

Direct Route to Well-Defined Poly(ionic liquid)s by Controlled Radical Polymerization in Water

Daniela Cordella,[†] Anthony Kermagoret,[†] Antoine Debuigne,[†] Raphaël Riva,[†] Ian German,[†] Mehmet Isik,[‡] Christine Jérôme,[†] David Mecerreyes,[‡] Daniel Taton,[§] and Christophe Detrembleur^{*,†}

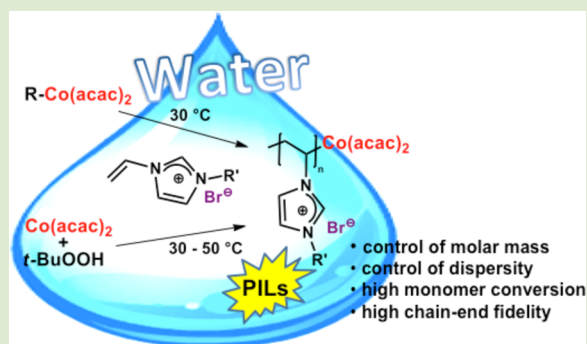
[†]Center for Education and Research on Macromolecules (CERM), Chemistry Department, University of Liege (ULg), Sart-Tilman, B6a, 4000 Liege, Belgium

[‡]Institute for Polymer Materials (POLYMAT), University of the Basque Country UPV/EHU, Joxe Mari Korta Center, Avda. Tolosa 72, 20018 Donostia-san Sebastian, Spain

[§]Laboratoire de Chimie des Polymères Organiques (LCPO), IPB-ENSCBP, Université de Bordeaux, F-33607 Pessac Cedex, France

Supporting Information

ABSTRACT: The precision synthesis of poly(ionic liquid)s (PILs) in water is achieved for the first time by the cobalt-mediated radical polymerization (CMRP) of *N*-vinyl-3-alkylimidazolium-type monomers following two distinct protocols. The first involves the CMRP of various 1-vinyl-3-alkylimidazolium bromides conducted in water in the presence of an alkyl-cobalt(III) complex acting as a monocomponent initiator and mediating agent. Excellent control over molar mass and dispersity is achieved at 30 °C. Polymerizations are complete in a few hours, and PIL chain-end fidelity is demonstrated up to high monomer conversions. The second route uses the commercially available bis(acetylacetonato)cobalt(II) (Co(acac)₂) in conjunction with a simple hydroperoxide initiator (*tert*-butyl hydroperoxide) at 30, 40, and 50 °C in water, facilitating the scaling-up of the technology. Both routes prove robust and straightforward, opening new perspectives onto the tailored synthesis of PILs under mild experimental conditions in water.



Poly(ionic liquid)s (PILs) have emerged as a special class of polyelectrolyte materials, featuring tunable solubility, high ionic conductivity, and a broad range of glass transition temperatures.¹ Due to their specific properties emanating from the ionic liquid (IL) units and their intrinsic polymeric nature, PILs find potential applications in various areas, such as analytical chemistry, biotechnology, gas separation, dispersants, solid ionic conductors for energy, catalysis, etc. The main synthetic strategies for PILs include direct chain-growth polymerization—whether controlled² or noncontrolled³—of ionic liquid (IL) monomers, step-growth polymerization,⁴ and postpolymerization modification of uncharged polymers by nitrogen quaternization.⁵ Exchange of the counterion (anion or cation) is typically efficient, providing an additional method for the variation of PIL properties.

In recent years, controlled radical polymerization (CRP) techniques have been applied to the synthesis of structurally well-defined PILs, with control attained over molar mass, dispersity, and end-group fidelity. Control of end-group functionality enables the precision engineering of IL-based block copolymers that possess unique self-assembly modes in solution⁶ or in the bulk.⁷ Confinement of PIL blocks within lamellar nanodomains of block copolymers has, for instance, led to polymer films with enhanced ionic conductivity.⁷ The design of novel PIL structures is therefore necessary for the

establishment of important structure/property relationships, required to expand the scope and realize the full potential of IL-based materials.

