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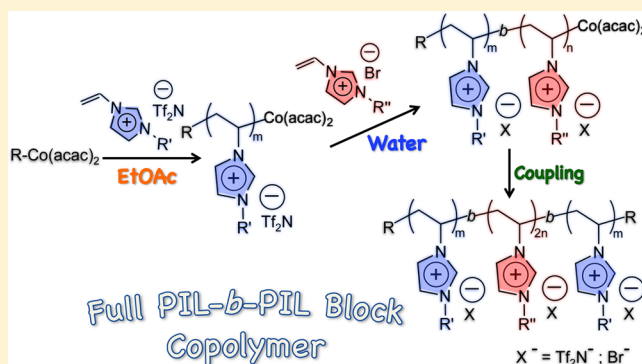
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## All Poly(ionic liquid)-Based Block Copolymers by Sequential Controlled Radical Copolymerization of Vinylimidazolium Monomers

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## Supporting Information

**ABSTRACT:** The organometallic-mediated radical polymerization (OMRP) of *N*-vinyl-3-alkylimidazolium-type monomers, featuring the bis(trifluoromethylsulfonyl)imide counteranion ( $\text{Tf}_2\text{N}^-$ ), in the presence of  $\text{Co}(\text{acac})_2$  as controlling agent, is reported. Polymerizations of monomers with methyl, ethyl, and butyl substituents are fast, reaching high monomer conversion in ethyl acetate as solvent at 30 °C, and afford structurally well-defined hydrophobic poly(ionic liquid)s (PILs) of *N*-vinyl type. Block copolymer synthesis is also achieved by sequential OMRP of *N*-vinyl-3-alkylimidazolium salts carrying different alkyl chains and different counteranions ( $\text{Tf}_2\text{N}^-$  or  $\text{Br}^-$ ). These block copolymerizations are carried out at 30 °C, either under homogeneous solution in methanol or in a biphasic medium consisting of a mixture of ethyl acetate and water. Unprecedented PIL-*b*-PIL block copolymers are thus prepared under these conditions. However, anion exchange occurs at the early stage of the growth of the second block. Finally, diblock copolymers generated in the biphasic medium can be readily coupled by addition of isoprene, forming all PIL-based and symmetrical ABA-type triblock copolymers in a one-pot process. Such a direct block copolymerization method, involving vinylimidazolium monomers bearing different alkyl chains, thus opens new opportunities in the precision synthesis of all PIL-based block copolymers of tunable properties.



## INTRODUCTION

Poly(ionic liquid)s (PILs) represent a special class of polyelectrolytes that are characterized by a tunable solubility, a high ionic conductivity, and chemical and thermal stability.<sup>1–15</sup> This unique combination of properties makes them excellent candidates for various applications, including solid ionic conductors for energy storage, membranes, dispersants, analytical chemistry, biotechnology, gas separation, and catalysis.<sup>5,6,11,16–27</sup> A large variety of PILs are now accessible either by directly polymerizing an ionic liquid monomers (ILM)<sup>3,5,7,9,28–41</sup> or by postmodification of a neutral polymer precursor.<sup>10,34,42–44</sup> The latter method involves the prior preparation of the polymer precursor, introduction of IL moieties generally being carried out by quaternization. Exchange of the counterion allows for further variation of PIL properties. Polymerizing ILMs by a chain-growth polymerization pathway gives a more direct access to PILs. Recently, controlled/living polymerization (CLP) techniques have been used to achieve well-defined

PILs,<sup>9,38,39,45–51</sup> broadening the scope of PILs structure, functionality, and applications.

Most of the investigated ILMs are conjugated imidazolium- or phosphonium-based vinyl monomers of norbornenyl,<sup>10,25</sup> styrenic, or methacrylate type<sup>39,45–47,52–56</sup> with various counteranions (mostly  $\text{Br}^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ , and bis(trifluoromethylsulfonyl)imide ( $(\text{SO}_2\text{CF}_3)_2\text{N}^- = \text{Tf}_2\text{N}^-$ ). CLP of these monomers can be achieved, for instance, by ring-opening metathesis polymerization (ROMP),<sup>57–61</sup> atom transfer radical polymerization (ATRP),<sup>38,39,47,51</sup> or reversible addition–fragmentation chain transfer (RAFT).<sup>11,32,49,62</sup> In contrast, the controlled polymerization of *N*-vinylimidazolium-type ILMs is less documented, owing to the high reactivity of related growing species.

These past years, substantial progress has been made in this direction, by implementing controlled radical polymerization

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techniques such as RAFT<sup>32,49,53,54,63–66</sup> and OMRP<sup>67–74</sup> to *N*-vinyl-3-alkylimidazolium-type ILMs in organic media. Besides controlling the homopolymerization of monomers with a bromine counteranion,<sup>32</sup> RAFT also enabled the preparation of related block copolymers (BCP's), e.g., poly(*N*-isopropylacrylamide)-*b*-poly(*N*-vinyl-3-ethylimidazolium bromide),<sup>32,35</sup> in DMF or methanol. Di- and triblock copolymers based on *N*-vinyl-3-alkylimidazolium and vinyl acetate units were accessible by OMRP in DMF/methanol mixture, using Co(acac)<sub>2</sub> as a controlling agent.<sup>9,75</sup> We have also recently reported the controlled OMRP of *N*-vinyl-3-alkylimidazolium ILMs in an aqueous environment and under mild conditions.<sup>76</sup>

In the past decade, design and self-assembling properties of BCP's constituted of a PIL block have been the topic of thorough studies. Such PIL BCPs combine the specific properties of PILs, such as responsiveness to ion exchange, ionic conductivity, and/or gas transport, with the self-assembling properties of BCP's, providing access to a range of nanostructured morphologies in solution and at the solid state.<sup>20,77–80</sup> In bulk, for instance, ionic and nonionic blocks segregate in highly ordered nanodomains due to the strong incompatibility of the two blocks. Interestingly, confinement of blocks within ordered nanodomains allows increasing the ionic conductivity by 1–2 orders of magnitude relative to statistical copolymer homologues or homopolymers.<sup>20,42,81,82</sup> The possibility to form all PILs block copolymers is even more attractive because nanodomains formed by their self-assembly in the bulk or in solution will be characterized by the responsiveness of the corresponding PIL. Novel smart materials would therefore be made available with potential applications as nanoreactors for catalysis or as ionic conductive materials for electrochemical devices, to cite only a few. To the best of our knowledge, however, there is no report on the preparation of all poly(*N*-vinyl-3-alkylimidazolium)-based BCP's, i.e., BCP's that would consist of different PIL blocks with different counterions and/or different alkyl substituents.

Such all PIL BCP's cannot be accessed by quaternization of a neutral precursor using different alkyl halides because this would unavoidably lead to a random copolymer rather than a BCP. The other option thus relies on a sequential and direct controlled polymerization method involving two different ILMs.

In this contribution, we first describe the conditions best suited for controlling the OMRP of hydrophobic *N*-vinylimidazolium ILMs bearing Tf<sub>2</sub>N<sup>−</sup> counteranions. The as-formed hydrophobic poly(*N*-vinylimidazolium) chains are then employed as macroinitiators for the OMRP of a hydrophilic vinylimidazolium ILM, leading to unprecedented AB-type PIL-*b*-PIL diblock copolymers. The two vinylimidazolium-based ILMs differ here by the nature of both the alkyl chain and the counteranion (Tf<sub>2</sub>N<sup>−</sup> and Br<sup>−</sup> for the hydrophobic and hydrophilic one, respectively). Block copolymerization can be conducted not only in homogeneous methanolic solution but also in a water/ethyl acetate biphasic mixture. Interestingly, the opposite strategy, i.e., chain extension from a hydrophilic poly(vinylimidazolium bromide) by a hydrophobic vinylimidazolium ILM, is also achievable in the same biphasic mixture. We show however that anion exchange, from one PIL block to another, cannot be avoided during growth of the second block. In other words, only the cationic backbone is of block type in these BCP's, while mobile anions are randomly distributed. Finally, radical coupling of as-obtained PIL-*b*-PIL diblock copolymers can be triggered by

addition of isoprene, forming symmetrical all PIL-based ABA-type triblock copolymers, in a one-pot process.

## EXPERIMENTAL SECTION

**Materials.** 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO) (98%, Aldrich), lithium bis(trifluoromethanesulfonyl)imide (LiTf<sub>2</sub>N) (99%, ABCR), and ethanol (96%, Aldrich) were used as received. Ethyl acetate (EtOAc) and methanol were dried over molecular sieves and degassed by bubbling argon for 20 min. Deionized water and acetone were degassed by bubbling argon for 20 min. Membrane Spectra/Por (cutoff: 1000 Da) was used for dialysis. *N*-Vinyl-3-ethylimidazolium bromide (VETImBr) was synthesized following the reported procedure. *N*-Vinyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide (VETImTf<sub>2</sub>N) and *N*-vinyl-3-buthylimidazolium bis(trifluoromethylsulfonyl)imide were prepared via anion-exchange following the procedure described in the literature.<sup>37</sup> The synthesis as well as the complete characterization of the alkyl-cobalt(III) adduct (R-Co(acac)<sub>2</sub>) is prepared according to our previously described procedure.<sup>83</sup> The alkyl-cobalt(III) adduct was stored as a CH<sub>2</sub>Cl<sub>2</sub> solution at −20 °C under argon.

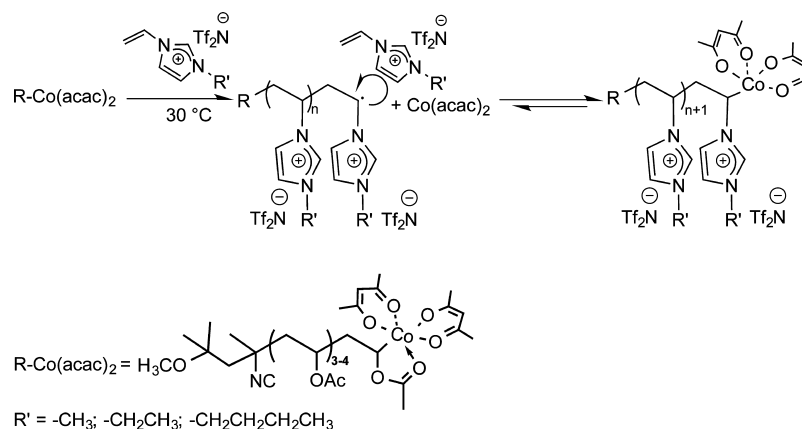
**Characterization.** <sup>1</sup>H NMR spectra of the polymers were recorded with a Bruker spectrometer (250, 400, or 500 MHz) at 298 K in acetone-*d*<sub>6</sub>, D<sub>2</sub>O, and DMSO-*d*<sub>6</sub>.

