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Synthesis by RAFT and Ionic Responsiveness of Double Hydrophilic Block Copolymers Based on Ionic Liquid Monomer Units

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ABSTRACT: Three imidazolium-based ionic liquid (IL) monomers, namely, 3-(1-ethyl imidazolium-3-yl)propylmethacrylamido bromide (IL-**1**), 2-(1-methylimidazolium-3-yl)ethyl methacrylate bromide (IL-**2**), and 2-(1-ethylimidazolium-3-yl)ethyl methacrylate bromide (IL-**3**), and methacrylic acid (MAA) were polymerized by the reversible addition fragmentation chain transfer (RAFT) process in methanolic solutions at 70 °C, using either 2-cyanopropyl dithiobenzoate (CTA-**1**) or (4-cyanopentanoic acid)-4-dithiobenzoate (CTA-**2**) as chain transfer agents (CTAs). Under these conditions, polymers exhibited molar masses predetermined by the initial molar ratio of the monomers to the dithioester precursor, as evidenced by ^{1}H NMR spectroscopy from chain ends analysis. These hydrophilic polymers were subsequently used as macro-CTAs in chain extension experiments in aqueous or in alcoholic solutions, affording IL-based double hydrophilic block copolymers (DHBCs) of the type PIL-**1**-*b*-PAm, PMAA-*b*-PIL-**2** and PMAA-*b*-PIL-**3**, where PAm and PIL stand for polyacrylamide and polymeric ionic liquid. These DHBCs could be further manipulated and made to self-assemble in micelle-like structures in water by exchanging the bromide (Br^-) counteranion of IL blocks for $^-N(SO_2CF_3)_2$. This anion exchange indeed turned the solution properties of the PIL blocks from hydrophilic to hydrophobic, as verified on the corresponding IL-based homopolymers which were immiscible with water after the anion switch. Investigations by ^{1}H NMR evidenced that the diblock copolymers exhibited salt-responsive behavior in aqueous solutions: anion exchange induced the formation of water-soluble micellar aggregates consisting of hydrophobic $^-N(SO_2CF_3)_2$-based IL blocks at the core stabilized by water-soluble PAm or PMAA at the shell.

Introduction

Ionic liquids (ILs) are organic salts that exhibit a low melting point; due to their unique physicochemical properties they currently receive increasing attention. ILs are chemically composed of an organic asymmetric cation (e.g., imidazolium, pyridinium, or tetraalkylammonium) and an inorganic anion such as halide, tetrafluoroborate, hexafluorophosphate, triflate, amidotriflate, etc.[1–11] The solubility of ILs is mainly determined by the anion which can be tuned, ranging from a high solubility to inmiscibility in water by simple anion exchange (ionic sensitivity). ILs are also attractive for environmental concerns and are often viewed as "green solvents" owing to their low vapor pressure, fire resistance, and chemical and thermal stability.[1–11] Besides their use in catalysis,[5,11] organic synthesis,[12,13] chemical separation,[14] and chemical storage and/or transportation,[15] applications of ILs have also emerged as a productive area in macromolecular science,[16,17] for instance as highly polar solvents in polymer synthesis,[16] as high performance plasticizers,[18] and as compatibilizers in nanocomposites and functional polymers.[19–24] In this respect, polymeric ionic liquids (PILs) made out of ILs are described as a new class of polymeric materials with unique properties combining those of ILs mentioned above and specific properties of polymers.[6,19–21,25–39] PILs are finding innovative applications in emerging areas such as biosensors,[25] supports of catalysts[26] as polymeric surfactants for the construction of porous polymers,[27,28] high CO_2 absorbing resins,[29] polymer electrolytes for electrochemical devices,[20,30,31] and microwave absorbing materials.[32]

Surprisingly and to the best of our knowledge, only Waymouth et al. have considered the possibility to arrange IL segments in a block copolymer architecture.[40,41] This was achieved via postsynthesis modification of neutral block copolymers based on polystyrene derived by nitroxide-mediated polymerization. The corresponding imidazolium-functionalized diblock copolymers were found to self-assemble in toluene, forming elongated micelles with the IL block as the core. It was also shown that these micelles could sequester a few water molecules for each IL repeating unit.

More recently, in their reports on the self-assembly of polybutadiene-*b*-poly(ethylene oxide) amphiphilic block copolymer in IL, Lodge et al.[42,43] showed that micellar structures (spherical and wormlike micelles as well as vesicles) could be achieved, for instance by varying the size of the corona, polybutadiene in this case. In contrast to the case of aqueous solutions, IL solutions of these block copolymers exhibited a temperature-independent micellar behavior. This could be further exploited to transfer the block copolymer micelles from IL to water by a thermo-reversible process.[43] These reports indicate that fields of block copolymers and of ionic liquids may benefit from their cross fertilization and that further investigations may well unveil interesting phenomena.

In this contribution, we report the synthesis of a series of PIL-based double hydrophilic block copolymers (DHBCs)[44] by sequential reversible addition fragmentation chain transfer (RAFT) polymerization of IL-based monomers and acrylamide or methacrylic acid. These novel block copolymers combine the anionic sensitivity of PILs with the self-assembly properties of block copolymers in water used as a selective solvent for one of the two blocks. Thus, it has been first verified that RAFT-

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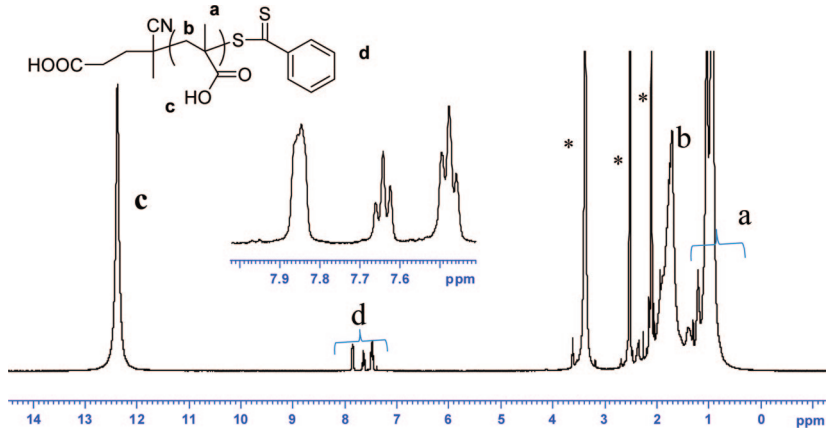


Figure 1. ^{1}H NMR (DMSO-d_6) of PMAA prepared from CTA **2** (entry 2, Table 1).

