

# Aqueous RAFT Polymerization of Imidazolium-Type Ionic Liquid Monomers: En Route to Poly(ionic liquid)-Based Nanoparticles through RAFT Polymerization-Induced Self-Assembly

Biao Zhang, Xibo Yan, Pierre Alcouffe, Aurelia Charlot,\* Etienne Fleury, and Julien Bernard\*

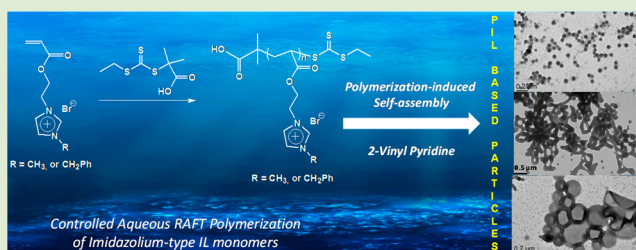
Université de Lyon, Lyon, F-69003, France

INSA-Lyon, IMP, Villeurbanne, F-69621, France

CNRS, UMR 5223, Ingénierie des Matériaux Polymères, Villeurbanne, F-69621, France

## S Supporting Information

**ABSTRACT:** The synthesis by aqueous RAFT polymerization of hydrophilic narrowly dispersed imidazolium-based poly(ionic liquid)s ( $\bar{M}_n$  typically below 1.20) is reported. Full monomer conversion is achieved within hours and high end-group fidelity of the living end groups affords the preparation of well-defined block copolymers. The resulting poly(ionic liquid) macroRAFT agents are finally exploited to polymerize 2-vinylpyridine in water and generate PIL-based nanoparticles of various morphologies (spheres, vesicles, or worms) in a one-pot surfactant-free process.



Polymeric ionic liquids (PILs) are a relatively new class of polymer electrolytes receiving ever-growing interest for their applications in the fields of catalysis,<sup>1</sup> gas separation,<sup>2</sup> multifunctional materials,<sup>3</sup> electrochemistry,<sup>4</sup> or energy-related technologies.<sup>5</sup> Standard synthetic routes to PILs rely on chain growth polymerization of IL, step growth polymerization, or postmodification of neutral polymers through quaternization and ion exchange.<sup>6</sup> In view of optimizing the performances of PIL-based materials, considerable efforts have been paid to the production of PIL chains with predetermined molecular weight and low molecular weight distribution or block copolymer architectures capable of phase-separating into a range of highly ordered morphologies.<sup>7</sup> Access to such tailor-made PILs has notably benefited from the outstanding advances in the area of the controlled radical polymerization techniques (CRP). Polymers possessing pendent imidazolium groups are by far the most investigated PILs. Depending on the nature of the imidazolium-based monomer (*N*-vinyl, (meth)acrylic, or styrenic derivatives), the growth of precisely defined PIL chains has been achieved by nitroxide-mediated polymerization (NMP),<sup>7c,8</sup> atom transfer radical polymerization (ATRP),<sup>9</sup> reversible addition–fragmentation chain transfer polymerization (RAFT),<sup>10</sup> or cobalt-mediated radical polymerization (CMRP).<sup>11</sup> Despite the affinity of numerous IL monomers for water (especially when the counteranion is Cl<sup>−</sup> or Br<sup>−</sup>) and the potential industrial applications of aqueous PIL formulations as stabilizers or lattices, the use of water as polymerization medium remains mostly unexplored in homogeneous conditions. To our knowledge, the only example of well-defined PILs generated by CRP in water has been recently reported by Detrembleur and co-workers.<sup>11b</sup> Controlled polymerizations of

*N*-vinyl-3-alkylimidazolium monomers were observed at moderate temperatures (30–50 °C) in the presence of an alkyl-cobalt(III) complex or commercially available bis-(acetylacetonato)-cobalt(II)/*tert*-butylhydroperoxide redox bi-component system. Surprisingly, despite the well-established compatibility of the RAFT technique with aqueous (homogeneous or dispersed) media in acidic or neutral pH conditions and a wide range of water-soluble monomers,<sup>12</sup> water has not been investigated as a solvent for the RAFT polymerization of IL monomers.