Macromolecular parameters of PILs (*M*<sub>n</sub>, *M*<sub>w</sub>/*M*<sub>n</sub>) were determined by size exclusion chromatography (SEC), with a SFD S5200 autosampler liquid chromatograph equipped with a SFD refractometer index detector 2000, carried out in tetrahydrofuran (THF) containing 10 mM LiTf<sub>2</sub>N (flow rate: 1 mL min<sup>−1</sup>) at 35 °C according to a previously reported procedure.<sup>37</sup> A PSS SDV analytical linear S 5 μm column (molar mass range: 100–150 000 Da), protected by a PL gel 5 μm guard column, was calibrated with PS standards. Samples of polymers bearing Tf<sub>2</sub>N<sup>−</sup> (~10–15 mg), dried under reduced pressure overnight at 50 °C, were dissolved with 1.5 mL of THF containing LiTf<sub>2</sub>N (10 mM) and filtered two times with nylon membrane filter (size 0.45 and 0.20 μm, respectively). For samples containing PVEtImBr, bromine counteranion was exchanged for bis(trifluoromethanesulfonyl)imide prior to SEC analysis according to the following procedure. A volume of 2 mL of deionized water was added in each sample (about 15 mg), and the solutions were stirred for 5 min. After adding an excess of LiTf<sub>2</sub>N (~50 mg), the sample was left under stirring (500 rpm) overnight. Water portion was removed with the pipet, and the precipitated polymer was washed three times with water in order to remove the residual LiBr. Samples with Tf<sub>2</sub>N<sup>−</sup> counteranions were dried under reduced pressure at 50 °C overnight, solubilized in THF containing LiTf<sub>2</sub>N (10 mM), and filtered two times with nylon membrane filter (size 0.45 and 0.20 μm, respectively).

Elemental analyses (Br, S) were realized at CNRS, Institut des Sciences Analytiques, Villeurbanne, France, and at Mikroanalytisches Labor Pascher, Remagen, Germany, using classical potentiometric and titrimetric methods, respectively. Values are expressed in wt %.

**Typical Procedure for the Homopolymerization of *N*-Vinyl-3-ethylimidazolium Bis(trifluoromethylsulfonyl)imide (VETImTf<sub>2</sub>N) in Ethyl Acetate ([VETImTf<sub>2</sub>N]/[R-Co(acac)<sub>2</sub>] = 50).** VETImTf<sub>2</sub>N (3.0 g, 7.5 × 10<sup>−3</sup> mol) is introduced in a Schlenk tube, dried overnight under vacuum, and degassed by three vacuum/argon cycles. Dried and degassed ethyl acetate (4.5 mL) is then added under argon to solubilize the monomer. A R-Co(acac)<sub>2</sub> solution in CH<sub>2</sub>Cl<sub>2</sub> (1 mL, 0.154 M, 1.54 × 10<sup>−4</sup> mol) is introduced under argon into a second Schlenk tube, and the solvent CH<sub>2</sub>Cl<sub>2</sub> is evaporated under reduced pressure. The monomer VETImTf<sub>2</sub>N in ethyl acetate is then transferred under argon by cannula into the Schlenk containing R-Co(acac)<sub>2</sub>, under stirring. The polymerization then occurs at 30 °C under stirring for 24 h. Samples are regularly withdrawn to evaluate the molecular parameters of the polymer (*M*<sub>n,SEC</sub>, *M*<sub>w</sub>/*M*<sub>n</sub>) by SEC and the monomer conversion by <sup>1</sup>H NMR. Results are summarized in Table 2, entry 1. After 24 h, a solution of TEMPO (4.6 × 10<sup>−4</sup> mol) in degassed ethyl acetate is added to quench the reaction.

The polymer is purified from unreacted monomer by the following procedure. The reaction medium in 10 mL of EtOAc is added

Scheme 1. OMRP of *N*-Vinyl-3-alkylimidazolium Bis((trifluoromethyl)sulfonyl)imide (VR'ImTf<sub>2</sub>N) Using R-Co(acac)<sub>2</sub>

dropwise into 50 mL of EtOH under stirring to precipitate the polymer and remove Co(acac)<sub>2</sub> and excess of TEMPO. The polymer is then dried under reduced pressure at 40 °C. This procedure is repeated two times in order to remove completely the residual monomer from the polymeric portion.

The same experimental procedure is used for the [VETImTf<sub>2</sub>N]/[R-Co(acac)<sub>2</sub>] ratios of 100 and 300, except that the volume of R-Co(acac)<sub>2</sub> added to initiate the polymerization is adapted to fit these ratios. Results are summarized in Table 2, entries 2 and 3, for the [VETImTf<sub>2</sub>N]/[R-Co(acac)<sub>2</sub>] ratios of 100 and 300, respectively.

**Synthesis of PVETImBr-Co(acac)<sub>2</sub> and Chain Extension by VMelImTf<sub>2</sub>N in Methanol.** VETImBr (1.53 g, 7.5 × 10<sup>-3</sup> mol) is introduced in a Schlenk tube, dried overnight under vacuum, and degassed under argon (three vacuum/argon cycles). Dried and degassed methanol (4.5 mL) is introduced into the tube under argon to solubilize the monomer. A solution of R-Co(acac)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> (1.4 mL, 0.11 M, 1.54 × 10<sup>-4</sup> mol) is introduced under argon into a second Schlenk tube, and CH<sub>2</sub>Cl<sub>2</sub> is evaporated under vacuum. The solution of monomer VETImBr in methanol is added into the Schlenk tube containing the R-Co(acac)<sub>2</sub> under stirring. The polymerization occurs at 30 °C for 7.5 h. A sample is withdrawn to determine the monomer conversion by <sup>1</sup>H NMR (91% conversion) and the molecular characteristics of the polymer by SEC after anion exchange with LiTf<sub>2</sub>N. The solution of the second monomer in methanol (3 g of VMelImTf<sub>2</sub>N in 4.5 mL of methanol) is then added under argon to the solution of the first PVETImBr-Co(acac)<sub>2</sub> block, and the reaction proceeds for 14 h at 30 °C. A sample is withdrawn after 1 h of reaction to evaluate molecular parameters by SEC (after anion exchange with LiTf<sub>2</sub>N) and the conversion by <sup>1</sup>H NMR in DMSO-*d*<sub>6</sub>. After 14 h, a solution of TEMPO in methanol (4.6 × 10<sup>-4</sup> mol) is added to quench the reaction in order to avoid coupling reaction. The diblock copolymer is then purified by dialysis in methanol. The results of the block copolymerization in methanol are shown in Figure 6.

**Synthesis of PVMelImTf<sub>2</sub>N-Co(acac)<sub>2</sub> in Ethyl Acetate, and Chain Extension by VETImBr in Ethyl Acetate/Water (1/1) Mixture.** VMelImTf<sub>2</sub>N (3.0 g, 7.5 × 10<sup>-3</sup> mol) is introduced in a Schlenk tube, dried overnight under vacuum, and degassed by three vacuum/argon cycles. Degassed EtOAc (4.5 mL) is introduced into the tube under argon to solubilize the monomer. A solution of R-Co(acac)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> (1.4 mL, 0.11 M, 1.54 × 10<sup>-4</sup> mol) is introduced under argon into a second Schlenk tube, and CH<sub>2</sub>Cl<sub>2</sub> is evaporated under vacuum. The solution of monomer VMelImTf<sub>2</sub>N in ethyl acetate is added into the Schlenk tube containing R-Co(acac)<sub>2</sub> under stirring. The polymerization occurs at 30 °C for 8 h. A sample is withdrawn to determine the monomer conversion by <sup>1</sup>H NMR (91% conversion) and the molecular characteristics of the polymer by SEC. Solution of the second monomer VETImBr in water (1.5 g VETImBr in 4.5 mL of solvent) is then added under argon to the organic solution of PVMelImTf<sub>2</sub>N-Co(acac)<sub>2</sub>, and the reaction proceeds for 16 h at 30 °C under stirring at 400 rpm. A solution of TEMPO in EtOAc (4.6 ×

10<sup>-4</sup> mol) is then added to quench the reaction in order to avoid coupling reaction. Results are illustrated in Figure 8.

**Synthesis of PVETImBr-Co(acac)<sub>2</sub> in Water and Chain Extension by VMelImTf<sub>2</sub>N in Ethyl Acetate/Water (1/1) Mixture Followed by Cobalt-Mediated Radical Coupling (CMRC).** VETImBr (1.53 g, 7.5 × 10<sup>-3</sup> mol) is introduced in a Schlenk tube, dried overnight under vacuum, and degassed by three vacuum/argon cycles. Degassed deionized water (4.5 mL) is added to the monomer under argon, and the mixture is stirred (500 rpm) until the monomer is completely solubilized. A solution of R-Co(acac)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> (1.4 mL, 0.11 M, 1.54 × 10<sup>-4</sup> mol) is introduced under argon into a second Schlenk tube, and CH<sub>2</sub>Cl<sub>2</sub> is evaporated under vacuum. Degassed acetone (1 mL) is then added to solubilize R-Co(acac)<sub>2</sub> and the solution of the monomer transferred by cannula into the Schlenk tube containing the solution of R-Co(acac)<sub>2</sub> under stirring. The polymerization occurs at 30 °C under stirring for 3 h. Samples are withdrawn to evaluate the monomer conversion by <sup>1</sup>H NMR in DMSO-*d*<sub>6</sub> (94% conversion) and the molar mass of the polymer by SEC in THF after anion exchange (Br<sup>-</sup>/Tf<sub>2</sub>N<sup>-</sup>), following the procedure previously described. The organic solution of the second monomer (3 g of VMelImTf<sub>2</sub>N in 4.5 mL of EtOAc) is then added under argon to the solution of PVETImBr-Co(acac)<sub>2</sub>, and the reaction proceeds for 16 h at 30 °C. After 2.5 h the solution is divided in two portions: in the first one is added a solution of TEMPO (4.6 × 10<sup>-4</sup> mol) in dried and degassed EtOAc to quench the reaction and analyze the copolymer; in the second one, 0.3 mL of isoprene is added, and the coupling reaction occurs at 30 °C overnight. The mixture is analyzed by <sup>1</sup>H NMR in DMSO-*d*<sub>6</sub> to check that residual VMelImTf<sub>2</sub>N is not polymerized during the coupling reaction. Results are summarized in Figure 12.

Synthesis of PVBuImBr-Co(acac)<sub>2</sub> in water, and chain extension by VMelImTf<sub>2</sub>N in ethyl acetate/water (1/1) mixture, are described in the Supporting Information.

## RESULTS AND DISCUSSION

To the best of our knowledge, the direct controlled polymerization of *N*-vinyl-3-alkylimidazolium monomers with the Tf<sub>2</sub>N<sup>-</sup> counteranion has never been reported. In contrast, styrenic-type ILMs featuring this anion have been polymerized by ATRP.<sup>37</sup> In a first step, ILMs with different alkyl groups (VRImTf<sub>2</sub>N; R = Et, Me, Bu) were thus tested under OMRP conditions, before studying the block copolymerization. As expected, ILMs exhibit marked differences of solubility, according to the counteranion. For instance, the Tf<sub>2</sub>N<sup>-</sup>-containing *N*-vinyl-3-ethylimidazolium monomer (VETImTf<sub>2</sub>N) is soluble in ethyl acetate (organophilic) while its Br-containing homologue (VETImBr) is not. Opposite solubility is noted in water for the two monomers, VETImBr being highly soluble (hydrophilic) while VETImTf<sub>2</sub>N is insoluble.