The majority of studies has focused on the direct CRP of styrenic- or (meth)acrylic monomers containing pendant imidazolium groups, featuring various counteranions (e.g., Br⁻, BF₄⁻, PF₆⁻, and (CF₃SO₂)₂N⁻).^{2,8} In contrast, processes for CRP of *N*-vinyl-3-alkylimidazolium salts (VImX) are relatively underdeveloped due to difficulties in controlling the highly reactive growing polymer chains. While their successful control by reversible addition–fragmentation chain transfer (RAFT)^{6c,9} and organometallic-mediated radical polymerization (OMRP)¹⁰ has recently been achieved, exclusively organic solvents were used as polymerization media. *N*-Vinyl-3-alkylimidazolium monomers, readily accessible through quaternization of *N*-vinylimidazole, can be made hydrophilic by installation of selected counterions, an illustration of which was their free radical polymerization under moderate conditions in water,^{1c,11} an environmentally benign and cost-efficient polymerization medium. Control of VImX polymerization in

Received: November 13, 2014

Accepted: December 4, 2014

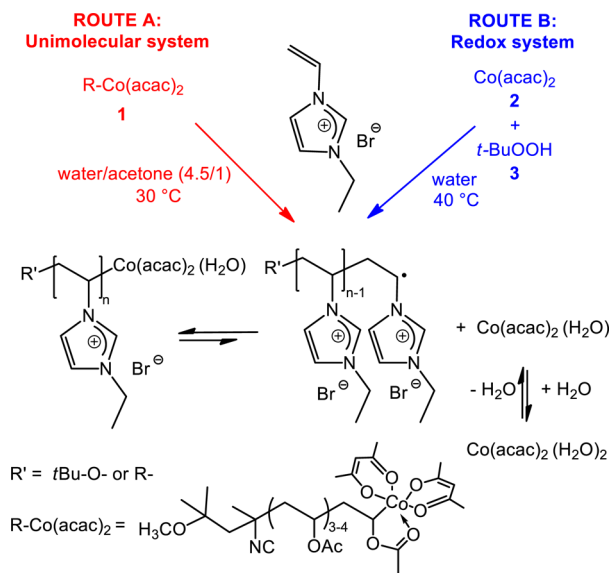
Published: December 5, 2014

water by CRP techniques would exploit this hydrophilicity while producing PILs of desired structure and functionality. Despite the significant efforts dedicated to the CRP in aqueous media by nitroxide-mediated polymerization (NMP),¹² single electron transfer living radical polymerization (SET LRP),¹³ atom transfer radical polymerization (ATRP),¹⁴ RAFT,¹⁵ and OMRP^{7i,16} to overcome the limitations of water-promoted side reactions, none of these processes however has yet been extended in scope to include the CRP of VImX monomers in water. Yet such an achievement would open huge perspectives in the design of in situ generation of PIL-based dispersive agents or latexes.

In this contribution, the synthesis of three structurally well-defined poly(*N*-vinyl-3-alkylimidazolium bromide)s, by direct CMRP in water, is described. Furthermore, the anticipated activating effect of water on CMRP¹⁷ facilitated their preparation under mild experimental conditions.

The direct CMRP of *N*-vinyl-3-ethylimidazolium bromide (VEtImBr) was achieved at moderate temperature (30, 40, or 50 °C), with water as solvent, using two distinct control strategies (Scheme 1). Route A employed an alkyl-cobalt(III)

Scheme 1. Routes for the CMRP of 1-Vinyl-3-ethylimidazolium Bromide (VEtImBr) in Water



complex (R-Co, 1) as a monocomponent initiator/mediating agent at a polymerization temperature of 30 °C. Alternatively, the commercially available components bis(acetylacetonato)-cobalt(II) (Co(acac)₂, 2) and *tert*-butylhydroperoxide (*t*-BuOOH, 3) were effective as mediating agent and initiator, respectively, for the synthesis of well-defined PVEtImBr at 30, 40, and 50 °C (Route B).