In the present contribution, we investigate the aqueous RAFT polymerization of two imidazolium-based monomers, namely, 1-[2-acryloyloethyl]-3-methylimidazolium bromide (AEMIBr) and 1-[2-acryloyloethyl]-3-benzylimidazolium bromide (AEBIBr; Scheme 1). We demonstrate that the use of a conventional trithiocarbonate chain transfer agent affords the rapid growth of PIL chains with controlled molar mass and high end-group fidelity of the living end-group. The resulting macroRAFT agents are further exploited to perform the first example of one-pot RAFT preparation of PIL-based block copolymer nanoparticles in water according to the principles of polymerization-induced self-assembly (PISA)<sup>13</sup> and to generate PIL-based particles with morphology evolving from spheres to worms and vesicles.

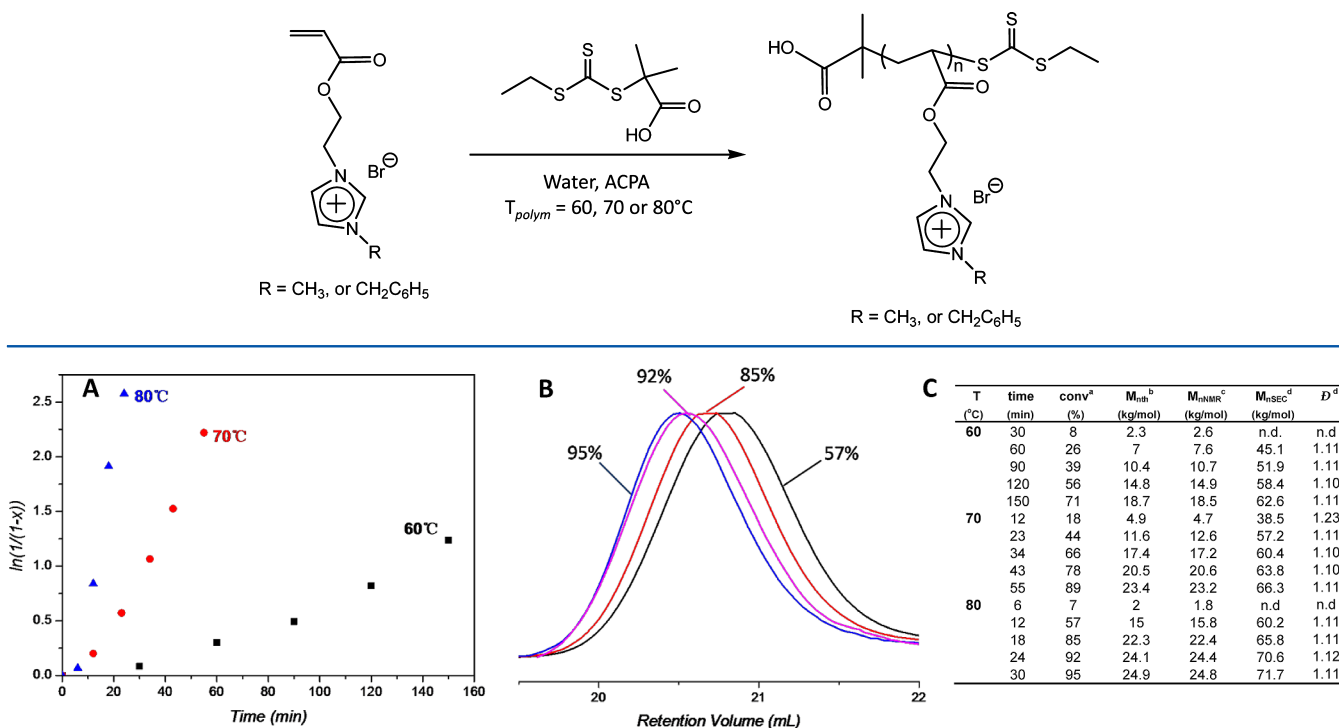
Aqueous RAFT polymerizations of AEMIBr were investigated at 60, 70, and 80 °C in the presence of a hydrolytically stable trithiocarbonate (TTC), *S*-ethyl-*S'*-( $\alpha,\alpha'$ -dimethyl- $\alpha''$ -