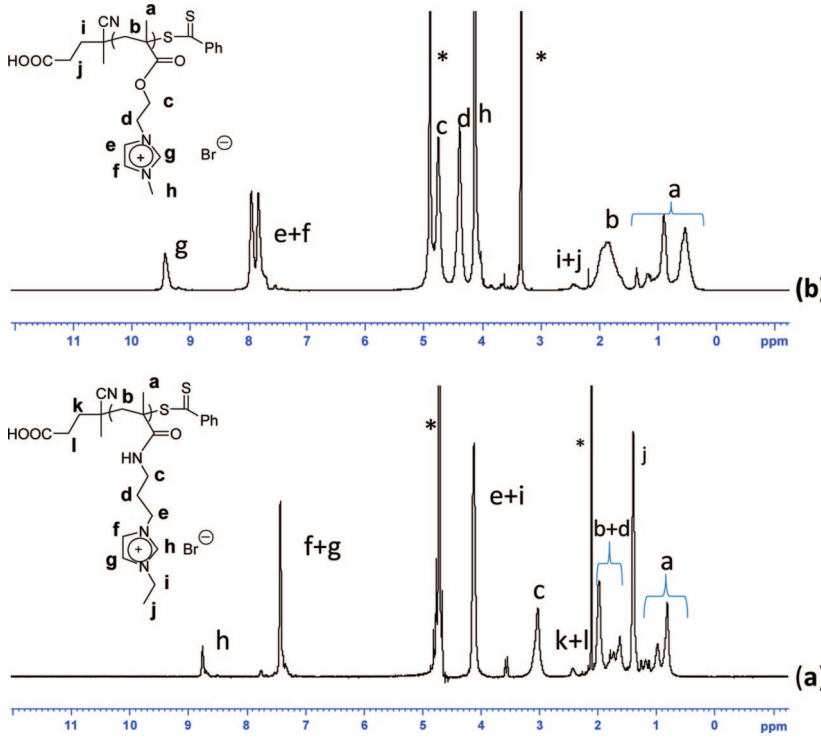


Figure 2. ^{1}H NMR of (a) PIL-**1** in D_2O (entry 7, Table 2); (b) PIL-**2** in methanol-d_4 (entry 9, Table 2).

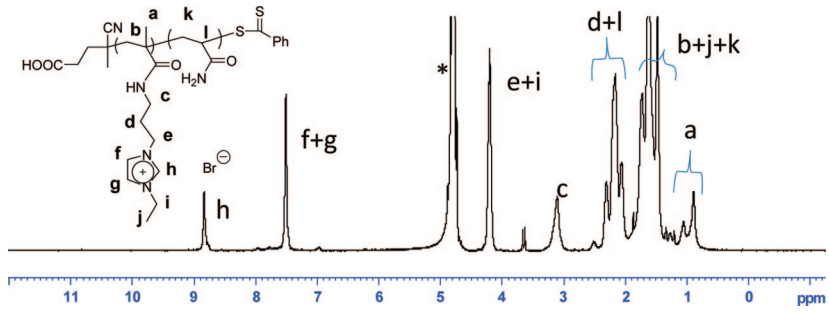


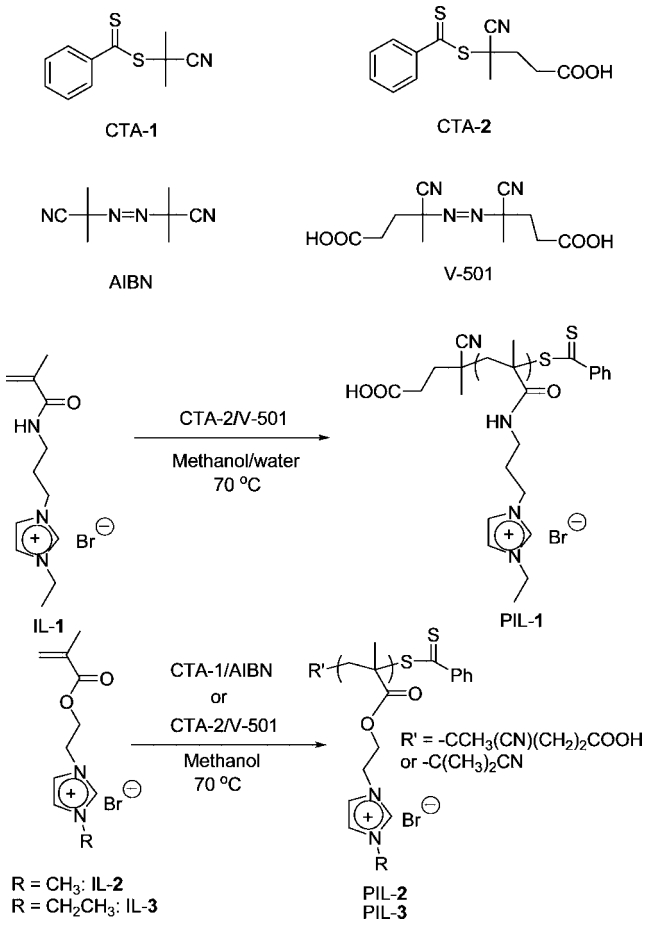
Figure 3. ^{1}H NMR of PIL-**1**-*b*-PAm in D_2O (entry 12, Table 3).

mediated polymerization of the IL-based monomers in methanolic solutions leads to well-defined PILs, which to the best of our knowledge has never been described before. Chain extension experiments by RAFT performed in aqueous solutions then afforded the targeted water-soluble DHBCs. As evidenced by ^{1}H NMR and light scattering characterization, such IL-based DHBCs show anion sensitivity in water, their self-assembly giving rise to micelles consisting of hydrophobic PIL blocks at the core and water-soluble polyacrylamide or poly(methacrylic acid) at the shell.

Experimental Section

Materials. All chemical manipulations were carried out under inert conditions. Azobis(2-methylpropionitrile) (AIBN, 99%) and 4,4′-azobis(4-cyanopentanoic acid) (V-501) were received from Aldrich and were purified by recrystallization from

Scheme 1. Homo Polymerization of Ionic Liquid Monomers (IL-1, IL-2 and IL-3) by RAFT



methanol. Trimethylsilyldiazomethane (Aldrich, 2 M solution in diethyl ether) was used as received. Methacrylic acid (MAA) and methyl methacrylate (MMA) were distilled under reduced pressure prior to use. Acrylamide (Am) was recrystallized from chloroform. Bromobenzene (Fluka, 99%), carbon disulfide (Sigma-Aldrich, 99.9%), and iodine crystals (Fluka) were used as received. Magnesium turnings (Unilab) were dried before use. RAFT agents, namely 2-cyanopropyl dithiobenzoate (CTA-1) and (4-cyanopentanoic acid)-4-dithiobenzoate (CTA-2), were prepared according to the literature procedure.[45,46] The ionic liquid monomers, IL-2 and IL-3 were prepared as per literature procedure.[47]