Both routes provided excellent control over molar mass and dispersity, while PIL chain end fidelity was demonstrated by highly selective radical coupling of growing PIL chains using isoprene as a coupling agent.

The water-insoluble alkyl-cobalt complex 1^{7a} was first dissolved in a minimum amount of acetone and then added to an aqueous solution of VEtImBr at 30 °C (water/acetone = 4.5/1 v/v). The polymerization was rapid, consistent with water coordination at cobalt promoting Co-C chain-end bond lability,¹⁷ with virtually complete consumption recorded after 6 h when using an initial VEtImBr/I molar ratio of 75 (target

mass = 15 200 g mol⁻¹). Figure 1 shows the linear increase of molar mass with the monomer conversion at different

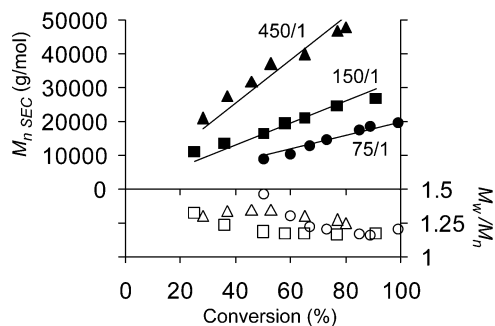


Figure 1. Plot of $M_{n,SEC}$ and M_w/M_n vs monomer conversion for the polymerization of VEtImBr in water at 30 °C for different [VEtImBr]/[I] ratios. See Figure S1 in the Supporting Information for SEC traces.

monomer loadings, while mass dispersity decreases with conversion, consistent with a controlled CMRP process.

Higher molar mass PVEtImBr with similarly narrow mass distribution was accessed by increasing the initial VEtImBr/I molar ratio (Figure 1; Table 1; Figure S1, Supporting Information). As anticipated, the lower initiator loadings led to longer polymerization times required to achieve high conversions (Table 1).

Table 1. Homopolymerization of VEtImBr Initiated by 1 in Water at 30 °C^a

entry	[VEtImBr]/[I]	time (h)	conv. (%) ^b	$M_{n,SEC}$ ^c (g/mol)	M_w/M_n ^c		
1	75/1	0.1	50	9000	1.46		
		0.25	60	10400	1.30		
		0.5	67	13000	1.22		
		2	85	17500	1.17		
		3	89	18700	1.16		
		6	>99	19700	1.20		
2	150/1	0.1	25	11400	1.34		
		0.25	36	13700	1.28		
		0.5	50	16700	1.27		
		1	65	21400	1.22		
		2	77	25000	1.21		
		4	91	27000	1.22		
		3	450/1	0.15	28	25300	1.22
				0.25	37	30300	1.34
0.5	46			36000	1.35		
1	53			38000	1.35		
2	65			43000	1.30		
4	77			44500	1.25		

^aConditions: water/VEtImBr (v/w) = 3/1; water/acetone = 4.5/1 (v/v), 30 °C. ^bVEtImBr conversion measured by ¹H NMR in DMSO-*d*₆.

^cDetermined after anion exchange (Br⁻/Tf₂N⁻) by SEC analysis in THF containing 10 mM LiTf₂N (PS calibration) following the procedure described in ref 18.

¹H NMR analysis (250 MHz, D₂O) was performed on a purified sample taken from the polymerization where [VEtImBr]₀/[I] = 150 at 91% conversion ($M_{n,SEC}$ = 27 000 g mol⁻¹; Table 1, entry 2, 4 h). The spectrum features a resonance at 3.15 ppm, characteristic of the OCH₃ protons of the anticipated initiating group formed by decomposition of complex 1 (Figure S2, Supporting Information). Comparison of the methoxy peak integral with those of the imidazolium ring

proton signals at 7.5 ppm allowed the estimation of PVeImBr molar mass ($M_{n,NMR} = 30\,400\text{ g mol}^{-1}$), which closely matches the theoretical molar mass at 91% conversion ($M_{n,th} = 30\,000\text{ g mol}^{-1}$). This agreement, replicated for each sample where spectrum resolution permitted an accurate calculation, indicates the complete initiation of polymer chains by radicals derived from complex **1**.