Received: July 30, 2015

Accepted: August 21, 2015

Published: August 28, 2015

## Scheme 1. Aqueous RAFT Polymerization of Imidazolium-Based Acrylates

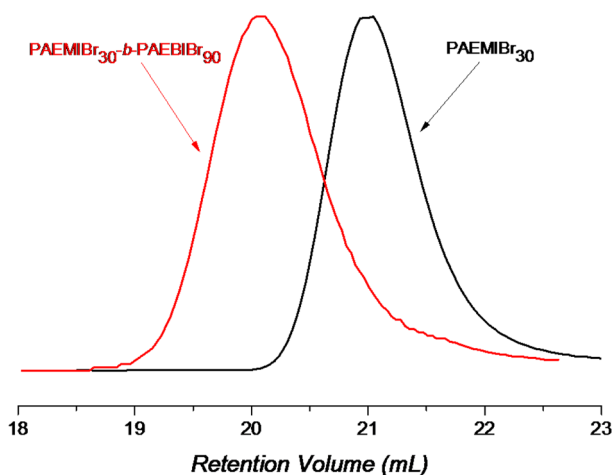


**Figure 1.** (A) Pseudo-first-order kinetic plots for the aqueous RAFT-mediated homopolymerizations of AEMIBr at 60 (blue triangles), 70 (red diamonds), and 80 °C (black squares; [AEMIBr] = 2.56 mol·L<sup>-1</sup>, 40% wt; [AEMIBr]/[EMP]/[ACPA] = 100/1/0.2); (B) Evolution of the SEC traces for the aqueous EMP-mediated polymerization of AEMIBr at 80 °C (SEC analyses performed in DMF/bis(trifluoromethylsulfonyl)imide lithium salt (LiTFSI) as eluent after anion exchange of the bromide counterions by LiTFSI); (C) Main features of the resulting PIL homopolymers. <sup>a</sup>Determined by <sup>1</sup>H NMR; <sup>b</sup>Calculated from monomer conversion; <sup>c</sup>Determined from relative integration of TTC chain end group and polymer backbone peaks; <sup>d</sup>Determined by SEC (in DMF/LiTFSI, PS standards).

acetic acid)trithiocarbonate (EMP), as chain transfer agent (CTA),<sup>14</sup> 4,4'-azobis(4-cyanovaleric acid) (ACPA) as initiator, and trioxane as internal standard ([AEMIBr] = 2.56 mol·L<sup>-1</sup>, 40% wt; [AEMIBr]/[EMP]/[ACPA] = 100/1/0.2). To overcome solubility issues in water, the CTA was systematically first dissolved in the ionic monomer. Aliquots of polymerization medium were withdrawn at selected time intervals and monomer conversions versus time were monitored by <sup>1</sup>H NMR analyses (see Supporting Information). Experimental data for the EMP-mediated homopolymerizations of AEMIBr are collected in Figure 1. After a short inhibition period (~5 and 30 min at 80 and 60 °C, respectively), linear pseudo-first order kinetic plots are observed up to high AEMIBr conversions (see Figure 1A). Evolution of the molecular weight and molecular weight distribution with conversion is given in Figure 1B. Consistent with a controlled polymerization process, molecular weights gradually increase with conversion and remain narrowly distributed ( $\bar{D} \leq 1.12$ , with the exception of aliquots withdrawn at the early stage of the polymerization). Accordingly, an excellent agreement between the experimental molecular weight estimated by <sup>1</sup>H NMR from relative integration of polymer backbone protons (methine protons) and TTC chain end group protons (methylene protons) and theoretical molecular weight is observed. At this point, it is important to note that when aqueous polymerization of AEMIBr is performed at 80 °C, high conversion of AEMIBr (95%) can be reached in 30 min without detection of bimodalities (see SEC traces in Figure 1B). As illustrated by Table S1 and Figure S8, PIL molecular weight can be easily