Instrumentation. ^{1}H NMR spectra were recorded on Bruker AC-400 spectrometer in appropriate deuterated solvents. Dynamic light scattering (DLS) experiments were performed (at four different angles 120°, 90°, 70°, and 50°, with a sample concentration of 1 g/L in water) using ALV Laser Goniometer, which consists of 22 mW He−Ne linear polarized laser with 632.8 nm wavelength and an ALV-5000/EPP Multiple Tau Digital Correlator with 125 ns initial sampling time. Molecular weights of PMMA were determined by gel permeation chromatography (GPC) using a PL-GPC50plus Integrated GPC System equipped with TSK columns (G2000, G3000, and G4000HXL with pore sizes of 20, 75, and 200 Å respectively, connected in series) and dual detector (RI and UV); THF was used as the mobile phase at a flow rate of 1 mL/min. Water soluble homo and block copolymers were injected in Varian 2510 GPC system with TSKgel super AW columns (AW2500, AW4000, and AW5000 with pore sizes of 25, 450, and 1000 Å, respectively, connected in series) equipped with dual detector (RI and UV) using water (with 8.5 g/L $NaNO_3$) as a mobile phase at a flow rate of 0.4 mL/min.

Synthesis of 3-(1-Ethylimidazolium-3-yl)propylmethacrylamido Bromide (IL-1). 3-(1-Ethylimidazolium-3-yl)propylmethacrylamido bromide (IL-**1**) was synthesized similarly to the methacrylate monomers. In a first stage, to a solution of 10 g (0.079 mol) of 1-aminepropyl imidazole in 30 mL of dry DMF, a solution of 10.4 mL (0.1 mol) of acryloyl choride in dry DMF was added dropwise at 0 °C. The reaction mixture was warmed to 20 °C and kept for stirring. The reaction was stopped after 14 h by precipitation into ethyl acetate. The product was dissolved in saturated aqueous sodium bicarbonate solution and recovered by extraction in dichloromethane. The extracts were dried over magnesium sulfate and the solvent was removed in vacuum. The product, *N*-imidazole 3-propylmethacrylamide, was obtained in a 60% yield without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (s, 1H, N−C*H*−N), 7.01 (s, 1H, N−*H*C═CH−N), 6.94 (s, 1H, N−HC═C*H*−N), 6.70 (bs, 1H, N*H*), 5.68 and 5.32 (AB, 2H, vinyl), 3.99 (t, 2H, CH_2-Im), 3.31 (t, 2H, CH_2−NH), 2.04 (m, 2H, CH_2−CH_2−CH_2), 1.93 (s, 3H, CH_2−CH_3).

Next, 3-(1-ethylimidazolium-3-yl)propylmethacrylamido bromide (IL-**1**) was synthesized by quaternization of *N*-imidazole 3-propylmethacrylamide. Under vigorous stirring, 5.67 g (0.052 mol) of bromoethane was added dropwise to 7.17 g (0.039 mol) of *N*-imidazole 3-propylmethacrylamide in a 250 mL one-neck round-bottom flask and the mixture was refluxed for 16 h. The resulting ionic liquid was allowed to cool to room temperature and was then washed several times with ethyl acetate. The product was filtered and dried in a vacuum oven until constant weight (8,05 g yield: 66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.23 (s, 1H, N−C*H*−N), 7.83 (s, 1H, N−*H*C═CH−N), 7.47 (s, 1H, N−HC═C*H*−N), 5.93 and 5.32 (AB, 2H, vinyl), 4.35 (m, 4H, CH_2-Im-CH_2), 3.65 (t, 2H, CH_2-NH), 2.25 (m, 2H, CH_2−CH_2-CH_2), 1.96 (s, 3H, ═C−CH_3), 1.57 (t, 3H, CH_2−CH_3). ^{13}C NMR (100 MHz, CD_3OD): δ 170.92, 141.14, 136.96, 124.11, 121.41, 119.36, 48.80, 46.44, 37.54, 31.01, 19.88, and 16.29.

Polymerization Procedure. All polymerizations were carried out under inert conditions using Schlenk techniques.

RAFT Polymerization of MAA. A 10 mL Schlenk tube was flame dried and charged with 2 g (23.23×10^{-3} mol) of MAA, 64.8 mg (23.23×10^{-5} mol) of CTA-2, 6.5 mg (23.23×10^{-6} mol) of initiator V-501 and 4 mL of methanol. The Schlenk tube was subjected to five freeze thaw cycles and placed in a thermostatted oil bath previously maintained at 70 °C. Polymerization reaction was quenched after appropriate time by sudden cooling. The obtained polymer was washed with cold acetone (3 × 20 mL) and dried in vacuum for 10 h to remove unreacted MAA. The corresponding PMAA was obtained as as pink color powder: ^{1}H NMR (DMSO-d_6): δ 12.37 ppm (s, broad, 1H, COO*H* of PMAA); 7.84 (m, 2H, *o*-2H-Ph of chain end CTA); 7.66 (m, 1H, *p*-H-Ph of chain end CTA); 7.49 (m, 2H, *m*-2H-Ph of chain end CTA), 2.35 ppm (m, 4H, CH_2CH_2 of chain end from CTA); 2−0.5 ppm (m, 5H, methylene and methyl protons of PMAA).

RAFT Polymerization of MMA. MMA was polymerized using CTA-**1** or CTA-**2**. In a typical procedure, a 10 mL Schlenk tube was flame dried and charged with 1 g (10×10^{-3} mol) of MMA, 46.3 mg (0.166×10^{-3} mol) of CTA-2, 4.63 mg (0.166×10^{-4} mol) of initiator V-501 and 4 mL of THF. The Schlenk tube was subjected to five freeze−thaw cycles and placed in a thermostated oil bath previously maintained at 70 °C. Polymerization reaction was quenched after appropriate time by sudden cooling. The obtained polymer was washed with cold diethyl-ether (3 × 20 mL) and dried in vacuum for 10 h.