In a preliminary assessment of the scope of aqueous VImX polymerization, complex **1** was tested for the polymerization of two other water-soluble vinyl imidazolium monomers: *N*-vinyl-3-methylimidazolium bromide (VMeImBr) and *N*-vinyl-3-butylimidazolium bromide (VBuImBr). The linear increase of M_n vs conversion and the low dispersities observed up to high monomer conversion are again indicative of controlled processes (Tables S1 and S2, Figures S3 and S4, Supporting Information).

In order to verify that a high proportion of PIL chains were still active at high monomer conversion, isoprene was added to the VEImBr polymerization medium once near complete consumption of the monomer was achieved. The addition of isoprene has previously been found to rapidly and quantitatively couple polymer chains prepared by CMRP mediated by $\text{Co}(\text{acac})_2$ while releasing the metal complex from the chain end.¹⁹ Thus, PVeImBr with $M_{n,SEC} = 27\,000\text{ g mol}^{-1}$ and $M_w/M_n = 1.22$, obtained after 91% monomer conversion in 4 h of polymerization at 30 °C, was successfully coupled when an excess of isoprene was added. The respective SEC chromatograms of the polymer samples taken prior to and after isoprene addition (Figure 2) show a complete shift of the trace of the

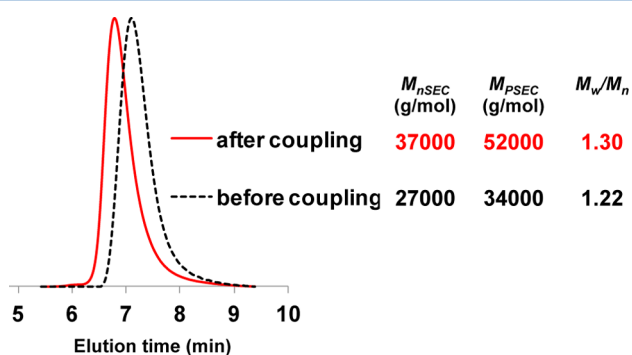


Figure 2. SEC traces and macromolecular data of PVeImBr before and after coupling by the addition of isoprene.

parent PVeImBr to higher molar mass upon coupling. No further incorporation of residual monomer was noted by ¹H NMR analysis of either the crude reaction medium after coupling or the corresponding purified polymer (Figure S5, Supporting Information). This observation confirmed that the increase of the molar mass upon addition of isoprene resulted from chain coupling, consistent with previous investigations carried out on other polymers end-capped by $\text{Co}(\text{acac})_2$.¹⁹ This quantitative coupling reaction evidenced that PILs produced by CMRP in water at high monomer conversion exhibited high chain-end fidelity. The capacity of Co-bound PVeImBr for high-yielding addition to neutral radical acceptors highlights the potential for further chain extension and chain-end functionalization reactions, to facilitate the structural elaboration of PIL-based materials.

Though straightforward, the preparation of PVeImBr by route A requires the prior synthesis of the oxygen-sensitive,

thermally labile complex **1** as a monocomponent initiator/mediating agent. As an alternative strategy, we assessed the capacity of a bicomponent initiator/mediating agent combination, comprising the commercially available bis-(acetylacetonato)cobalt(II) $\text{Co}(\text{acac})_2$ (**2**) and *tert*-butyl hydroperoxide (*t*-BuOOH) (**3**; Route B, Scheme 1), for control of VEImBr polymerization. Additionally, route B requires no acetone to aid solubility over that of route A. In this system, *t*-BuOOH plays the role of the oxidant and radical source, while $\text{Co}(\text{acac})_2$ operates both as a reducing agent and a mediating agent. Two equivalents of $\text{Co}(\text{acac})_2$ relative to *t*-BuOOH were thus employed: 1 equiv in order to activate *t*-BuOOH toward generation of a *tert*-butyloxy radical; the remainder is required to reversibly trap propagating PIL chains.