**OMRP of *N*-Vinyl-3-alkylimidazolium Bis((trifluoromethyl)sulfonyl)imide (VRImTf<sub>2</sub>N; R = Ethyl, Methyl, or Butyl).** The preformed alkyl–cobalt(III) adduct (R-Co(acac)<sub>2</sub>; Scheme 1),<sup>83</sup> which has proven efficient for controlling the polymerization of unconjugated vinyl monomers, such as vinyl esters (vinyl acetate, vinyl levulinate),<sup>68,83–86</sup> vinylamides (*N*-vinylpyrrolidone, *N*-vinylcaprolactame, *N*-vinylacetamide),<sup>87–90</sup> ethylene/vinyl acetate,<sup>91</sup> and *N*-vinyl-3-ethylimidazolium bromide,<sup>9</sup> was here employed as controlling agent for the OMRP of VETImTf<sub>2</sub>N (Scheme 1).

Unlike VETImBr that is a solid compound, VETImTf<sub>2</sub>N is a viscous liquid at 30 °C. Its homopolymerization was thus carried out first in concentrated conditions ([VETImTf<sub>2</sub>N] = 7.5 M) at 30 °C, by adding a dichloromethane solution of R-Co(acac)<sub>2</sub> that served as both initiator and controlling agent. Under these experimental conditions, the polymerization was fast with a high monomer conversion (~70%) achieved after 1 h (Table 1). A burst effect at the early stages of the

**Table 1. Polymerization of *N*-Vinyl-3-ethylimidazolium Bis((trifluoromethyl)sulfonyl)imide (VETImTf<sub>2</sub>N) Initiated by R-Co(acac)<sub>2</sub> at 30 °C in Dichloromethane ([VETImTf<sub>2</sub>N] = 7.5 M)<sup>a</sup>**

time (h)	conv <sup>b</sup> (%)	<i>M</i> <sub>nSEC</sub> <sup>c</sup> (g/mol)	<i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub> <sup>d</sup>
0.25	19	9400	1.08
0.5	45	13300	1.21
0.75	54	11500	1.21
1	70	12200	1.20
1.25	72	13000	1.21
2	82	15500	1.20
24	100	18900	1.21

<sup>a</sup>Conditions: [VETImTf<sub>2</sub>N]/[R-Co(acac)<sub>2</sub>] = 50, [VETImTf<sub>2</sub>N] = 7.5 M, 30 °C. <sup>b</sup>VETImTf<sub>2</sub>N conversion measured by <sup>1</sup>H NMR in acetone-*d*<sub>6</sub>. <sup>c</sup>*M*<sub>n</sub> determined by SEC analysis in THF (containing 10 mM LiTf<sub>2</sub>N), using PS calibration. <sup>d</sup>Dispersity determined by SEC in THF (containing 10 mM LiTf<sub>2</sub>N).

polymerization was observed with a jump in the molar mass (*M*<sub>n</sub>) of the polymer (Figure 1a) at low conversion. Molar masses then increased with the monomer conversion but not in a linear fashion. The dispersity remained however low (*M*<sub>w</sub>/*M*<sub>n</sub> ~ 1.2) until complete conversion. As evidenced in Figure 1b, time dependence of ln([M]<sub>0</sub>/[M]) evolves linearly, in agreement with a constant concentration of active species during the entire polymerization process. Observation of the burst effect at the early stage of the polymerization and nonlinear increase of *M*<sub>n</sub> vs conversion are indicative of a process that is not perfectly controlled.

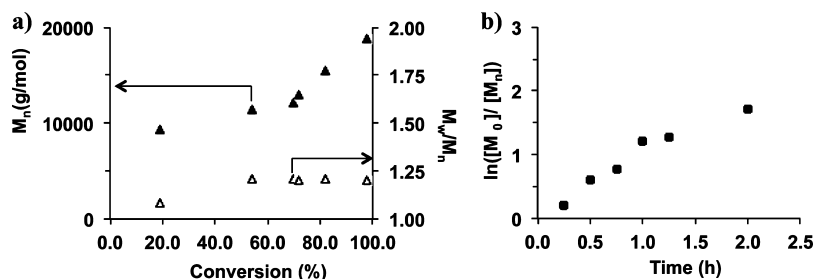
Polymerization of VETImTf<sub>2</sub>N was then carried out in more diluted conditions ([VETImTf<sub>2</sub>N] = 1.66 M), using ethyl acetate as solvent, keeping the other experimental parameters constant (see Experimental Section). Ethyl acetate was selected as a good solvent of the monomer and the polymer (at least in the polymer molar mass range targeted in this paper). As expected, when diluting the reaction medium, the polymerization was slower compared to the previous experiment carried out at higher concentration. Reaction reached 95% conversion after 7 h of reaction at 30 °C (Table 2, entry 1) and molar masses increased linearly with the conversion while the dispersity remained low all along the polymerization process (*M*<sub>w</sub>/*M*<sub>n</sub> ≤ 1.1) (Table 2 and Figure 2a). The discrepancy

**Table 2. Polymerization of *N*-Vinyl-3-ethylimidazolium Bis((trifluoromethyl)sulfonyl)imide (VETImTf<sub>2</sub>N) Initiated by R-Co(acac)<sub>2</sub> in Ethyl Acetate (1.66 M) at 30 °C Using Different [VETImTf<sub>2</sub>N]/[R-Co(acac)<sub>2</sub>] Ratios<sup>a</sup>**

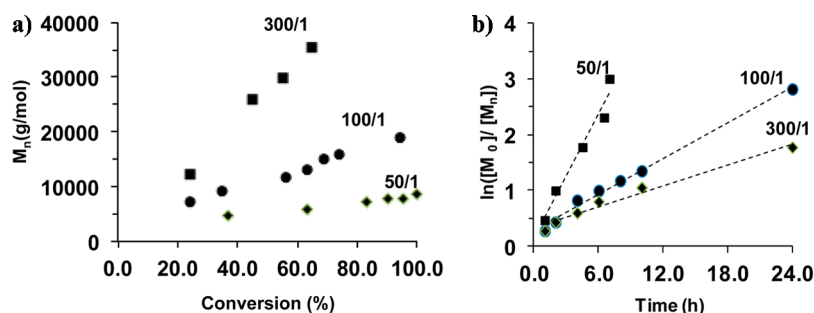
entry	[VETImTf <sub>2</sub> N]/[R-Co(acac) <sub>2</sub> ]	time (h)	conv <sup>b</sup> (%)	<i>M</i> <sub>nSEC</sub> <sup>c</sup> (g/mol)	<i>M</i> <sub>n,th</sub> <sup>d</sup> (g/mol)	<i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub> <sup>e</sup>
1	50/1	1	37	4800	7400	1.08
		2	63	5700	12700	1.09
		4.5	83	7200	16700	1.08
		6.5	90	7700	18100	1.09
		7	95	7900	19100	1.08
		24	100	8500	20100	1.1
		24 <sup>f</sup>	94	19000	37800	1.09
2	100/1	1	24	7200	9600	1.13
		4	56	11700	22500	1.08
		6	63	13200	25300	1.07
		8	69	15000	27700	1.08
		10	74	15900	29700	1.08
		24 <sup>f</sup>	94	19000	37800	1.09
		24 <sup>f</sup>	83	36900	100100	1.20
3	300/1	1	24	12200	28900	1.09
		2	35	11200	42200	1.05
		4	45	26300	54300	1.12
		6	55	29800	66300	1.13
		10	65	35400	78400	1.12
		24 <sup>f</sup>	83	36900	100100	1.20
		24 <sup>f</sup>	83	36900	100100	1.20

<sup>a</sup>Conditions: [VETImTf<sub>2</sub>N]/[R-Co(acac)<sub>2</sub>] = 50 (entry 1), 100 (entry 2), and 300 (entry 3); EtOAc/VETImTf<sub>2</sub>N (v/w) = 1.5/1; 30 °C.

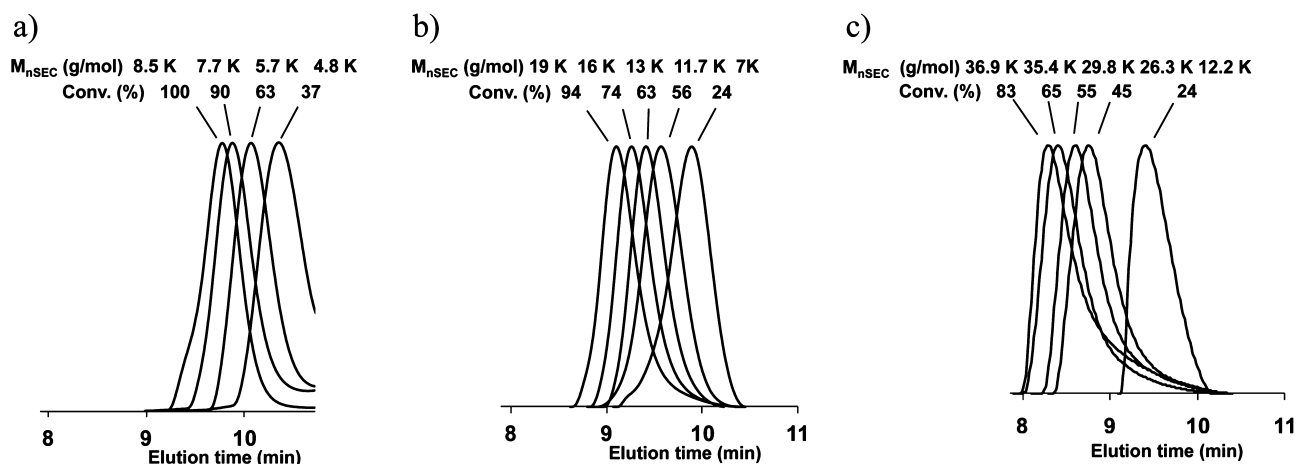
<sup>b</sup>VETImTf<sub>2</sub>N conversion measured by <sup>1</sup>H NMR in acetone-*d*<sub>6</sub>. <sup>c</sup>*M*<sub>n</sub> determined by SEC analysis in THF (containing 10 mM LiTf<sub>2</sub>N), using PS calibration. <sup>d</sup>Theoretical molar mass determined by the equation *M*<sub>n,th</sub> = ([VETImTf<sub>2</sub>N]/[R-Co(acac)<sub>2</sub>]) × Mr(VETImTf<sub>2</sub>N), where Mr(VETImTf<sub>2</sub>N) states for the molar mass of the monomer. <sup>e</sup>Dispersity determined by SEC in THF (containing 10 mM LiTf<sub>2</sub>N). <sup>f</sup>*M*<sub>n</sub> referred to the purified compound.