Table 1. RAFT Polymerization of MAA[a]

entry	[MAA]:[CTA]:[INT]	time (h)	conv (%)	$M_{n\,theo}$[b] (g·mol^{-1})	$M_{n\,NMR}$[c] (g·mol^{-1})	$M_{n\,GPC}$[d] (g·mol^{-1})	PDI[d]
1	260:1:0.20	6	48	10700	10850	nd	nd
2	260:1:0.15	5	15	3570	5530	nd	nd
3	100:1:0.10	4	36	3380	6500	3600	1.04
4	100:1:0.10	6	53	4850	8150	5000	1.10
5	100:1:0.10	12	82	7350	11950	8500	1.05

[a] Reaction conditions: monomer = 2 g of MAA; solvent = 4 mL of methanol; polymerization temperature = 70 °C. [b] Theoretical average molar mass: $M_{n\,theo}$ = ([MAA]/[CTA] × conv) × M_{MAA} + M_{CTA}, where M_{MAA} and M_{CTA} are the molar masses of MAA and CTA, respectively. [c] Number average experimental molar mass determined by ^{1}H NMR in DMSO-d_6 by quantification of chain ends. [d] Number average experimental molar mass and polydispersity (PDI) obtained in THF (1.0 mL/min) as eluent after MAA groups were converted to MMA units with trimethylsilyldiazomethane. nd = not determined.

Table 2. RAFT Polymerization of IL Monomers[a]

entry	RAFT agent	monomer	[IL]:[CTA]:[INT]	time (h)	conv (%)	$M_{n\,theo}$[b] (g·mol^{-1})	M_{NMR}[c] (g·mol^{-1})
6	CTA-1	IL-**1**	40:1:0.30	70	23	3400	6300
7	CTA-2	IL-**1**	40:1:0.20	165	53	6680	6930
8	CTA-2	IL-**2**	30:1:0.10	28	47	4100	nd
9	CTA-2	IL-**2**	35:1:0.10	74	60	5680	7980
10	CTA-2	IL-**3**	100:1:0.10	68	65	19050	19640

[a] Reaction conditions: monomer = 1 g; solvent = 4 mL of methanol; polymerization temperature = 70 °C. [b] Theoretical average molar mass: $M_{n\,theo}$ = ([IL]/[CTA] × conv) × M_{IL} + M_{CTA}, where M_{IL} and M_{CTA} are the molar masses of IL and CTA, respectively. [c] Number average experimental molar mass determined by ^{1}H NMR in D_2O by quantification of chain ends. nd = not determined.

Table 3. Synthesis of IL-Based DHBCs[a]

entry	CTA	monomer	MON:CTA:INT	solvent	time (h)	yield (%)	$M_{n\,theo}$[b] (g·mol^{-1})	M_{NMR}[c] (g·mol^{-1})
11	PIL-**1**	Am	95:1:0.4	1 mL H_2O + 1 mL MeOH	40	54	6300 + 3650	6300 + 6150
12	PIL-**1**	Am	210:1:0.4	1 mL H_2O + 1 mL MeOH	40	40	6300 + 6140	6300 + 8050
13	PIL-**1**	Am	125:1:0.2	1 mL H_2O + 1 mL MeOH	120	43	4810 + 3820	4810 + 4550
14	PIL-**2**	MAA	300:1 0.1	3 mL MeOH	20	65	7980 + 16790	7980 + 16070
15	PMAA	IL-**2**	15:1:0.1	3 mL MeOH	22	82	7100 + 3360	7100 + 3570
16	PMAA	IL-**3**	35:1:0.1	3 mL MeOH	45	70	9750 + 7590	9750 + 7940
17	PMMA	IL-**2**	10:1:0.1	3 mL MeOH + 1 mL THF	24	93	8350 + 2550	8350 + 2200
18	PMMA	IL-**2**	60:1:0.1	3 mL MeOH + 1 mL THF	20	72	8350 + 11880	8350 + 12920
19	PMMA	IL-**3**	50:1:0.2	3 mL MeOH + 1 mL THF	30	70	19000 + 10110	19000 + 11350
20	PMMA	IL-**3**	25:1:0.2	3 mL MeOH + 1 mL THF	16	48	19000 + 3470	19000 + 3700

[a] Reaction conditions: for entries 11 and 12: 100 mg of PIL-**1** with M_n = 6300 g·mol^{-1} was used as a macro CTA; For entry 13: 160 mg of PIL-**1** with M_n = 4810 g·mol^{-1} was used as a macro CTA; for entry 14: 150 mg of PIL-**2** with M_n = 7980 g·mol^{-1} was used as a macro CTA; for entry 15: 500 mg of PMAA with M_n = 7100 g·mol^{-1} was used as a macro CTA whereas 500 mg of PMMA with M_n = 8350 g·mol^{-1} was used as a macro CTA for entries 17 and 18; for entry 19: 380 mg of PMMA with M_n = 19 000 g·mol^{-1} was used as a macro CTA; for entries 19 and 20: AIBN was used as initiator and for the rest of the reactions V-501 was used as initiator. All the macro-CTAs used in these reactions from entries 11−18 were prepared by RAFT process using CTA-**2** and V-501, whereas the macro CTA PMMA used in entries 19 and 20 were prepared using CTA-**1** and AIBN. Polymerization temperature = 70 °C. [b] Same as in Tables 1 and 2. [c] Molar mass of both blocks determined from the composition of the block copolymer by ^{1}H NMR spectroscopy, knowing the molar mass of the first block (see text).

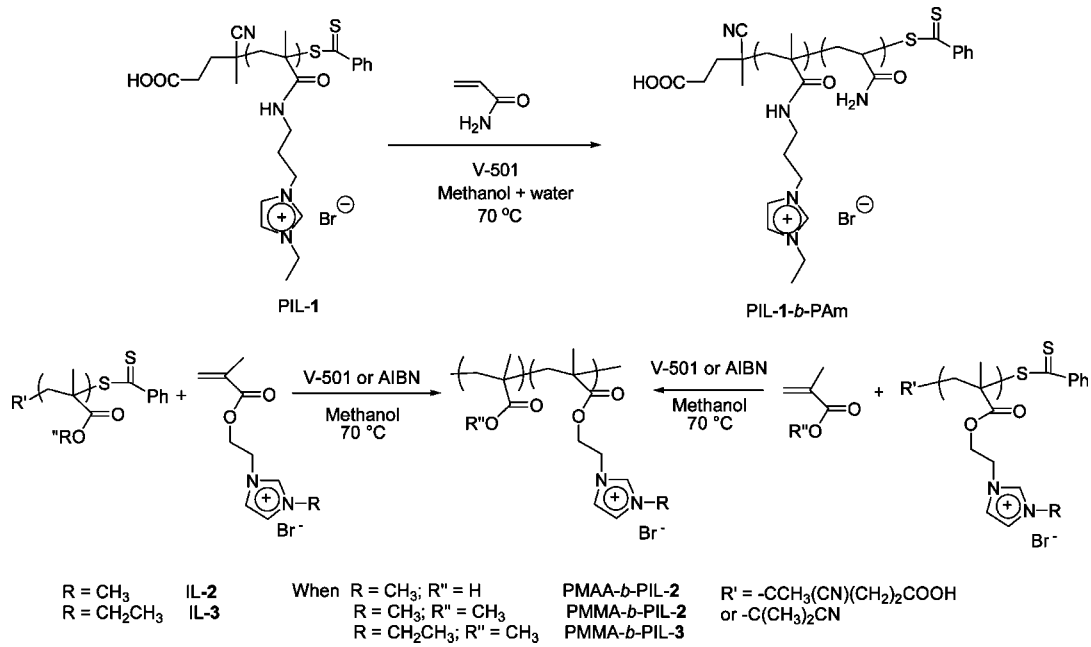
Synthesis of Polymeric Ionic Liquids PIL-1, PIL-2, and PIL-3 by RAFT. A typical RAFT polymerization was as follows. A 10 mL Schlenk tube was flame dried and charged with 1 g (3.31×10^{-3} mol) of monomer IL-**1**, 23.1 mg (82.79×10^{-6} mol) of CTA-**2**, 4.6 mg (16.43×10^{-6} mol) of V-501 initiator, and 4 mL of methanol. The Schlenk tube was subjected to five freeze−thaw cycles and placed in a thermostated oil bath previously maintained at 70 °C. Polymerization reaction was stopped after appropriate time by sudden cooling. The final polymer was obtained as a pinkish powder after washing with cold acetone (3 × 20 mL) to remove unreacted monomer IL-1 and drying under vacuum for 10 h. Same procedure was adopted to synthesize PIL-**2** and PIL-**3** by RAFT.