The CMRP of VEImBr by the $\text{Co}(\text{acac})_2/t$ -BuOOH redox system in water at 30 °C was well controlled, producing a PIL of narrow molecular weight distribution (Figure 3a). The

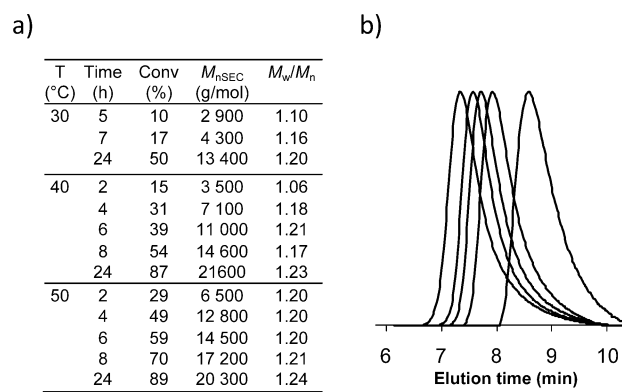


Figure 3. Polymerization of VEImBr initiated by *t*-BuOOH in water. (a) Polymerization conditions and experimental results. (b) SEC traces for PVeImBr prepared at 50 °C (for SEC traces obtained at 40 °C, see Figure S7, Supporting Information). Conditions: $[\text{VEImBr}]/[t\text{-BuOOH}]/[\text{Co}(\text{acac})_2] = 50/1/2$; water/VEImBr = 3.6/1 v/v.

polymerization was however significantly slower than that initiated by **1** at the same temperature, with only 10% monomer conversion achieved after 5 h. The nature of the initiating system requires close to complete decomposition of the peroxide, thus a combination of nearly all additional $\text{Co}(\text{acac})_2$ centers with growing chain radicals, before significant propagation can occur—an effect established for the CMRP of VAc.^{16b,20} The low conversion achieved was proposed therefore to be due to incomplete decomposition of *t*-BuOOH leaving a slight excess of $\text{Co}(\text{acac})_2$ in the polymerization medium that further shifts the CMRP equilibrium toward the dormant species (Scheme 1). To overcome this effect and speed up the propagation, the polymerization was also carried out at 40 and 50 °C (Figure 3). Under these experimental conditions, the polymerization rate was significantly higher and remained under control even at 50 °C and high monomer conversion, as indicated by the linear increase of molar masses with conversion and the production of PVeImBr of low mass dispersity (Figure 3 and Figures S6 and S7, Supporting Information).

In conclusion, we report the first example of controlled radical polymerization of hydrophilic *N*-vinyl-3-alkylimidazolium salts in water at moderate temperatures (30–50 °C) employing either a mono- or bicomponent cobalt-based initiation/control strategy. Polymerizations at 30 °C using an

alkylcobalt(III) complex as monocomponent initiator/mediating agent are complete within a few hours, producing poly(ionic liquid)s (PILs) of low mass dispersity even after very high monomer conversion. The second route exploits the redox reaction between the commercially available reagents *tert*-butylhydroperoxide and Co(acac)₂ to generate initiating radicals, with additional Co(acac)₂ acting as a mediating agent to enforce good molar mass control. Optimization of the polymerization conditions, with a view to increasing polymerization rate while maintaining controlled behavior, is ongoing. Both routes enable the controlled synthesis of hydrophilic PILs, expand the scope of this important class of polyelectrolytes, and provide pathways to novel IL-based block copolymers and higher polymer structures in water.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental section detailing ¹H NMR analysis, monomer and polymer preparations, tables, and SEC chromatograms. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: christophe.detrembleur@ulg.ac.be.

Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank the ITN Marie-Curie “Renaissance” funded by the People FP7 Programme, the “Fonds de la Recherche Scientifique” (FRS-FNRS), and the Belgian Science Policy in the frame of the Interuniversity Attraction Poles Program (P7/05)–Functional Supramolecular Systems (FS2) for financial supports. A.D. and C.D. are Research Associate and Research Director of the FRS-FNRS, respectively. The authors thank G. Cartigny and C. Dannemark for skillful assistance.