tuned by adjusting the [AEMIBr]/[EMP] ratio (40/1, 100/1 or 400/1). In all cases, polymerizations proceed in a controlled fashion and SEC traces remain sharp and unimodal even at the highest [AEMIBr]/[EMP] ratio (400) and conversion (71%,  $M_{n,SEC} = 149000$  g·mol<sup>-1</sup> after ionic exchange;<sup>15</sup>  $\bar{D} = 1.19$ , see Supporting Information). To emphasize the general applicability of aqueous imidazolium-based acrylate RAFT polymerization, we further investigated the RAFT polymerization of a second ionic liquid monomer (AEBIBr) in water at 70 and 80 °C ([AEBIBr] = 1.98 mol·L<sup>-1</sup>, 40% wt; [AEBIBr]/[EMP]/[ACPA] = 100/1/0.2). As observed for AEMIBr, the polymerization of AEBIBr is complete within hours (94% of conversion after 2 h of reaction at 80 °C) and exhibits an ideal behavior up to high conversion. Polymers having narrow molar mass distribution ( $\bar{D}$  typically below 1.20) and experimental molar mass concurring with theoretical values are obtained (see Table S2 and Figures S9 and S10). To assess the formation of well-controlled living chains, the blocking efficiency of the resulting PIL macroCTAs was subsequently evaluated.

Following purification procedures (dialysis and freeze-drying), a PAEMIBr macroCTA (PAEMIBr<sub>30</sub>,  $M_{n,NMR} = 7900$  g·mol<sup>-1</sup>;  $M_{n,SEC} = 47200$  g·mol<sup>-1</sup>;  $\bar{D} = 1.19$ ) was then used for the RAFT block copolymerization of AEBIBr in water. As illustrated by the SEC traces given in Figure 2, the chain extension of PAEMIBr<sub>30</sub> proceeds effectively resulting in the generation of unimodal and narrow molecular weight distributed PIL block copolymer (PAEMIBr<sub>30</sub>-*b*-PAEBIBr<sub>90</sub>,  $M_{n,th} = 38400$  g·mol<sup>-1</sup>,  $M_{n,NMR} = 39200$  g·mol<sup>-1</sup>;  $M_{n,SEC} = 89200$  g·mol<sup>-1</sup>  $\bar{D} = 1.21$ ). Similar transfer efficiency and quality