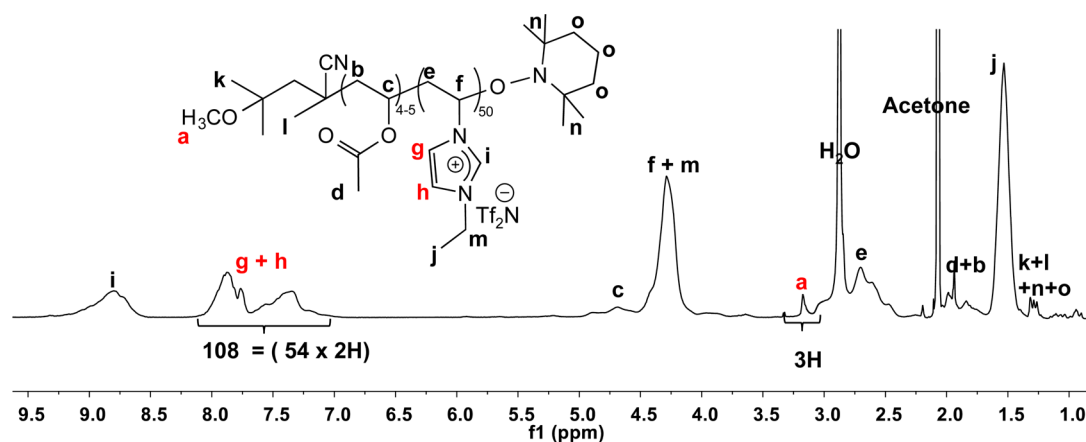
**Figure 1.** (a) Dependence of the number-average molar mass with the monomer conversion and (b) time dependence of ln([M]<sub>0</sub>/[M]) for OMRP of VETImTf<sub>2</sub>N. Conditions: [VETImTf<sub>2</sub>N]/[R-Co(acac)<sub>2</sub>] = 50, [VETImTf<sub>2</sub>N] = 7.5 M, 30 °C.



**Figure 2.** (a) Number-average molar mass evolution with the monomer conversion and (b) time dependence of  $\ln([M]_0/[M])$  for the VEtImTf<sub>2</sub>N polymerization initiated by R-Co(acac)<sub>2</sub> in ethyl acetate at 30 °C using different [VEtImTf<sub>2</sub>N]/[R-Co(acac)<sub>2</sub>] ratios. Conditions: see Table 2.



**Figure 3.** SEC traces for the VEtImTf<sub>2</sub>N polymerization initiated by R-Co(acac)<sub>2</sub> in ethyl acetate at 30 °C: (a) [VEtImTf<sub>2</sub>N]/[R-Co(acac)<sub>2</sub>] = 50/1 (Table 2, entry 1); (b) [VEtImTf<sub>2</sub>N]/[R-Co(acac)<sub>2</sub>] = 100/1 (Table 2, entry 2); (c) [VEtImTf<sub>2</sub>N]/[R-Co(acac)<sub>2</sub>] = 300/1 (Table 2, entry 3).

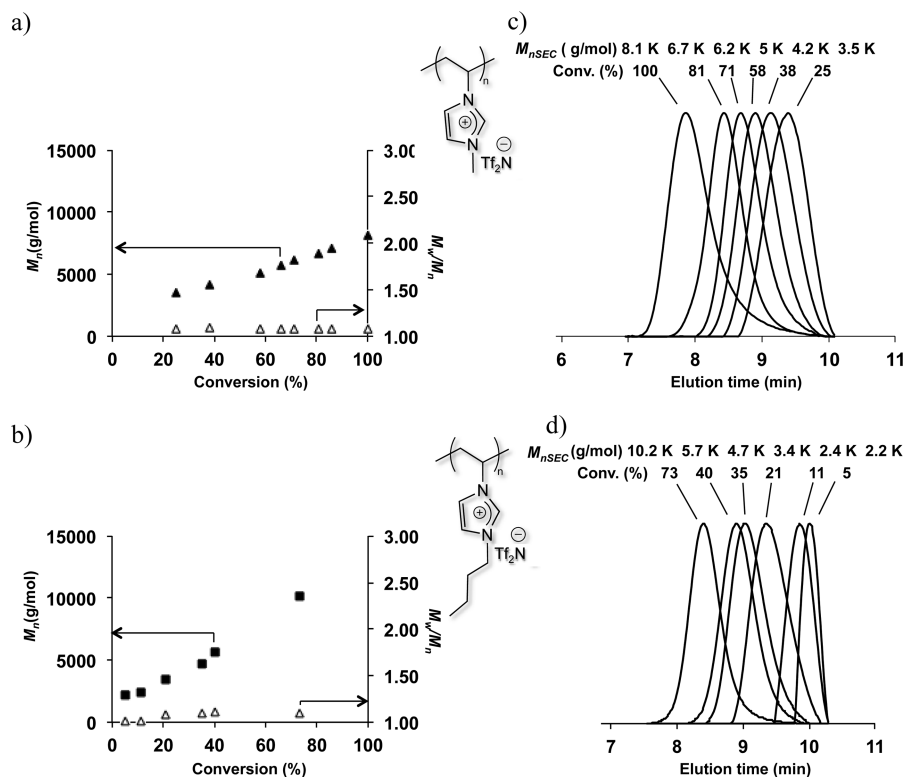


**Figure 4.** 500 MHz <sup>1</sup>H NMR spectrum in acetone-*d*<sub>6</sub> of the purified P(VEtImTf<sub>2</sub>N) prepared from R-Co(acac)<sub>2</sub> in ethyl acetate at 30 °C after 24 h (Table 2, entry 1) and deactivated by TEMPO.

between theoretical and experimental molar masses was likely the result of the difference in hydrodynamic volume between PVEtImTf<sub>2</sub>N and the linear polystyrene (PS) standards used for SEC calibration. Time evolution of  $\ln([M]_0/[M])$  is also linear, witnessing the steady concentration of radicals during polymerization (Figure 2b).

SEC traces are symmetrical and shift toward the high molar mass side, as reaction proceeds (Figure 3a); hence, ethyl acetate proved a compatible solvent for this polymerization and dilution allowed gaining in control of the reaction.

Figure 4 shows the <sup>1</sup>H NMR spectrum of a purified PVEtImTf<sub>2</sub>N sample collected after 24 h of reaction and deactivated by the addition of TEMPO. The absolute molar mass of the polymer can be determined by comparing the integral of protons a at 3.15 ppm, corresponding to the methoxy group of the initiating fragment at the  $\alpha$ -chain end, with that of protons g + h centered at 7.6 ppm and that is characteristic of the imidazolium ring. The experimental value ( $M_{n,abs} = 21\,500$  g/mol) is very close to the theoretical one ( $M_{th} = 20\,000$  g/mol), confirming that each R-Co(acac)<sub>2</sub> initiates one polymer chain that grows all along the polymerization



**Figure 5.** Number-average molar mass and dispersity evolutions with the monomer conversion for (a) VMelTf<sub>2</sub>N and (b) VBulTf<sub>2</sub>N polymerizations initiated by R-Co(acac)<sub>2</sub> in ethyl acetate at 30 °C and evolution of SEC traces of (c) PVMelTf<sub>2</sub>N and (d) PVBulTf<sub>2</sub>N. Conditions: [VMe(Bu)ImTf<sub>2</sub>N]/[R-Co(acac)<sub>2</sub>] = 50/1; EtOAc/VMe(Bu)ImTf<sub>2</sub>N (v/w) = 1.5/1.

process. It has to be mentioned that is also possible to calculate the molar mass of the polymer by taking into account protons (j) instead of protons (g + h). The same molar mass is obtained within the <sup>1</sup>H NMR accuracy (DP = 56 when protons (j) are taken into account, compared to 54 when considering protons (g + h)). We preferred to consider protons (g + h) instead of (j) because (g + h) appear for all poly-(vinylimidazolium)s with no overlapping with protons of the alkyl chains, facilitating the integrations.

When the polymerization of VETImTf<sub>2</sub>N was carried out using different ratios ([VETImTf<sub>2</sub>N]/[R-Co(acac)<sub>2</sub>] = 50, 100, and 300), the molar mass of the polymer could be adjusted accordingly (Table 2 and Figure 2). The three polymerizations appeared to be controlled, as assessed by the linear increase of the molar mass with the conversion and the low dispersity of the polymers (Figure 2a). Molar masses as high as 10<sup>5</sup> g/mol could be achieved by using a [VETImTf<sub>2</sub>N]/[R-Co(acac)<sub>2</sub>] ratio of 300, and the dispersity remained low. SEC traces are shifted toward the high molar mass side with the progress of the reaction (Figure 3). However, the polymerization slowed down for higher ratios as the result of a lower amount of R-Co(acac)<sub>2</sub> in the system and therefore of growing polymer chains (Figure 2b). From all these experiments, it can be concluded that OMRP of VETImTf<sub>2</sub>N is controlled in ethyl acetate at 30 °C.

Substituting a methyl or a butyl group for an ethyl group (VMelTf<sub>2</sub>N or VBulTf<sub>2</sub>N instead of VETImTf<sub>2</sub>N) did not affect the control of the polymerization in ethyl acetate. Molar masses indeed increased linearly with the monomer conversion, while the dispersity remained below 1.12 (Figure 5a,b and Table 3). SEC overlay clearly shows the growth of the chains

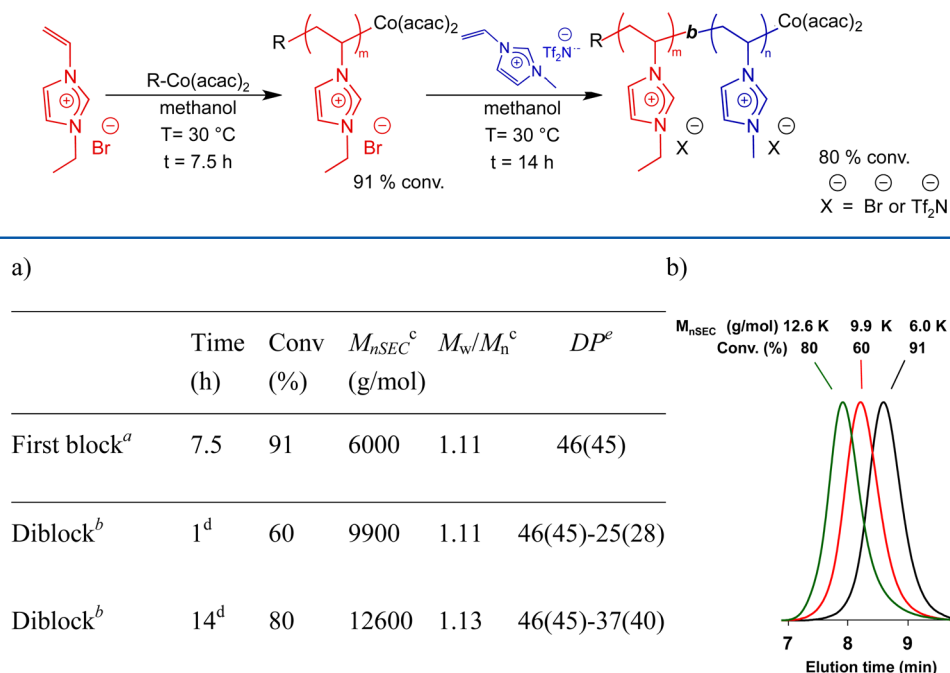
during the polymerization process (Figure 5c,d). OMRP of VBulTf<sub>2</sub>N was however slower, presumably for steric reasons.

