financing the Collaborative Large-scale integrating project ORION (FP7- NMP-LA-2009-229036).

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