■ REFERENCES

- (1) (a) Green, O.; Grubjesic, S.; Lee, S.; Firestone, M. A. *Polym. Rev.* **2009**, *49*, 339. (b) Mecerreyes, D. *Prog. Polym. Sci.* **2011**, *36*, 1629. (c) Yuan, J.; Mecerreyes, D.; Antonietti, M. *Prog. Polym. Sci.* **2013**, *38*, 1009. (d) Green, M. D.; Long, T. E. *Polym. Rev.* **2009**, *49*, 291. (e) Schultz, A. R.; Lambert, P. M.; Chartrain, N. A.; Ruohoniemi, D. M.; Zhang, Z.; Jangu, C.; Zhang, M.; Williams, C. B.; Long, T. E. *ACS Macro Lett.* **2014**, *3*, 1205. (f) Abdelhedi-Miladi, I.; Montarnal, D.; Obadia, M. M.; Ben Romdhane, H.; Drockenmuller, E. *ACS Macro Lett.* **2014**, *3*, 1187. (g) Suga, T.; Sakata, M.; Aoki, K.; Nishide, H. *ACS Macro Lett.* **2014**, *3*, 703. (h) Men, Y.; Schlaad, H.; Yuan, J. *ACS Macro Lett.* **2013**, *2*, 456.
- (2) (a) He, H.; Zhong, M.; Luebke, D.; Nulwala, H.; Matyjaszewski, K. *J. Polym. Sci., Part A: Polym. Chem.* **2014**, *52*, 2175. (b) Tang, H.; Tang, J.; Ding, S.; Radosz, M.; Shen, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 1432. (c) Nakamura, Y.; Nakanishi, K.; Yamago, S.; Tsujii, Y.; Takahashi, K.; Morinaga, T.; Sato, T. *Macromol. Rapid Commun.* **2014**, *35*, 642. (d) He, H.; Luebke, D.; Nulwala, H.; Matyjaszewski, K. *Macromolecules* **2014**, *47*, 6601.
- (3) (a) Bara, J. E.; Lessmann, S.; Gabriel, C. J.; Hatakeyama, E. S.; Noble, R. D.; Gin, D. L. *Ind. Eng. Chem. Res.* **2007**, *46*, 5397. (b) Ohno, H.; Yoshizawa, M.; Ogihara, W. *Electrochim. Acta* **2004**, *50*, 255. (c) Marcilla, R.; Blazquez, J. A.; Rodriguez, J.; Pomposo, J. A.

Mecerreyes, D. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 208. (d) Cardiano, P.; Mineo, P. G.; Neri, F.; Lo Schiavo, S.; Piraino, P. *J. Mater. Chem.* **2008**, *18*, 1253.

(4) (a) Mudraboyina, B. P.; Obadia, M. M.; Allaoua, I.; Sood, R.; Serghei, A.; Drockenmuller, E. *Chem. Mater.* **2014**, *26*, 1720. (b) Dimitrov-Raychev, P.; Beghdadi, S.; Serghei, A.; Drockenmuller, E. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 34.

(5) (a) Aitken, B. S.; Buitrago, C. F.; Heffley, J. D.; Lee, M.; Gibson, H. W.; Winey, K. I.; Wagener, K. B. *Macromolecules* **2012**, *45*, 681. (b) Yuan, J.; Antonietti, M. *Polymer* **2011**, *52*, 1469.

(6) (a) Stancik, C. M.; Lavoie, A. R.; Schuetz, J.; Achurra, P. A.; Lindner, P.; Gast, A. P.; Waymouth, R. M. *Langmuir* **2004**, *20*, 596. (b) Stancik, C. M.; Lavoie, A. R.; Achurra, P. A.; Waymouth, R. M.; Gast, A. P. *Langmuir* **2004**, *20*, 8975. (c) Mori, H.; Yahagi, M.; Endo, T. *Macromolecules* **2009**, *42*, 8082. (d) Mori, H.; Ebina, Y.; Kambara, R.; Nakabayashi, K. *Polym. J.* **2012**, *44*, 550. (e) Karjalainen, E.; Chenna, N.; Laurinmaeki, P.; Butcher, S. J.; Tenhu, H. *Polym. Chem.* **2013**, *4*, 1014.