**Synthesis of PIL-*b*-PIL Diblock Copolymers by Sequential OMRP in Methanol.** The successful OMRP of *N*-vinyl-3-alkylimidazolium ILMs bearing Br<sup>−</sup> or Tf<sub>2</sub>N<sup>−</sup>

**Table 3.** Homopolymerization of *N*-Vinyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide (VMelTf<sub>2</sub>N) and *N*-Vinyl-3-butylimidazolium Bis(trifluoromethylsulfonyl)imide (VBulTf<sub>2</sub>N) Initiated by R-Co(acac)<sub>2</sub> at 30 °C in Ethyl Acetate<sup>a</sup>

monomer	time (h)	conv <sup>b</sup> (%)	$M_{nSEC}$ <sup>c</sup> (g/mol)	$M_w/M_n$ <sup>d</sup>
VMelTf <sub>2</sub> N	0.75	25	3500	1.08
	1.50	38	4200	1.09
	2.50	58	5100	1.08
	3.50	66	5700	1.08
	4.50	71	6200	1.08
	6.50	81	6700	1.08
	8.50	86	7100	1.08
	24	100	8100	1.08
VBulTf <sub>2</sub> N	1	5	2200	1.01
	2	11	2400	1.02
	4	21	3400	1.08
	6	35	4700	1.10
	8	40	5700	1.11
	24	73	10200	1.10

<sup>a</sup>Conditions: [VMe(Bu)ImTf<sub>2</sub>N]/[R-Co(acac)<sub>2</sub>] = 50; EtOAc/VMe(Bu)ImTf<sub>2</sub>N (v/w) = 1.5/1; 30 °C. <sup>b</sup>VMe(Bu)ImTf<sub>2</sub>N conversion measured by <sup>1</sup>H NMR in acetone-*d*<sub>6</sub>. <sup>c</sup> $M_n$  determined by SEC analysis in THF (containing 10 mM LiTf<sub>2</sub>N) using PS calibration. <sup>d</sup>Dispersity determined by SEC in THF (containing 10 mM LiTf<sub>2</sub>N).

Scheme 2. OMRP of VETImBr Followed by Chain Extension with VMeImTf<sub>2</sub>N in Methanol

**Figure 6.** (a) Block copolymerization of *N*-vinyl-3-ethylimidazolium bromide (VETImBr) and *N*-vinyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (VMeImTf<sub>2</sub>N) in methanol and (b) SEC chromatograms of PVETImBr-Co(acac)<sub>2</sub> first block and PVETImBr-*b*-PVMeImTf<sub>2</sub>N diblock copolymer. <sup>a</sup>Conditions: methanol/VETImBr = 3/1 (v/w), [VETImBr]/[R-Co(acac)<sub>2</sub>] = 50, 30 °C. <sup>1</sup>H NMR in D<sub>2</sub>O. <sup>b</sup>Conditions: reaction medium from first-block after 1 h of reaction to which is added VMeImTf<sub>2</sub>N; methanol/VMeImTf<sub>2</sub>N = 1.5/1 (v/w); [VMeImTf<sub>2</sub>N]/[PVETImBr-Co(acac)<sub>2</sub>] = 50/1; 30 °C. <sup>1</sup>H NMR in DMSO-*d*<sub>6</sub>. <sup>c</sup> $M_n$  determined (after anion exchange with LiTf<sub>2</sub>N). <sup>d</sup>Polymerization time after the addition of the second monomer (VMeImTf<sub>2</sub>N). <sup>e</sup>Degree of polymerization of each block determined by <sup>1</sup>H NMR analysis; in parentheses: the theoretical DP.

counteranions prompted us to investigate the block copolymerization of monomers bearing not only different alkyl chain (methyl or ethyl) but also different counteranions (Br<sup>−</sup> or Tf<sub>2</sub>N<sup>−</sup>). At first, methanol was selected as a common solvent of both monomers (and related polymers). PVETImBr-Co(acac)<sub>2</sub> was thus prepared as first block by OMRP of *N*-vinyl-3-ethylimidazolium bromide (VETImBr), in methanol at 30 °C (Scheme 2), until high monomer conversion (91%; Figure 6). <sup>1</sup>H NMR analysis of this macroinitiator allowed the degree of polymerization to be determined (DP = 45) by comparing the integral of the methoxy group in the  $\alpha$ -position, at 3.15 ppm, with that of protons of the imidazolium ring at 7.6 ppm as previously described (Figure 7a).

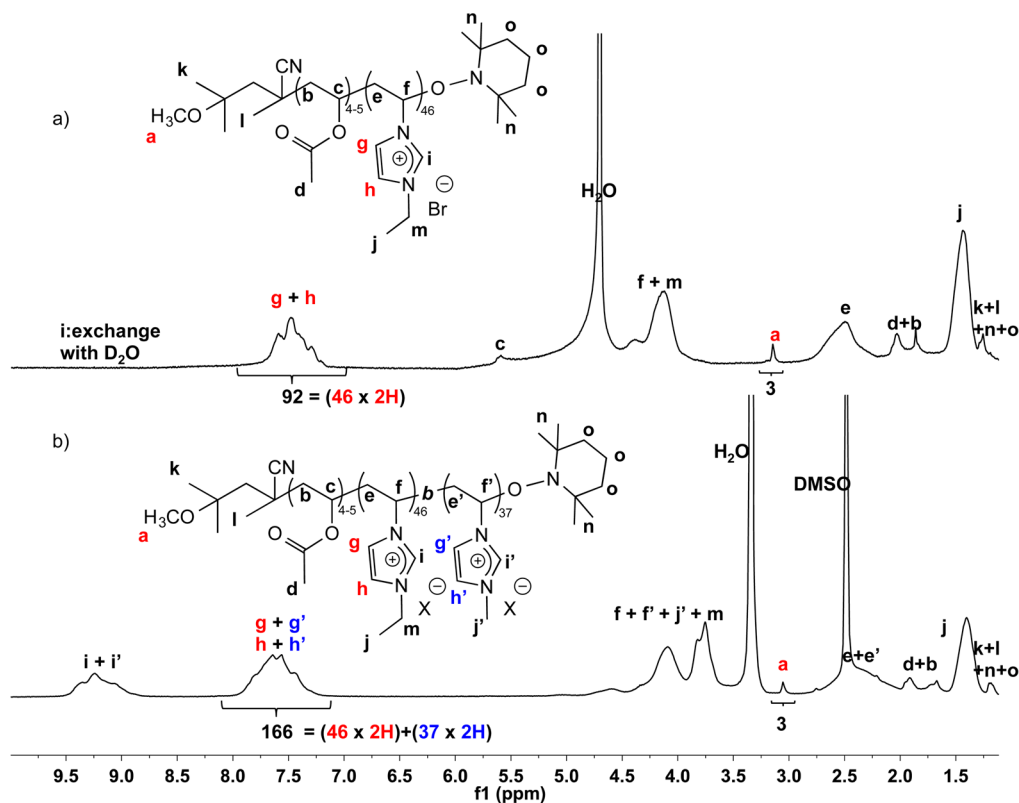
*N*-Vinyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (VMeImTf<sub>2</sub>N) was then added onto the solution of the PVETImBr-Co(acac)<sub>2</sub> macroinitiator, chain extension occurring at 30 °C. Molar mass was increased, from  $M_{n,SEC}$  = 6000 g/mol to 9900 and 12 600 g/mol, after 60 and 80% monomer conversion, respectively, SEC traces remaining monomodal and narrow (Figure 6b). These observations are consistent with the formation of a PVETImBr-*b*-PVMeTf<sub>2</sub>N diblock copolymer. By doing so, however, in particular because methanol is a common solvent of both blocks, fast anion exchange might have occurred, forming a block copolymer with randomly distributed Br<sup>−</sup> and Tf<sub>2</sub>N<sup>−</sup> counteranions. However, <sup>1</sup>H NMR analysis in DMSO-*d*<sub>6</sub> of purified copolymers did not permit to probe this counteranion exchange. In contrast, the overall composition of the copolymers collected after 60 and 80% conversion could be calculated, by comparing the signal of the methoxy group at 3.15 ppm with that of aromatic protons from the imidazolium

ring, of the first and second block, at 7.6 ppm. After 60% monomer conversion, DPs of the first and second blocks were equal to 46 and 25, respectively. At 80% conversion, the DP of the second block was found equal to 37. These values are close to those expected (Figure 6a). Chain extension can thus be successfully achieved by OMRP, allowing a direct access to PIL-*b*-PIL block copolymers, though ion exchange can be strongly suspected.

**Synthesis of PIL-*b*-PIL Diblock Copolymers by Sequential OMRP in an Ethyl Acetate/Water Biphasic Mixture.** Block copolymerization was also carried out in a biphasic reaction medium consisting in an ethyl acetate/water (1/1 vol) mixture. The reason why we resorted to this rather unconventional reaction medium was to try to minimize the anion exchange reaction, thanks to a compartmentalization effect of ILMs and related PILs, in two distinct phases.