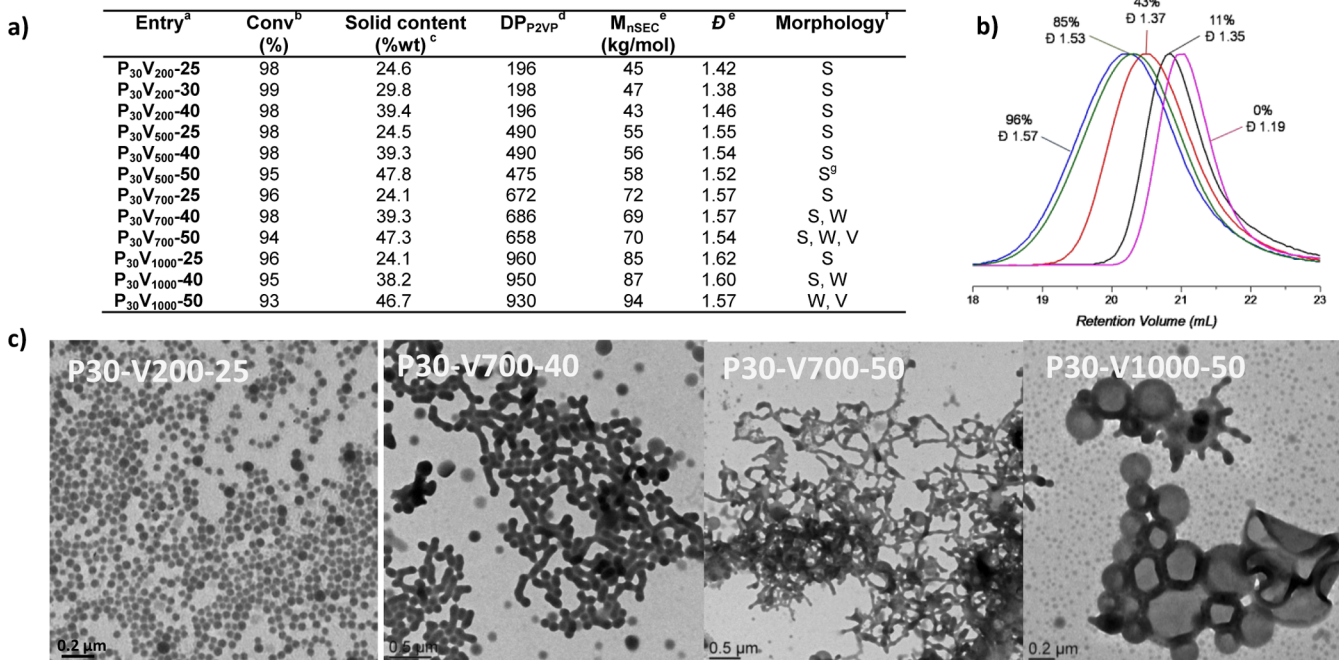


**Figure 2.** SEC traces of PAEMIBr macroCTA and PAEMIBr-*b*-PAEBIBr block copolymer (SEC in DMF/LiTfSI after anion exchange).

of control is observed for the chain extension of PAEMIBr macroCTA with *N*-isopropylacrylamide (see Figure S12).

The control and the livingness of RAFT polymerization of IL monomers in water finally prompted us to explore the preparation of concentrated aqueous solutions of PIL-based nanoparticles. Whereas several examples of poly(ionic liquid) colloidal particles have been reported over the past decade,<sup>16</sup> the generation of PIL-based nanoparticles with controlled morphologies using PISA concepts has not been explored yet.

To do so, the RAFT emulsion polymerization of 2-vinylpyridine (2VP), a precursor of *N*-alkylpyridinium-based poly(ionic liquid) chains, was investigated in the presence of PAEMIBr<sub>30</sub> macroCTA at 80 °C. Series of PAEMIBr<sub>30</sub>-*b*-P2VP<sub>*x*</sub> block copolymers were prepared by tuning the total solids concentration from 25 to 50 wt % (at full monomer conversion) and the targeted degree of polymerization (DP) of the P2VP block from 200 to 1000. 2VP polymerization data are given in Figure 3. Complete conversion of 2VP is achieved within hours (Figure S14). SEC traces of PAEMIBr<sub>30</sub>-*b*-P2VP<sub>*x*</sub> block copolymers are clearly shifted toward higher molar masses versus PAEMIBr<sub>30</sub> and block copolymers dispersity gradually increases with targeting high degree of polymerization (from  $\bar{D} \sim 1.38$ – $1.62$  for PAEMIBr<sub>30</sub>-*b*-P2VP<sub>200</sub> and PAEMIBr<sub>30</sub>-*b*-P2VP<sub>1000</sub>, respectively). As revealed by TEM studies, the resulting PAEMIBr<sub>30</sub>-*b*-P2VP<sub>*x*</sub> block copolymers formed nanoparticles with various shapes depending on the length of the P2VP block and on the total solids concentration. PISA targeting DP  $\leq 500$  for the P2VP block reproducibly afforded spherical particles with narrow size distribution ( $D_h$  ranging from 80 nm (PDI = 0.036) to 180 nm (PDI = 0.051) for P<sub>30</sub>V<sub>200</sub>-25 and P<sub>30</sub>V<sub>500</sub>-40, respectively), whatever the total solids concentration. When higher DP are targeted for the P2VP block, increasing the total solids concentration above 25% leads to the observation of worms, branched worms, and vesicles, as reported in previous reports of PISA (see Figure 3).<sup>13</sup> Finally, we undertook cross-linking of the P2VP inner domains with 1,4-dibromobutane (0.1 equiv per 2VP repeating unit).<sup>17</sup> This procedure allowed for maintaining the integrity of the nano-objects in good solvents of both blocks (see DLS and