Synthesis of PIL-1-b-PAm by RAFT (Table 3, Entry 11). In a typical procedure, a 10 mL Schlenk tube was flame dried and charged with 400 mg (6.34×10^{-5} mol) of the previously synthesized PIL-1 used as macro-CTA (M_n = 6300 g·mol^{-1}), 430 mg (6.04×10^{-3} mol) of acrylamide, 7 mg (2.5×10^{-5} mol) of V-501, 1 mL of methanol and 1 mL of water. The Schlenk tube was subjected to five freeze−thaw cycles and placed in a thermostated oil bath previously maintained at 70 °C. Reaction was stopped after cooling with a cold bath of acetone. Characterization by ^{1}H NMR is shown in Figure 3.

Synthesis of PMAA-b-PIL-2 by RAFT. This block copolymer could be synthesized following two different procedures. *Procedure 1* (PIL-**2**-b-PMAA, entry 14, Table 3): in this case, PIL-**2** was used as a macro-CTA. A 10 mL Schlenk tube was flame dried and charged with 150 mg (1.88×10^{-5} mol) of PIL-**2** (M_n = 7980 g·mol^{-1}), 485 mg (5.64×10^{-3} mol) of MAA, 0.5 mg (1.78×10^{-6} mol) of V-501 and 3 mL of methanol. The Schlenk tube was subjected to five freeze−thaw cycles and placed in a thermostated oil bath previously maintained at 70 °C. Polymerization reaction was stopped after appropriate time by sudden cooling and was quenched in cold acetone. *Procedure 2* (PMAA-b-PIL-**2**, entry 15, Table 3): in this case, PMAA was used as macro-CTA. A 10 mL Schlenk tube was flame dried and charged with 500 mg (7×10^{-5} mol) of RAFT-derived PMAA (M_n = 7100 g·mol^{-1}), 275 mg (1×10^{-3} mol) of IL-**2**, 2 mg (7.14×10^{-6} mol) of V-501, and 3 mL of methanol. The Schlenk tube was subjected to five freeze−thaw cycles and placed in a thermostated oil bath previously maintained at 70 °C. Polymerization reaction was stopped after appropriate time by sudden cooling using a bath of cold acetone.

Synthesis of PMMA-b-PIL-3 by RAFT (PMMA-b-PIL-3, Entry 19, Table 3). In a typical experiment, a 10 mL Schlenk tube was flame dried and charged with 380 mg (2×10^{-5} mol) of PMMA used as macro-CTA (M_n = 19 000 g·mol^{-1}; PDI = 1.12), 300 mg (1.03×10^{-3} mol) of IL-**3**, 1 mg (6.09×10^{-6} mol) of AIBN, 3 mL of methanol, and 1 mL of THF. The Schlenk tube was subjected to five freeze−thaw cycles and placed in a thermostated oil bath previously maintained at 70

Scheme 2. Synthesis of Diblock Copolymers by RAFT



°C. Polymerization reaction was stopped after appropriate time by sudden cooling. The PMMA-*b*-PIL-**2** sample was synthesized following the same procedure.

Chemical Modification of PMAA-Based Compounds. The carboxylic acid groups in PMAA-based polymers were modified into methacrylate units using trimethylsilyldiazomethane.[48,49] In a typical experiment, 50 mg of PMAA-based polymer was dissolved in a mixture of methanol and THF. To this solution, a large excess of trimethylsilyldiazomethane (2 M stock solution in diethyl ether) was added dropwise and the reaction mixture was stirred at room temperature for 3−4 h.

Results and Discussion

Double hydrophilic block copolymers (DHBCs) are a particular class of amphiphilic block copolymers that generally associate a polyelectrolyte block with a stabilizing block in water, but they can also be composed of two polyelectrolytes.[44] Similarly to amphiphilic block copolymers constituted of hydrophobic and hydrophilic moieties, DHBCs can self-associate to form micelle-like structures. The self-assembly process in water is generally induced by a change of pH, or by temperature or by ionic strength variations. Upon applying one of these stimuli, one block turns insoluble in water while the other stabilizes the colloidal aggregate. The novel IL-based DHBCs described here were synthesized by sequential reversible addition fragmentation chain transfer (RAFT)[50] polymerization in solution. Among advantages of RAFT, hydrophilic monomers can be directly polymerized by this process in aqueous or alcoholic media without resorting to protection/deprotection chemistry so as to obtain, for instance, pH-responsive or temperature-sensitive polymers.[51–57] Access to water-soluble (co)polymers by RAFT polymerization has been recently reviewed by McCormick et al.[57] To our knowledge, however, no report on RAFT polymerization of IL-based monomers and on the synthesis of related DHBCs has been reported in the literature. For that purpose, three IL methacrylamido or methacrylic monomers, namely 3-(1-ethylimidazolium-3-yl)propylmethyacrylamide bromide (IL-**1**), 2-(1-methylimidazolium-3-yl)ethyl methyacrylate bromide (IL-**2**), and 2-(1-ethylimidazolium-3-yl)ethyl methyacrylate bromide (IL-**3**) were designed. In addition, two different RAFT agents, namely, 2-cyanopropyl dithiobenzoate (CTA-**1**) and (4-cyanopentanoic acid)-4-dithiobenzoate (CTA-**2**), were readily prepared from bis(phenylthiocarbonyl) disulfide, following an already reported procedure.[45] The intermediate bis(phenylthiocarbonyl) disulfide was obtained via elimination process, adapted from the procedure reported by Sanderson et al.[46] Both thiocarbonylthio CTA-**1** and CTA-**2** consist of a tertiary leaving R-group that is particularly suited for RAFT polymerization of methacrylic monomers, including hydrophilic ones. It is thus expected that both CTA-**1** and CTA-**2** can effectively control the RAFT polymerization of the three IL monomers. Polyacrylamide (PAm) and poly(methacrylic acid) (PMAA) were chosen as the water-soluble stabilizing blocks to be associated with PIL in DHBCs. The synthesis of the former polymer and of related DHBCs by RAFT is well documented.[51,57] In contrast, only a few reports have been dedicated to RAFT (block) polymerization of MAA.[58–61] Yang and Cheng first investigated the kinetics of RAFT polymerization of this monomer using carboxymethyl dithiobenzoate as CTA.[61] In the following lines, we first describe the synthesis of well-defined PMAA and PILs by RAFT (Scheme 1) before that of the IL-based DHBCs.