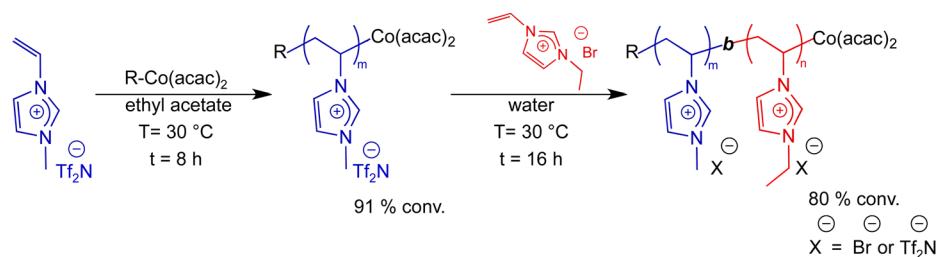
Since R-Co(acac)<sub>2</sub> cannot be directly solubilized in pure water, *N*-vinyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (VMeImTf<sub>2</sub>N) was polymerized in ethyl acetate first (Scheme 3). After 8 h at 30 °C, a well-defined PVMeImTf<sub>2</sub>N-Co(acac)<sub>2</sub> ( $M_{n,SEC}$  = 6100 g/mol;  $M_{n,NMR}$  = 17 800 g/mol,  $M_w/M_n$  = 1.08) was formed, reaching 91% monomer conversion (Figure 8). Crossover to PVETImBr was then carried out by addition of VETImBr in solution in water at 30 °C under vigorous stirring (400 rpm). After 16 h of reaction, a monomer conversion of 80% was obtained, the reaction medium being quenched by adding a solution of TEMPO in ethyl acetate. As shown in Figure 8, the formation of a block copolymer is evidenced with the increase in molar mass, from 6100 to 10 600 g/mol, while the dispersity remains low ( $M_w/$





**Figure 7.** (a)  $^1\text{H}$  NMR spectrum in  $\text{D}_2\text{O}$  of the purified first block  $\text{P}(\text{VETImBr})$  prepared from  $\text{R-Co}(\text{acac})_2$  in methanol at  $30^\circ\text{C}$  after 7.5 h (Figure 6a) and deactivated by TEMPO. (b)  $^1\text{H}$  NMR spectrum in DMSO of the  $\text{PVETImX-}b\text{-PVMImX}$  diblock copolymer, quenched by TEMPO, after dialysis in methanol ( $\text{X}^- = \text{Br}^-$  or  $\text{Tf}_2\text{N}^-$ ).

**Scheme 3. OMRP of  $\text{VMeImTf}_2\text{N}$  in Ethyl Acetate and Synthesis of  $\text{PVMImX-}b\text{-PVETImX}$  Diblock Copolymer in an Ethyl Acetate/Water Mixture at  $30^\circ\text{C}$**

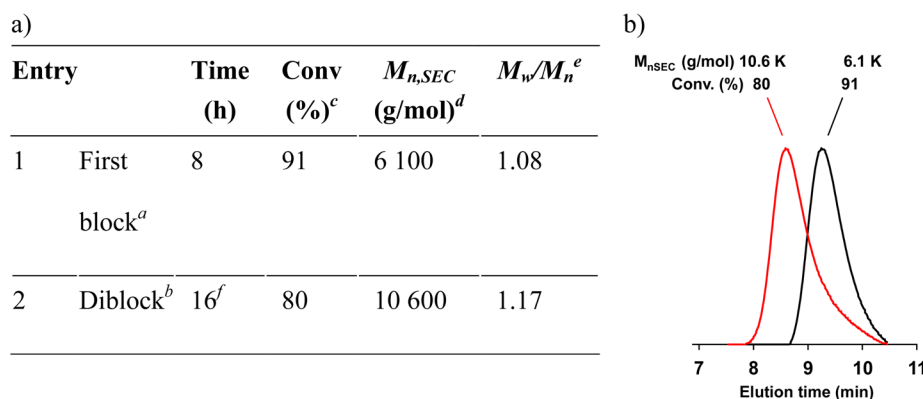


$M_n = 1.17$ ). Only a slight tailing at the low molar mass side is observed, the origin of which is discussed further.

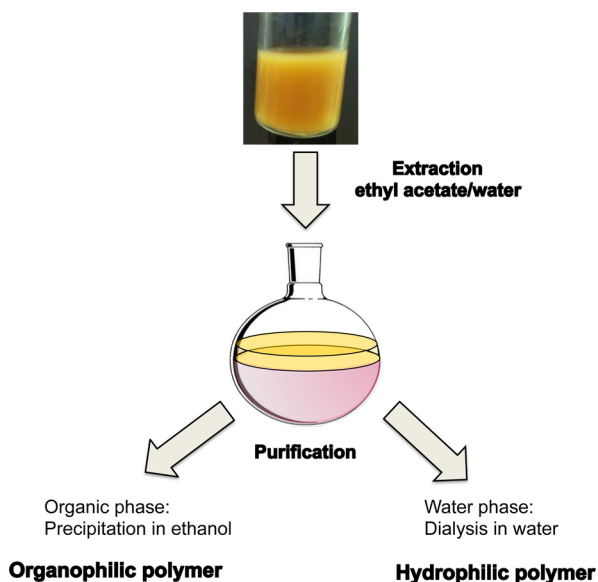
Phase separation between the aqueous and the organic phase did occur after a few minutes of reaction if stirring was not maintained. Interestingly, no phase separation was observed at high monomer conversion (reaction time of 16 h). The system looked like a viscous emulsion that remained stable (no phase separation) for several weeks after stopping agitation (Figure 9), suggesting that (part of) the block copolymer could stabilize the interface. Characterization of the reaction mixture by dynamic light scattering (DLS) and by transmission electron microscopy (TEM) was unfortunately not possible, and because dilution was required for such analyses, dilution (with water and/or ethyl acetate) led to almost immediate phase separation. The precise location of the block copolymer, i.e., in either the organic and/or aqueous phase, and the probability for anion exchange to occur during block copolymer synthesis are important aspects that are addressed hereafter.

Figure 9 illustrates the procedure used for recovering the copolymer. In order to avoid further polymerization or coupling reaction during the purification step, the copolymer was deactivated by adding an excess of TEMPO at the completion of the polymerization (according to a well-established procedure),<sup>9</sup> and the reaction medium was stirred at room temperature for 4 h. Then, dilution with the same volume of ethyl acetate/water led to the separation of two phases, and each of them could be isolated. Corresponding polymers could be analyzed after removal of residual monomer. Thus, the polymer that was found soluble in the organic phase was purified by precipitation in ethanol, while that soluble in water was purified by dialysis against water (membrane cutoff: 1 kDa). Intriguingly, the polymer content as collected in the organic phase proved higher than that recovered from the aqueous phase:  $\text{polymer}_{\text{organic phase}}/\text{polymer}_{\text{water phase}} \text{ (w/w)} \approx 2.7/1$ .

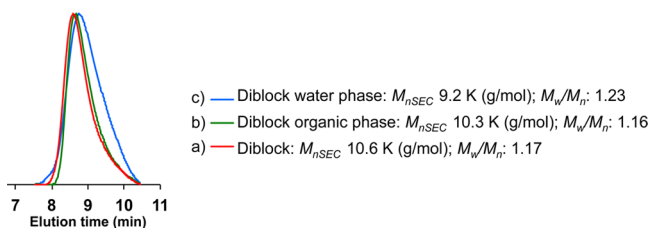
Characterization by SEC of the two polymers, after anion exchange with  $\text{Tf}_2\text{N}^-$ , is illustrated in Figure 10, and comparison



**Figure 8.** (a) Synthesis of PVMeImTf<sub>2</sub>N-Co(acac)<sub>2</sub> in ethyl acetate and block copolymerization with VEtImBr in an ethyl acetate/water mixture at 30 °C and (b) SEC traces of PVMeImTf<sub>2</sub>N-Co(acac)<sub>2</sub> first block, and PVMeImX-*b*-PVEtImY diblock copolymer after 16 h of reaction (X and Y state for the counteranion that can be Br or Tf<sub>2</sub>N). <sup>a</sup>Conditions: EtOAc/VMelImTf<sub>2</sub>N = 1.5/1 (v/w), [VMelImTf<sub>2</sub>N]/[R-Co(acac)<sub>2</sub>] = 50; 30 °C. <sup>b</sup>Conditions: reaction medium from (a), after 8 h of reaction to which is added the aqueous solution of VEtImBr, water/VEtImBr = 3/1 (v/w), water/ethyl acetate = 1/1 (v/v), [VEtImBr]/[PVMeImTf<sub>2</sub>N-Co(acac)<sub>2</sub>] = 50/1; 30 °C. <sup>c</sup>VMelImTf<sub>2</sub>N conversion measured by <sup>1</sup>H NMR in acetone-*d*<sub>6</sub> for first block and in DMSO-*d*<sub>6</sub> for diblock. <sup>d</sup> $M_n$  determined after anion exchange (Br<sup>−</sup>/Tf<sub>2</sub>N<sup>−</sup>) of diblock by SEC analysis in THF (containing 10 mM LiTf<sub>2</sub>N), using PS calibration. <sup>e</sup>Dispersity determined by SEC in THF (containing 10 mM LiTf<sub>2</sub>N). <sup>f</sup>Polymerization time after the addition of the second monomer (VEtImBr).



**Figure 9.** Final aspect of the reaction medium for the block polymerization of VMelImTf<sub>2</sub>N with VEtImBr in a biphasic system ethyl acetate/water (after quenching with TEMPO) and procedure for recovering and purifying the two different fractions of polymers.

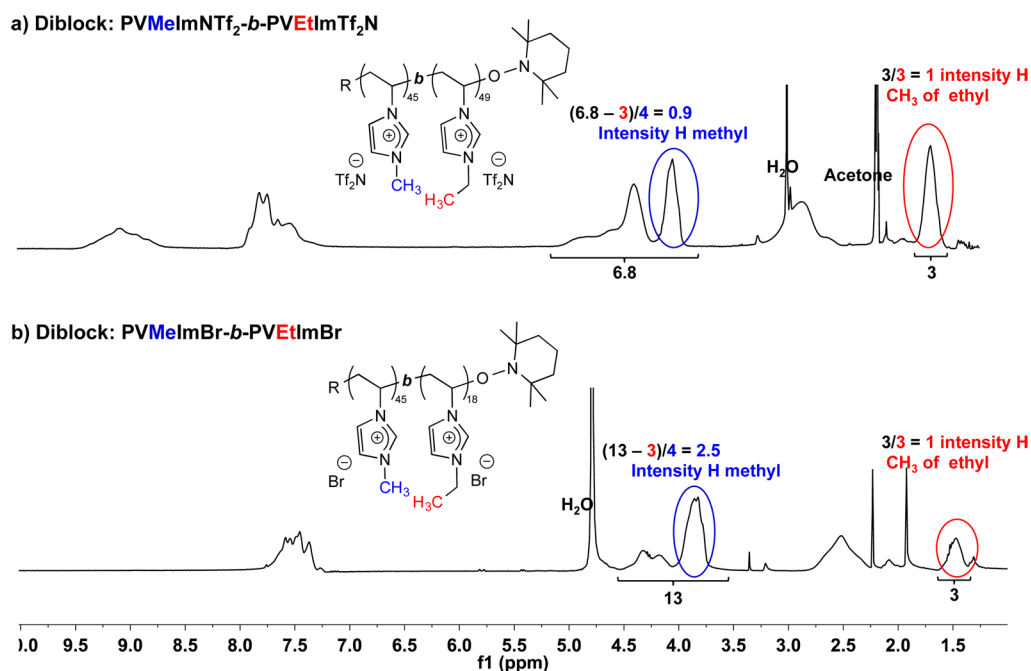


**Figure 10.** SEC traces of PVMeImX-*b*-PVEtImY diblock copolymer prepared in the biphasic system: (a) crude copolymer, (b) polymer fraction soluble in ethyl acetate, and (c) polymer fraction soluble in water. SEC traces have been obtained after anion exchange Br<sup>−</sup>/Tf<sub>2</sub>N<sup>−</sup> (X and Y state for the counteranion that can be Br or Tf<sub>2</sub>N).

is made with the crude polymer collected at the end of the polymerization before phase separation. The polymer extracted from the organic phase shows a SEC trace very similar to that of the crude copolymer, while that recovered from the aqueous phase exhibits a slightly lower molar mass with a tailing in the low molar mass region.