(7) (a) Green, M. D.; Choi, J.-H.; Winey, K. I.; Long, T. E. *Macromolecules* **2012**, *45*, 4749. (b) Gao, R.; Wang, D.; Heflin, J. R.; Long, T. E. *J. Mater. Chem.* **2012**, *22*, 13473. (c) Ye, Y.; Choi, J.-H.; Winey, K. I.; Elabd, Y. A. *Macromolecules* **2012**, *45*, 7027. (d) Ye, Y.; Sharick, S.; Davis, E. M.; Winey, K. I.; Elabd, Y. A. *ACS Macro Lett.* **2013**, *2*, 575. (e) Choi, J.-H.; Ye, Y.; Elabd, Y. A.; Winey, K. I. *Macromolecules* **2013**, *46*, 5290. (f) Chanthad, C.; Masser, K. A.; Xu, K.; Runt, J.; Wang, Q. *J. Mater. Chem.* **2012**, *22*, 341. (g) Schneider, Y.; Modestino, M. A.; McCulloch, B. L.; Hoarfrost, M. L.; Hess, R. W.; Segalman, R. A. *Macromolecules* **2013**, *46*, 1543. (h) Weber, R. L.; Ye, Y.; Schmitt, A. L.; Banik, S. M.; Elabd, Y. A.; Mahanthappa, M. K. *Macromolecules* **2011**, *44*, 5727. (i) Coupillaud, P.; Fèvre, M.; Wirotius, A.-L.; Aissou, K.; Fleury, G.; Debuigne, A.; Detrembleur, C.; Mecerreyes, D.; Vignolle, J.; Taton, D. *Macromol. Rapid Commun.* **2014**, *35*, 422.

(8) (a) Vijayakrishna, K.; Jewrajka, S. K.; Ruiz, A.; Marcilla, R.; Pomposo, J. A.; Mecerreyes, D.; Taton, D.; Gnanou, Y. *Macromolecules* **2008**, *41*, 6299. (b) Vijayakrishna, K.; Mecerreyes, D.; Gnanou, Y.; Taton, D. *Macromolecules* **2009**, *42*, 5167.

(9) (a) Yuan, J.; Schlaad, H.; Giordano, C.; Antonietti, M. *Eur. Polym. J.* **2011**, *47*, 772. (b) Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2009**, *62*, 1402.

(10) Detrembleur, C.; Debuigne, A.; Hurtgen, M.; Jérôme, C.; Pinaud, J.; Fèvre, M.; Coupillaud, P.; Vignolle, J.; Taton, D. *Macromolecules* **2011**, *44*, 6397.

(11) (a) Salamone, J. C.; Israel, S. C.; Taylor, P.; Snider, B. *Polymer* **1973**, *14*, 639. (b) Yuan, J.; Antonietti, M. *Macromolecules* **2011**, *44*, 744. (c) Men, Y.; Drechsler, M.; Yuan, J. *Macromol. Rapid Commun.* **2013**, *34*, 1721.

(12) (a) Nicolas, J.; Charleux, B.; Guerret, O.; Magnet, S. *Macromolecules* **2004**, *37*, 4453. (b) Nicolas, J.; Charleux, B.; Guerret, O.; Magnet, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 6186. (c) Charleux, B.; Nicolas, J. *Polymer* **2007**, *48*, 5813. (d) Phan, T. N. T.; Bertin, D. *Macromolecules* **2008**, *41*, 1886. (e) Nicolas, J.; Guillauneuf, Y.; Lefay, C.; Bertin, D.; Gignes, D.; Charleux, B. *Prog. Polym. Sci.* **2013**, *38*, 63. (f) Detrembleur, C.; Teyssié, P.; Jérôme, R. *Macromolecules* **2002**, *35*, 1611.