RAFT Homopolymerization of MAA and of IL-Based Monomers (Scheme 1). MAA was homopolymerized by RAFT in methanol at 70 °C using CTA-**2** and V-501 as radical source (Table 1). Protons of MAA monomer units and benzoate protons of PMAA chain ends introduced by the CTA-**2** of such RAFT-derived PMAAs could be clearly identified by ^{1}H NMR spectroscopy in DMSO-d_6 (Figure 1). From the relative peak integration values at $\delta \approx 12.3$ ppm due to the acidic proton (COO*H*) of PMAA and at 7.66 ppm (para proton of the phenyl group of CTA-**2**), the molar mass of these PMAAs could be accurately calculated (Table 1). It was first verified that the integrations between the COOH proton and the other five protons of PMAA [$-CH_2-C(CH_3)(COOH)$] were in a 1:5 ratio in DMSO-d_6. Though PMAA is apparently soluble in water and in dimethylformamide (DMF), the determination of its molar mass by aqueous GPC or even by GPC in DMF at 60 °C in the presence of LiBr was unsuccessful, presumably due to the retention of this polymer onto the GPC columns. This could be overcome by characterizing the corresponding poly(methyl methacrylate) (PMMA) by GPC with THF as eluent, after converting the carboxylic acid groups of PMAA into methacry-

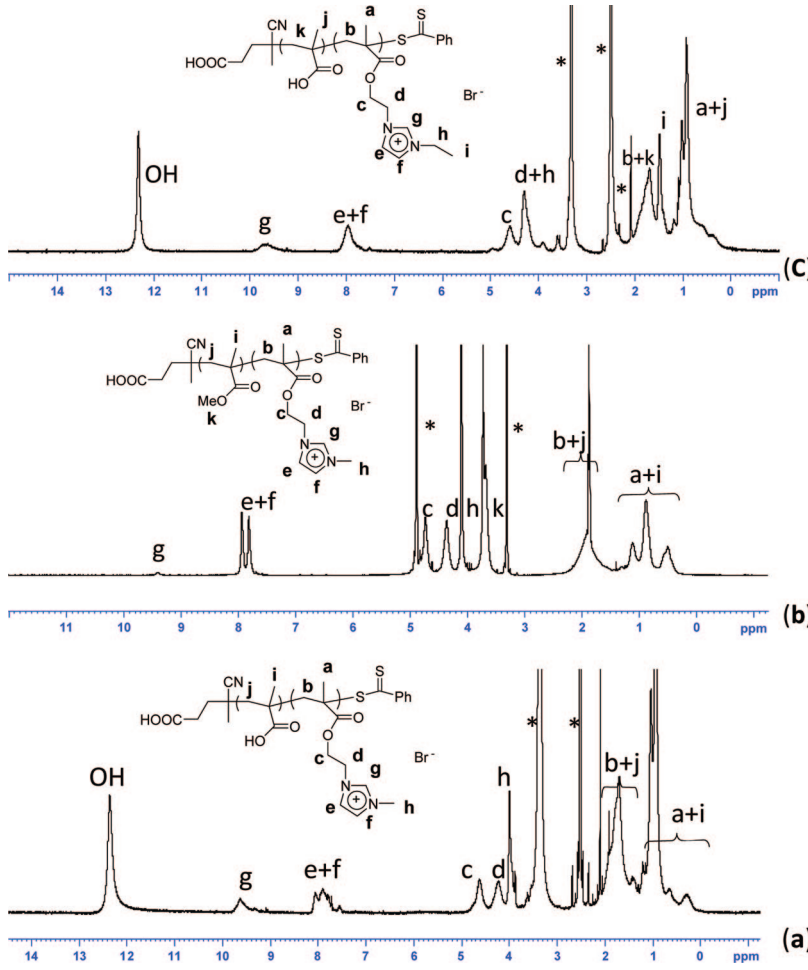


Figure 4. [1]H NMR of: (a) PMAA-*b*-PIL-**2** in DMSO-d_6; (b) PMMA-*b*-PIL-**2** in methanol-d_4; (c) PMAA-*b*-PIL-**3** in DMSO-d_6.