Copolymers collected from both organic and aqueous phases were then analyzed by <sup>1</sup>H NMR in acetone-*d*<sub>6</sub> and D<sub>2</sub>O, respectively (Figure 11). Both samples showed characteristic signals of the two types of monomer units, i.e., a peak due to methyl group for the first block (3.9 ppm) and peaks attributed to the ethyl group of the second block at 4.2 ppm for  $-\text{CH}_2-\text{CH}_3$  and at 1.4 ppm for  $-\text{CH}_2-\text{CH}_3$ . Composition of each copolymer could thus be determined, and the corresponding diblock copolymers could be written as follows: PVMeImX<sub>45</sub>-*b*-PVEtImY<sub>49</sub> and PVMeImX<sub>45</sub>-*b*-PVEtImY<sub>18</sub> in the organic and in the aqueous phase, respectively (X and Y state for the counteranions that cannot be discriminated at this stage). The composition of the copolymer in the organic phase was found relatively close to the theoretical value. In contrast, the DP of the second block in the water-soluble copolymer was lower than the theoretical value (DP<sub>th</sub> = 50). The lower incorporation of the second monomer in the copolymer is mirrored by a lower molar mass, as shown by SEC analysis (Figure 10). We carefully checked that the difference in molar mass of the copolymers collected from the two fractions did not originate from the two different purification protocols (precipitation vs dialysis for the polymer soluble in ethyl acetate and in water, respectively). Indeed, <sup>1</sup>H NMR analysis of solvents used for both protocols did not reveal the presence of copolymer, confirming that no fractionation or polymer loss occurred during the sample recovery.

For the copolymer soluble in ethyl acetate, contents in sulfur and bromine were found equal to 14.22% S and 4% Br, as determined by elemental analysis, while values obtained for the water-soluble copolymer were 0.45% S and 33.5% Br. These results clearly evidence that the two copolymers have a different composition in anions. The copolymer soluble in ethyl acetate mainly contains Tf<sub>2</sub>N<sup>−</sup> counteranion (82% Tf<sub>2</sub>N<sup>−</sup> vs 18% Br<sup>−</sup>) while the water-soluble copolymer is richer in bromine anions



**Figure 11.**  $^1\text{H}$  NMR spectra of PVMeImX-*b*-PVETImY diblock copolymer synthesized in biphasic system: isolated from (a) the organic (in acetone- $d_6$ ) and (b) the aqueous phase (in  $\text{D}_2\text{O}$ ).

(98%  $\text{Br}^-$  vs 2%  $\text{Tf}_2\text{N}^-$ ). In light of these observations, a mechanism accounting for the formation of both PIL-*b*-PIL diblock copolymers occurring in the biphasic medium can be proposed (see Scheme 4).

The hydrophobic PVMeImTf $_2$ N-Co(acac) $_2$  precursor is expected to initiate the OMRP of VETImBr (Scheme 4, stage I), leading to a PVMeImTf $_2$ N-*b*-PVETImBr diblock copolymer. The latter compound, however, cannot be isolated, owing to rapid anion exchange between PVMeImTf $_2$ N-Co(acac) $_2$  and VETImBr at the early stage of the process. This anion exchange can *in situ* generate a hydrophobic VETImTf $_2$ N monomer that can migrate to the organic phase (Scheme 4, stage II), where it can be initiated by the PVMeImTf $_2$ N-Co(acac) $_2$ , giving rise to a diblock copolymer that is enriched in Tf $_2$ N anions, i.e., of PVMeImTf $_2$ N-*b*-PVETImTf $_2$ N-type, in the organic phase (Scheme 4, stage III). In the meantime, the PVMeImTf $_2$ N-Co(acac) $_2$  macroinitiator can be changed into a more hydrophilic polymer, i.e., with  $\text{Br}^-$  anions, migrating into the water phase, where it can initiate the OMRP of VETImBr (Scheme 4, stage II). This could explain the formation of the Br-rich diblock copolymer that was collected in the water phase (Scheme 4, stage III).

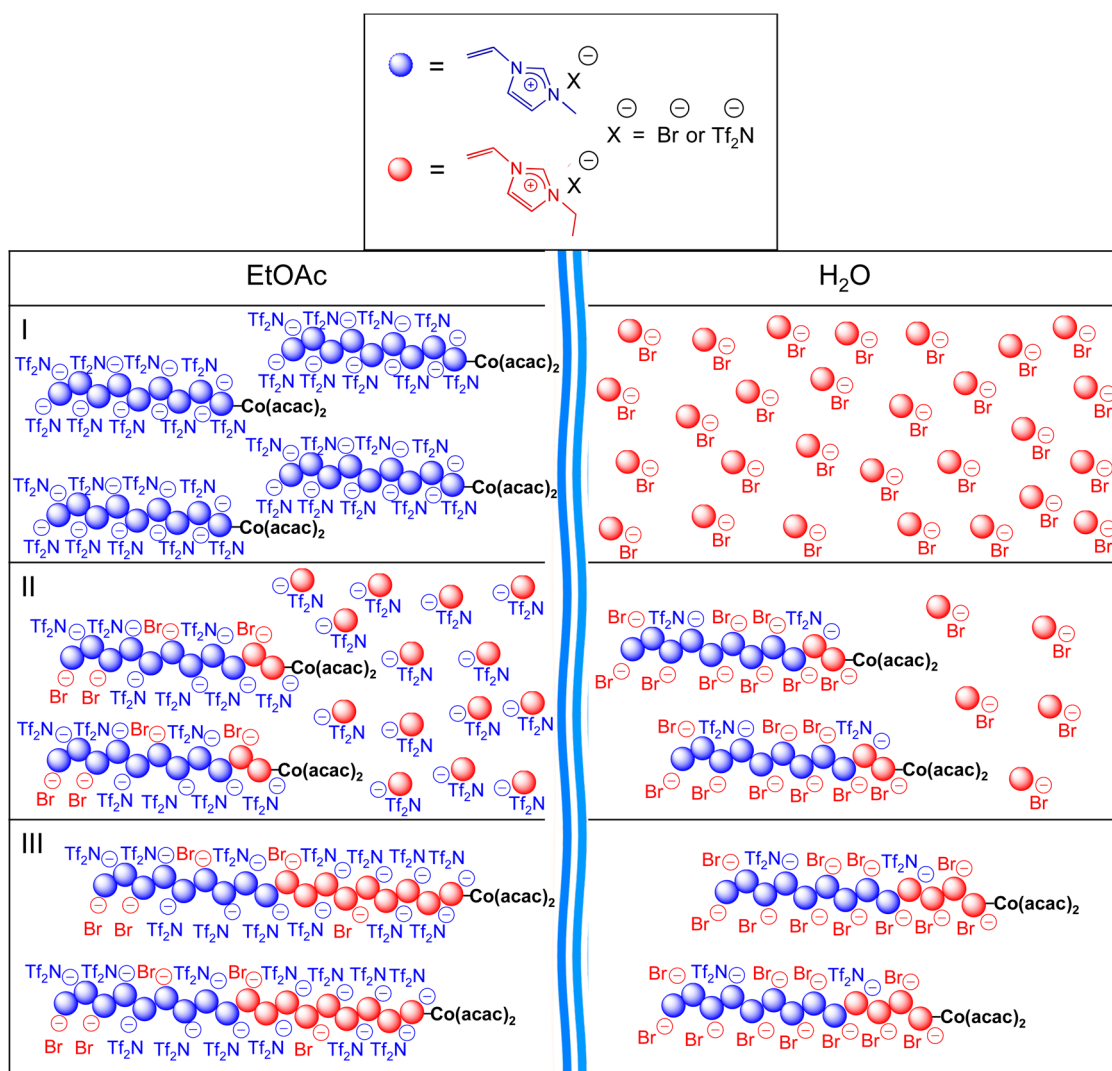
NMR and SEC analyses indeed demonstrate that the copolymer formed in the organic phase is slightly longer than that recovered in the aqueous phase; hence, polymerization in the organic phase seems favored. In contrast, sufficient counteranion exchange seems necessary to drive the macroinitiator from the organic phase to the aqueous one, to initiate the copolymerization in this medium. The slow migration of the macroinitiator from the organic to the water phase, combined to the decrease of the concentration of monomer in the aqueous phase, might be the reason why the copolymer produced in water is of slightly lower molar mass, in comparison to that produced in the organic phase. After polymerization, the fast anion exchange still takes place but does not change the overall composition in each phase. Therefore, it is reasonable to assume that 4 h after deactivation

of the chains by TEMPO, the system has reached its equilibrium.

The mechanism was further validated by carrying out the same copolymer synthesis, but by increasing the amount of VETImBr by a factor of 2 for the preparation of the second block (keeping constant all other parameters). A stable emulsion was again observed at the end of the reaction (at 80% conversion), and the copolymer was then deactivated by TEMPO as previously discussed. Extraction of the copolymer by ethyl acetate and water was carried out according to the previous experiment, and copolymers isolated in each phase were analyzed by  $^1\text{H}$  NMR and elemental analysis. Figure S1 clearly shows that the DP of the second block is about twice increased, when doubling the monomer content compared to the macroinitiator. In accordance with the mechanism proposed for block copolymer formation in the biphasic medium (Scheme 4), the length of the second block formed in ethyl acetate was longer compared to that formed in water (DP = 103 in ethyl acetate vs DP = 48 in water; Figure S1). Moreover, elemental analysis shows that the copolymer soluble in ethyl acetate mainly contains Tf $_2$ N counteranion (81% Tf $_2$ N $^-$  vs 19%  $\text{Br}^-$ ) while the water-soluble copolymer is richer in bromine anions (93%  $\text{Br}^-$  vs 7% Tf $_2$ N $^-$ ), in line with the previous experiment and the mechanism proposal. The polymer content as collected in the organic phase proved slightly higher than that recovered from the aqueous phase:  $\text{polymer}_{\text{organic phase}}/\text{polymer}_{\text{water phase}}$  (w/w)  $\approx 1.4/1$ .

All these results establish, for the first time, that anion exchange occurs rapidly and substantially during all PIL-based block copolymer synthesis. This does not preclude the synthesis of *N*-vinylimidazolium-type BCP's having different alkyl chains, but mobile counteranions cannot be confined in one type of PIL backbone and can readily diffuse from one PIL block to another, even in a biphasic medium. BCP's reported here are rather nonconventional in the sense that they consist of a block-type cationic copolymer backbone where each block

**Scheme 4.** Proposed Mechanism for the Formation of Block Copolymers in Ethyl Acetate/Water Mixture from PVMeImTf<sub>2</sub>N as a First Block and VEtImBr as the Second Monomer: I, Initial Stage; II, Intermediate Stage; III, Final Stage



is characterized by a different alkyl chain, but where mobile anions are randomly distributed along the polymer chain.