(13) (a) Zhang, Q.; Wilson, P.; Li, Z.; McHale, R.; Godfrey, J.; Anastasaki, A.; Waldron, C.; Haddleton, D. M. *J. Am. Chem. Soc.* **2013**, *135*, 7355. (b) Percec, V.; Popov, A. V.; Ramirez-Castillo, E.; Monteiro, M.; Barboiu, B.; Weichold, O.; Asandei, A. D.; Mitchell, C. M. *J. Am. Chem. Soc.* **2002**, *124*, 4940. (c) Zhang, Q.; Wilson, P.; Anastasaki, A.; McHale, R.; Haddleton, D. M. *ACS Macro Lett.* **2014**, *3*, 491.

(14) (a) Wang, X. S.; Lascelles, S. F.; Jackson, R. A.; Armes, S. P. *Chem. Commun.* **1999**, 1817. (b) Nishikawa, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1999**, *32*, 2204. (c) Wang, X. S.; Armes, S. P. *Macromolecules* **2000**, *33*, 6640. (d) Bortolamei, N.; Isse, A. A.; Magenau, A. J. D.; Gennaro, A.; Matyjaszewski, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 11391. (e) Konkolewicz, D.; Krysz, P.; Góis, J. R.; Mendonça, P. V.; Zhong, M.; Wang, Y.; Gennaro, A.; Isse, A. A.

Fantin, M.; Matyjaszewski, K. *Macromolecules* **2014**, *47*, 560. (f) Texter, J.; Vasantha, V. A.; Crombez, R.; Maniglia, R.; Slater, L.; Mourey, T. *Macromol. Rapid Commun.* **2012**, *33*, 69.

(15) (a) Lowe, A. B.; McCormick, C. L. *Prog. Polym. Sci.* **2007**, *32*, 283. (b) Guinaudeau, A.; Coutelier, O.; Sandeau, A.; Mazieres, S.; Nguyen, T. H. D.; Le Drogo, V.; Wilson, D. J.; Destarac, M. *Macromolecules* **2014**, *47*, 41. (c) Alidedeoglu, A. H.; York, A. W.; McCormick, C. L.; Morgan, S. E. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 5405. (d) Chaduc, I.; Crepet, A.; Boyron, O.; Charleux, B.; D'Agosto, F.; Lansalot, M. *Macromolecules* **2013**, *46*, 6013. (e) McCormick, C. L.; Lowe, A. B. *Acc. Chem. Res.* **2004**, *37*, 312.

(16) (a) Peng, C.-H.; Fryd, M.; Wayland, B. B. *Macromolecules* **2007**, *40*, 6814. (b) Debuigne, A.; Caille, J.-R.; Detrembleur, C.; Jerome, R. *Angew. Chem., Int. Ed.* **2005**, *44*, 3439. (c) Detrembleur, C.; Debuigne, A.; Bryaskova, R.; Charleux, B.; Jerome, R. *Macromol. Rapid Commun.* **2006**, *27*, 37.

(17) (a) Debuigne, A.; Champouret, Y.; Jerome, R.; Poli, R.; Detrembleur, C. *Chem.–Eur. J.* **2008**, *14*, 4046. (b) Debuigne, A.; Poli, R.; Jerome, R.; Jerome, C.; Detrembleur, C. *ACS Symp. Ser.* **2009**, *1024*, 131.

(18) (a) Bis(trifluorosulfonyl)imide (TFSI) anions were substituted for bromine anions (Br). (b) He, H.; Zhong, M.; Adzima, B.; Luebke, D.; Nulwala, H.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2013**, *135*, 4227.

(19) (a) Debuigne, A.; Jerome, C.; Detrembleur, C. *Angew. Chem., Int. Ed.* **2009**, *48*, 1422. (b) Kermagoret, A.; Debuigne, A.; Jérôme, C.; Detrembleur, C. *Nat. Chem.* **2014**, *6*, 179.

(20) Bryaskova, R.; Detrembleur, C.; Debuigne, A.; Jerome, R. *Macromolecules* **2006**, *39*, 8263.