**Figure 3.** (a) Features of PAEMIBr<sub>30</sub>-*b*-P2VP<sub>*x*</sub> block copolymers prepared by RAFT polymerization-induced self-assembly. <sup>a</sup>The notation P<sub>30</sub>V<sub>200</sub>-25 refers to a PAEMIBr<sub>30</sub>-mediated polymerization of 2VP targeting a DP of 200 and a total solids content of 25% wt, respectively. All the polymerizations were performed in water for 14 h at 80 °C using PAEMIBr<sub>30</sub> as macroCTA (80.3 mg,  $1.0 \times 10^{-5}$  mol·L<sup>-1</sup>) and VA-044 as initiator ([macroCTA]<sub>0</sub>/[VA-044]<sub>0</sub> = 2); <sup>b</sup>Determined by <sup>1</sup>H NMR; <sup>c</sup>Solid content = (mass of 2VP × conv + mass of PAEMIBr<sub>30</sub>)/(total mass of the reaction mixture); <sup>d</sup>Determined from 2VP conversion; <sup>e</sup>Determined by SEC (in DMF/LiTfSI, PS standards); <sup>f</sup>Morphologies observed by TEM; S, W, and V refer to spheres, worms, and vesicles, respectively; <sup>h</sup>Few vesicles were also observed in this sample. (b) Evolution of SEC traces for PAEMIBr<sub>30</sub>-mediated polymerization of 2VP at 80 °C ([2VP]/[PAEMIBr<sub>30</sub>] = 700). (c) TEM pictures of nano-objects obtained by RAFT polymerization-induced self-assembly.

TEM pictures of cross-linked nanoparticles in acidic water, Figures S15–16), while advantageously transforming pendent pyridine groups located in the core of the nanoparticles into pyridinium bromide units.

In summary, aqueous RAFT polymerization was successfully exploited for the preparation of well-defined poly(ionic liquid)s. Homopolymers with DP up to 300 and dispersity below 1.20 were obtained within hours using EMP as chain transfer agent. Achievement of high chain-end fidelity allowed for effective chain extension of the PIL chains with ionic or neutral monomers and paved the way to the generation of stable PIL-based nanoparticles with various morphologies using the PISA concept. These features make these nanoparticles promising candidates as binders for lithium-ion battery applications.<sup>5b</sup>

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Experimental methods, kinetic studies, full characterization of the homopolymers, block copolymers, and nanolatexes. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00534.

(PDF)

## ■ AUTHOR INFORMATION

### Corresponding Authors

\*E-mail: aurelia.charlot@insa-lyon.fr.

\*E-mail: julien.bernard@insa-lyon.fr.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

B. Z. acknowledges the CSC for a Ph.D. grant. The authors thank Dr. Sandra Binauld and Pr. Eric Drockenmuller for fruitful discussions. The authors also acknowledge the CT $\mu$  for access to microcopy facilities.

## ■ REFERENCES

- (1) Fellingner, T.-M.; Thomas, A.; Yuan, J.; Antonietti, M. *Adv. Mater.* **2013**, *25*, 5838.
- (2) Carlisle, T. K.; Wiesenauer, E. F.; Nicodemus, G. D.; Gin, D. L.; Noble, R. D. *Ind. Eng. Chem. Res.* **2013**, *52*, 1023.
- (3) (a) Zhang, K.; Feng, X.; Sui, X.; Hempenius, M. A.; Vancso, G. J. *Angew. Chem., Int. Ed.* **2014**, *53*, 13789. (b) Cui, J.; Zhu, W.; Gao, N.; Li, J.; Yang, H.; Jiang, Y.; Seidel, P.; Ravoo, B. J.; Li, G. *Angew. Chem., Int. Ed.* **2014**, *53*, 3844. (c) Obadia, M.; Mudraboyina, B. P.; Serghei, A.; Montarnal, D.; Drockenmuller, E. *J. Am. Chem. Soc.* **2015**, *137*, 6078.
- (4) Yoo, S. J.; Li, L.-J.; Zeng, C.-C.; Little, R. D. *Angew. Chem., Int. Ed.* **2015**, *54*, 3744.
- (5) (a) Kim, T.-Y.; Lee, H.-W.; Stoller, M.; Dreyer, D. R.; Bielawski, C. W.; Ruoff, R. S.; Suh, K.-S. *ACS Nano* **2011**, *5*, 436. (b) Eshetu, G. G.; Armand, M.; Scrosati, B.; Passerini, S. *Angew. Chem., Int. Ed.* **2014**, *53*, 13342.
- (6) Yuan, J.; Mecerreyes, D.; Antonietti, M. *Prog. Polym. Sci.* **2013**, *38*, 1009.
- (7) (a) Gu, Y.-Y.; Lodge, T. P. *Macromolecules* **2011**, *44*, 1732. (b) Ye, Y.; Sharick, S.; Davis, E. M.; Winey, K. I.; Elabd, Y. A. *ACS Macro Lett.* **2013**, *2*, 575. (c) Weber, R. L.; Ye, Y.; Schmitt, A. L.; Banik, S. M.; Elabd, Y. A.; Mahanthappa, M. K. *Macromolecules* **2011**, *44*, 5727. (d) 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. (e) Jiang, Y.; Freyer, J. L.; Cotanda, P.; Brucks, S. P.; Killops, K. L.; Bandar, J. S.;

Torsitano, C.; Balsara, N. P.; Lambert, T. H.; Campos, L. M. *Nat. Commun.* **2015**, *6*, 5950.