Of particular interest, the synthesis of PVMeImX-*b*-PVEtImX block copolymer also proved feasible following the inverse strategy, i.e., by preparing the hydrophilic PVEtImBr- $\text{Co}(\text{acac})_2$  in water first, until high monomer conversion (94%;  $M_{n,\text{SEC}} = 11\,000$  g/mol;  $M_w/M_n = 1.11$ ; Figure 12a), followed by OMRP of VMImTf<sub>2</sub>N in ethyl acetate at 30 °C. Note again that the synthesis of the hydrophilic macroinitiator required a low amount of acetone in order to solubilize the R- $\text{Co}(\text{acac})_2$  controlling agent in water (as already reported in our previous works).<sup>76</sup>

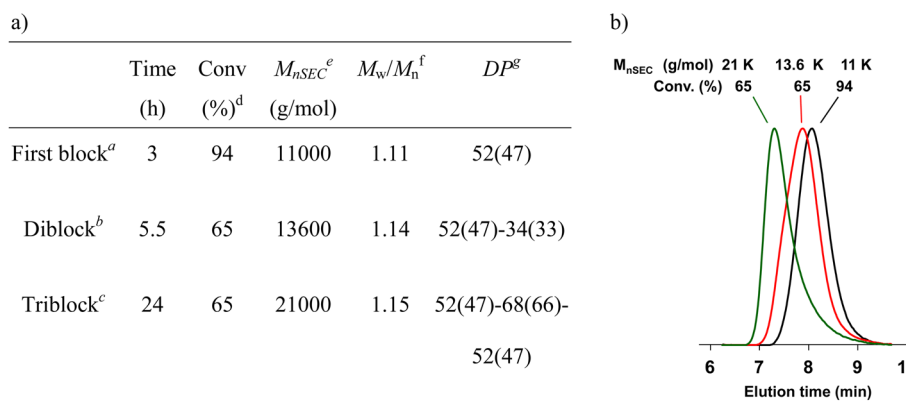
Chain extension could be successfully achieved, indeed, as attested by the complete shift of the SEC trace of the first block to the higher molar mass region upon addition of the second monomer (Figure 12b). A stable system was again observed after 5.5 h of reaction (65% monomer conversion), no phase separation being noted even after several days without stirring.

In order to take advantage of the presence of the  $\text{Co}(\text{acac})_2$  moiety at the diblock copolymer chain ends, isoprene was added to provide an unprecedented ABA triblock copolymer. The addition of isoprene to freshly OMRP-derived polymer chains has indeed been reported to rapidly and quantitatively

lead to coupled chains by cobalt-mediated radical coupling (CMRC).<sup>91–94</sup> When applied to AB diblock copolymer precursors, CMRC leads to corresponding symmetrical ABA triblock copolymers in a few seconds. Here, CMRC was applied to one of AB-type diblock copolymers prepared in the ethyl acetate/water biphasic mixture (Scheme 5). Addition of an excess of isoprene to the PVMeImX-*b*-PVEtImX- $\text{Co}(\text{acac})_2$  copolymer solution ( $M_n = 13\,600$  g/mol,  $M_w/M_n = 1.14$ ) gave the expected symmetrical ABA-type triblock copolymer ( $M_n = 21\,000$  g/mol). Figure 12 indeed shows that most of the diblock copolymer was indeed coupled, the dispersity remaining as low as 1.15. The viscosity of the polymerization medium rapidly increased after addition of isoprene, the mixture resembling a stable emulsion. Dilution of the reaction medium again led to phase separation, avoiding any DLS or TEM characterizations. Based on DP of the first block determined by <sup>1</sup>H NMR analysis, DP of the diblock and triblock could be calculated and were found consistent with the targeted values (Figure 12a).

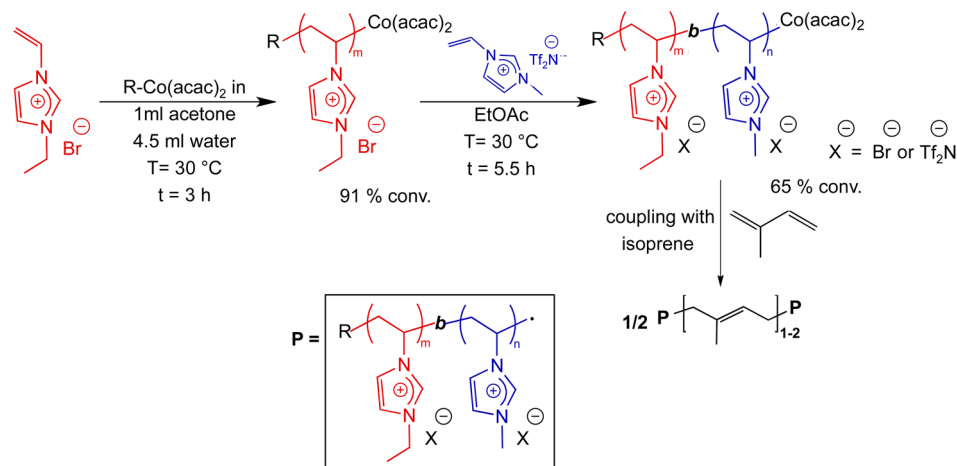
As a final example, block copolymerization between vinylimidazolium bearing a short (methyl) and a longer (butyl) alkyl chain was considered in the same biphasic system. *N*-Vinyl-3-butylimidazolium bromide was first polymerized in water,





**Figure 12.** (a) Synthesis of PVetImBr–Co(acac)<sub>2</sub> in water, PVetImX-*b*-PVMelImX by chain extension of PVetImBr–Co(acac)<sub>2</sub> with VMeImTf<sub>2</sub>N in ethyl acetate/water, and PVetImX-*b*-PVMelImX-*b*-PVetImX by CMRC and (b) SEC chromatograms of PVetImBr–Co(acac)<sub>2</sub> first block, PVetImX-*b*-PVMelImX diblock copolymer, and PVetImX-*b*-PVMelImX-*b*-PVetImX triblock copolymer. <sup>a</sup>Conditions: water/VetImBr (v/w) = 3/1; water/acetone = 4.5/1 (v/v). [VetImBr]/[R–Co(acac)<sub>2</sub>] = 50; 30 °C. <sup>b</sup>Conditions: reaction medium from footnote a to which is added the solution of VMeImTf<sub>2</sub>N in ethyl acetate, after 5.5 h of reaction. Ethyl acetate/VMeImTf<sub>2</sub>N = 1.5/1 (v/v); water/ethyl acetate = 1/1 (v/v); [VMeImTf<sub>2</sub>N]/[PVetImBr–Co(acac)<sub>2</sub>] = 50/1, 30 °C. <sup>c</sup>Reaction medium from footnote b to which is added a large excess of isoprene (≈0.3 mL). <sup>d</sup>VetImBr conversion measured by <sup>1</sup>H NMR in D<sub>2</sub>O for first block and in DMSO-*d*<sub>6</sub> for diblock. <sup>e</sup> $M_n$  determined after anion exchange (Br<sup>−</sup>/Tf<sub>2</sub>N<sup>−</sup>) of diblock and triblock by SEC analysis in THF (containing 10 mM LiTf<sub>2</sub>N), using PS calibration. <sup>f</sup>Dispersity determined by SEC in THF (containing 10 mM LiTf<sub>2</sub>N). <sup>g</sup>Degree of polymerization of each block determined by <sup>1</sup>H NMR analysis; in parentheses: the theoretical DP.

**Scheme 5. Reaction Scheme for the Synthesis of Symmetrical PVetImX-*b*-PVMelImX-*b*-PVetImX Triblock Copolymer in Ethyl Acetate/Water Biphasic Mixture**



providing a well-defined PVBuImBr–Co(acac)<sub>2</sub> with 92% monomer conversion after 4 h of reaction at 30 °C (Figure S2). Block copolymerization was then accomplished by adding a solution of VMeImTf<sub>2</sub>N in ethyl acetate. The molar mass of the macroinitiator was accordingly increased, and the SEC trace remained monomodal and narrow during chain extension. <sup>1</sup>H NMR analysis of the copolymer showed the presence of the two monomer units in the copolymer (Figure S3) and enabled to calculate the DP of each block that were close to the target values. Although counteranion exchange most probably occurred also in this case, a well-defined all PIL-*b*-PIL block copolymer, where each block contained a different alkyl chain, was successfully formed.

## CONCLUSIONS

Synthesis of structurally well-defined poly(*N*-vinyl-3-alkylimidazolium)s with the hindered bis(trifluoromethylsulfonyl)imide (Tf<sub>2</sub>N<sup>−</sup>) counteranion can be readily achieved by organometallic-mediated radical polymerization (OMRP), using a presynthesized alkyl–cobalt(III) complex serving as

both initiating system and controlling agent. Polymerizations can be conducted in ethyl acetate at 30 °C, providing fast control over molar masses and dispersities, up to high monomer conversion. Synthesis of all poly(ionic liquid)-based amphiphilic block copolymers is also investigated for the first time. Targeted compounds are constituted of both a hydrophilic and a lipophilic poly(*N*-vinylimidazolium) blocks that differ not only by the nature of the alkyl chain (methyl, ethyl, or butyl) but also by the counteranion (Tf<sub>2</sub>N<sup>−</sup> and Br<sup>−</sup> for the hydrophobic and hydrophilic monomers, respectively). Block copolymers can be successfully prepared in solution in methanol at 30 °C, though anion exchange likely occurs under such homogeneous conditions, leading to a random distribution of mobile counteranions along the copolymer chains. In these conditions, however, this anion exchange can be hardly evidenced. Alternatively, block copolymer synthesis can be accomplished in a water/ethyl acetate biphasic mixture. Though well-defined block copolymers can be obtained under such unusual conditions, counteranions cannot be confined on a specific poly(*N*-vinyl-3-alkylimidazolium) block. Therefore,

use of a biphasic reaction mixture cannot prevent the anion exchange reaction from happening. This can be evidenced by elemental analysis of compounds recovered from both phases. Addition of isoprene to AB-type poly(ionic liquid) (PIL)-based diblock copolymer formed in the biphasic medium enables the quantitative synthesis of unprecedented symmetrical and all PIL-based ABA-type triblock copolymers, by cobalt-mediated radical coupling. These results highlight that OMRP is particularly suited for the preparation of all *N*-vinylimidazolium-type PIL-based block copolymers under mild experimental conditions, not only in organic but also in biphasic media. Current efforts are devoted to the synthesis of amphiphilic block copolymers exclusively carried out in a water-borne polymerization medium. Work is also in progress to associate various PIL blocks of significantly distinct properties arising from different alkyl chains in the 3-position of the imidazolium ring.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Figures S1–S3. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.5b01013.

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### Notes

The authors declare no competing financial interest.

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