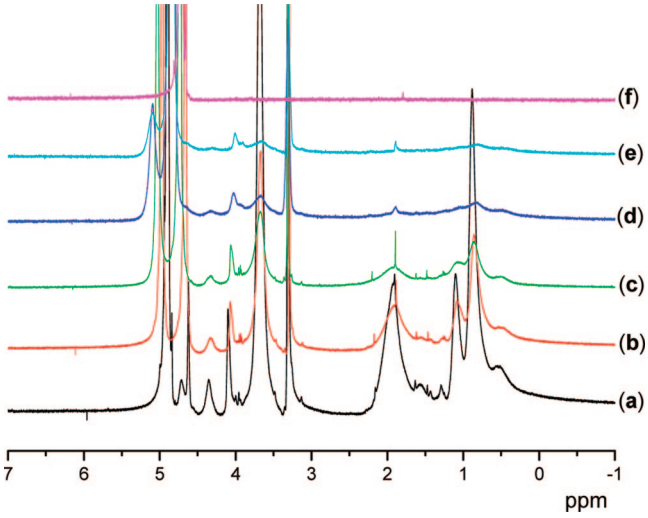


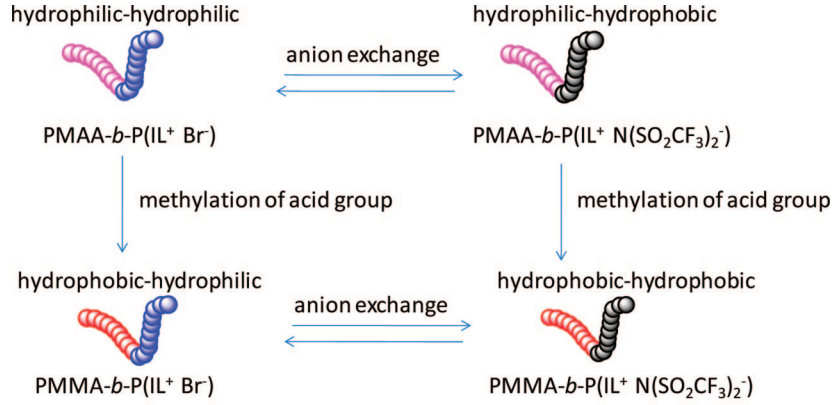
Figure 5. [1]H NMR monitoring of PMMA-*b*-PIL-**2** in methanol-d_4 with gradual addition of D_2O: (a) in methanol-d_4; (b) to (e) with gradual addition of D_2O to (a); and (f) in D_2O.

late units with trimethylsilyldiazomethane.[48,49] Using this indirect method, we verified that the polymerization kinetics followed a first-order variation with respect to the monomer concentration and that M_n values grew linearly with monomer conversion; polydispersity indices were in the range of 1.1, as expected for well-controlled polymerizations.

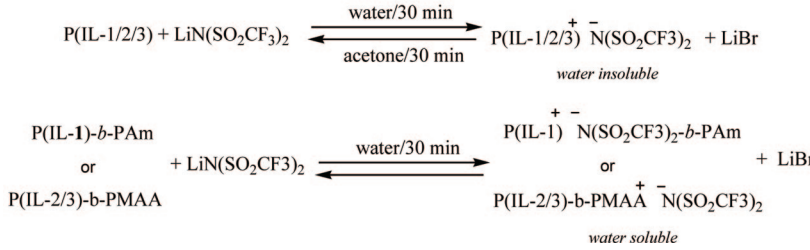
Next, RAFT polymerizations in solution of the three IL monomers, IL-**1**, IL-**2**, and IL-**3** were investigated at 70 °C, using CTA-**1** or CTA-**2** and AIBN or V-501 as radical source (Scheme 1). The results are summarized in Table 2. Compared to the case of methacrylate-based IL-**2** and IL-**3**, the RAFT polymerization of the methacrylamido IL-**1** required a higher initiator to CTA ratio for efficient reaction (Table 2). Unfortunately, as in the case of PMAA, PILs could not be eluted neither by aqueous GPC nor by GPC using dimethylformamide as the mobile phase (with 1 g/L LiBr) at 60 °C. Nevertheless, their characterization by [1]H NMR spectroscopy obtained after purification showed all the expected peaks, including those due to the resonance of protons in α-position to the thiocarbonylthio moiety of the RAFT agent (Figure 2). For instance, in PIL-**1** prepared by RAFT using CTA-**2**, the four methylene protons of the polymer chain, assigned as "e" and "i" resonate at 4.1 ppm (Figure 2a) whereas the four methylene protons arising from CTA-**2** at chain end, assigned as "k" and "l" appear around 2.3 ppm. Experimental molar masses determined in this way are in good agreement with theoretical values based on the [MAA]/[CTA-**2**] molar ratio (Table 2). All these RAFT-derived imidazolium-carrying PILs possess bromide (Br^-) as counteranion and are highly soluble in water, methanol, DMF, and DMSO but not in acetone. The presence of a thiocarbonylthio chain end in these PILs and in PMAA was subsequently exploited to derive DHBCs by RAFT-driven chain extension in aqueous solutions, as discussed below.

Synthesis by RAFT of PIL-b-PAm and PMAA-b-PIL DHBCs (Scheme 2). PIL-**1** was used as a macro-CTA in the RAFT polymerization of acrylamide carried out in a methanol/water mixture at 70 °C, using V-501 as initiator (Scheme 2, Table 3). The solution behavior in methanol of the generated

Scheme 3. Chemical Manipulation of IL-Based Block Copolymers Anion Exchange Reactions in Homo and Block Copolymers of IL Monomers



Anion exchange reactions in homo and block copolymers of IL monomers



PIL-**1**-*b*-PAm DHBCs was dependent on the PAm content, methanol being a bad solvent for the PAm block and a selective one for PIL. For instance, the sample with a major content in PAm (e.g., entry 12, Table 3) was insoluble in methanol. Washing this sample with cold methanol therefore eliminated any PIL-**1** macro-CTA left over, if present. In contrast, all PIL-**1**-*b*-PAm DHBCs proved soluble in water, allowing their composition to be determined by ^{1}H NMR spectroscopy in D_2O (Figure 3) after a thorough washing with methanol as mentioned above. The presence of both monomer units was confirmed, all peaks being assigned as shown in Figure 3.

The RAFT-prepared PMAA described above (Table 1) was also used as a macro-CTA to polymerize methacrylate-based IL-**2** and IL-**3** monomers and to gain access to PMAA-*b*-PIL DHBCs (Scheme 2). Figure 4, a and c, shows the ^{1}H NMR spectra of PMAA-*b*-PIL-**2** and PMAA-*b*-PIL-**3** DHBCs, run in DMSO-d_6. Like for the homo-PMAAs described above, the integration ratio between the COOH proton at 12.3 ppm to the

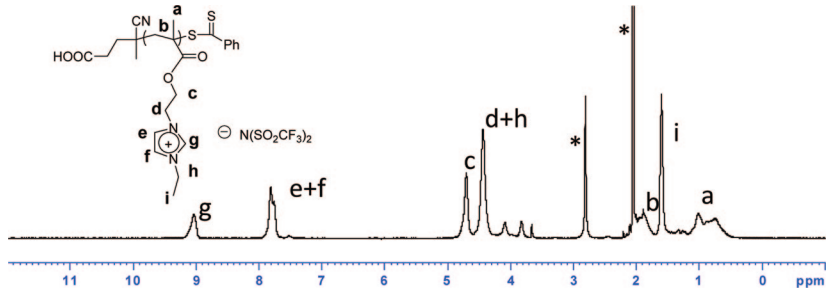


Figure 6. ^{1}H NMR of PIL-**3** $^-$ $N(SO_2CF_3)_2$ in acetone-d_6.