(8) Green, M. D.; Choi, J.-H.; Winey, K. I.; Long, T. E. *Macromolecules* **2012**, *45*, 4749.

(9) (a) Tang, H.; Tang, J.; Ding, S.; Radosz; Shen, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 1432. (b) Ma, X.; Ashaduzzaman, Md.; Kunitake, M.; Crombez, R.; Texter, J.; Slater, L.; Mourey, T. *Langmuir* **2011**, *27*, 7148. (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, M. *Macromolecules* **2014**, *47*, 6601.

(10) (a) Vijaykrishna, K.; Jewrajka, S. K.; Ruiz, A.; Marcilla, R.; Pomposo, J. A.; Mecerreyes, D.; Taton, D.; Gnanou, Y. *Macromolecules* **2008**, *41*, 6299. (b) Mori, H.; Yahagi, M.; Endo, T. *Macromolecules* **2009**, *42*, 8082.

(11) (a) Detrembleur, C.; Debuigne, A.; Hurtgen, M.; Jérôme, C. *Macromolecules* **2011**, *44*, 6397. (b) Cordella, D.; Kermagoret, A.; Debuigne, A.; Riva, R.; German, I.; Isik, M.; Jérôme, C.; Mecerreyes, D.; Taton, D.; Detrembleur, C. *ACS Macro Lett.* **2014**, *3*, 1276.

(12) McCormick, C. L.; Sumerlin, B. S.; Lokitz, B. S.; Stempka, J. E. *Soft Matter* **2008**, *4*, 1760.

(13) (a) Charleux, B.; Delaittre, G.; Rieger, J.; D'Agosto, F. *Macromolecules* **2012**, *45*, 6753. (b) Warren, N. J.; Armes, S. P. *J. Am. Chem. Soc.* **2014**, *136*, 10174. (c) Zhang, Q.; Zhu, S. *ACS Macro Lett.* **2015**, *4*, 755–758.

(14) Convertine, A. J.; Lokitz, B. S.; Vasileva, Y.; Myrick, L. J.; Scales, C. W.; Lowe, A. B.; McCormick, C. L. *Macromolecules* **2006**, *39*, 1724.

(15) He, H.; Zhong, M.; Adzima, B.; Luebke, D.; Nulwala, H.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2013**, *135*, 4227.

(16) (a) Men, Y.; Kuzmicz, D.; Yuan, J. *Curr. Opin. Colloid Interface Sci.* **2014**, *19*, 76. (b) Yan, F.; Texter, J. *Chem. Commun.* **2006**, 2696. (c) Tauer, K.; Weber, N.; Texter, J. *Chem. Commun.* **2009**, 6065. (d) Yuan, J.; Antonietti, M. *Macromolecules* **2011**, *44*, 744. (e) Tokuda, M.; Shindo, T.; Minami, H. *Langmuir* **2013**, *29*, 11284. (f) Tokuda, M.; Sanada, T.; Shindo, T.; Suzuki, T.; Minami, H. *Langmuir* **2014**, *30*, 3406. (g) Killops, K. L.; Brucks, S. D.; Rutkowski, K. L.; Freyer, J. L.; Jiang, Y.; Valdes, E. R.; Campos, L. M. *Macromolecules* **2015**, *48*, 2519. (h) Yu, R.; Tauer, K. *Polym. Chem.* **2014**, *5*, 5644.

(17) Klinger, D.; Wang, C. X.; Connal, L. A.; Audus, D. J.; Jang, S. G.; Kraemer, S.; Killops, K. L.; Fredrickson, G. H.; Kramer, E. J.; Hawker, C. J. *Angew. Chem., Int. Ed.* **2014**, *53*, 7018.