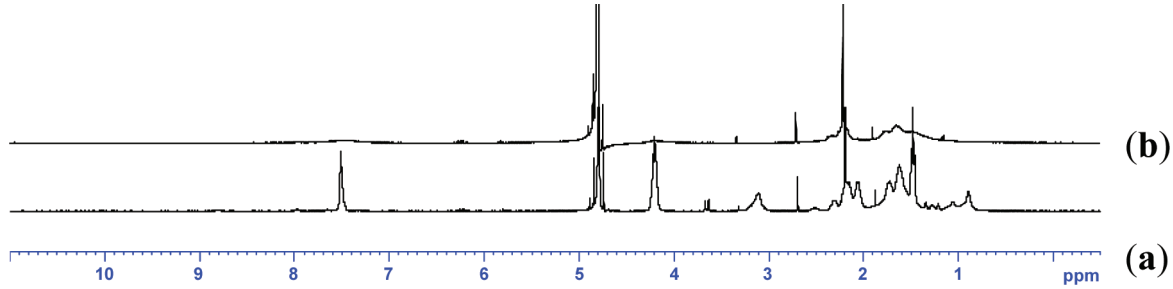


Figure 7. ^{1}H NMR spectra (in D_2O) of block copolymer PIL-**1**-*b*-PAm (a) before and (b) after anion exchange from Br^- to $^-N(SO_2CF_3)_2$. The peaks resonating at around 7.5 ppm, 4.2 ppm, 3.1 ppm and few between 2.3 to 0.8 ppm correspond to PIL-**1** part in the block copolymer PIL-**1**-*b*-PAm. These peaks disappeared after anion exchange (as seen in (b)) due to micellization.

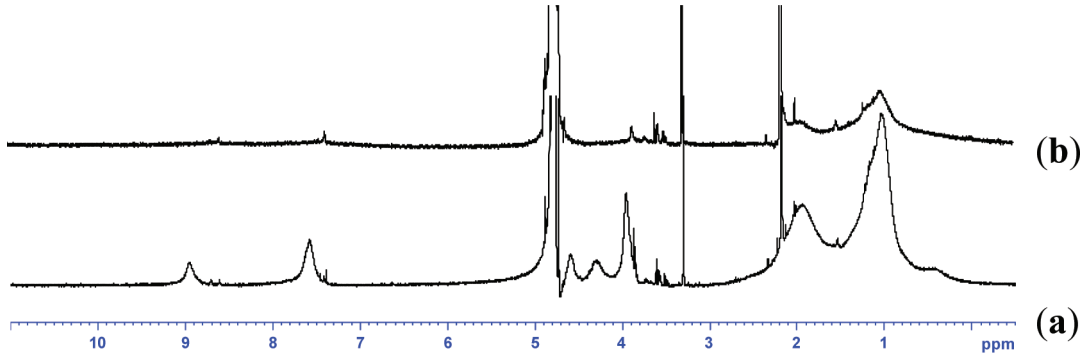


Figure 8. ^{1}H NMR spectra (in D_2O) of block copolymer PIL-**2**-*b*-PMAA (a) before and (b) after anion exchange [Br^- to $^-N(SO_2CF_3)_2$]. The peaks resonating at around 9, 7.8, 4.2, and 4.8−3.8 ppm and a few between 2.3 and 0.3 ppm correspond to PIL-**2** part in the block copolymer PIL-**2**-*b*-PMAA. These peaks disappeared after anion exchange (as seen in (b)) due to micellization.

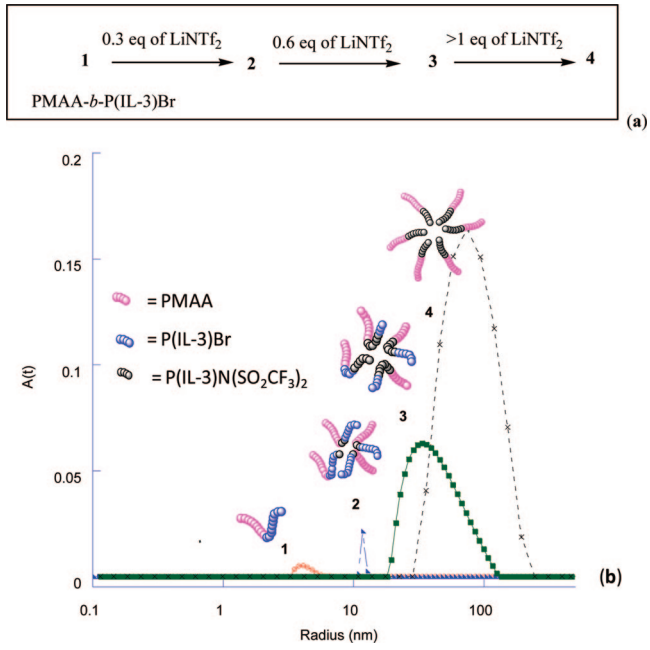


Figure 9. (a) Schematic representation for the controlled addition of $LiN(SO_2CF_3)_2$ to PMAA-*b*-P(IL-**3**)Br. (b) CONTIN plot for PMAA-*b*-P(IL-**3**)Br in water with controlled addition of $LiN(SO_2CF_3)_2$ to trigger the micellar aggregation. An illustrative graphical representation for 1, 2, 3, and 4, the micellar aggregation of PMAA-*b*-P(IL-**3**)Br after anion exchange (from Br^- to $^-N(SO_2CF_3)_2$) at various levels are presented. DLS was recorded at 25 °C at an angle of 90° with a concentration of 1 g/L.

5 other protons of PMAA [-CH_2−C(CH_3)(COOH)] was equal to 1:5 in DMSO-d_6. Comparison of the integration value of the COO*H* proton with that of methylene protons at 4.6 ppm (O−CH_2 of PIL-**2**) provides the molar ratio of both blocks. Knowing the molar mass of the PMAA precursor, the molar mass of the PIL block could thus be calculated. Notably, the same type of DHBC could also be achieved from PIL-**2** as macro-CTA whose chain extension with MAA as second monomer gave rise to PIL-**2**-*b*-PMAA DHBC (Table 3, run 14).

Solution Properties and Ion Sensitivity of PILs and IL-Based DHBCs (Scheme 3). The solution properties of such DHBCs can be manipulated by several means, either by modification of the hydrophilic PMAA block into a hydrophobic PMMA one through its esterification and/or by anion exchange on the PIL block to make it hydrophobic (Scheme 3). For instance, methylation of the COOH groups of the PMAA block in PMAA-*b*-PIL-**2** DHBC using trimethylsilyldiazomethane afforded the corresponding PMMA-*b*-PIL-**2** amphiphilic block copolymer, as verified by ^{1}H NMR in deuterated methanol (Figure 4b). Since the targeted molar mass of PMMA is moderate, methanol is here selective for both PMMA and PIL-**2**, so that signals of both types of units can be clearly detected. The ability of these PMMA-*b*-PIL-**2** samples to self-associate into micelles was further investigated. A series of ^{1}H NMR spectra were thus recorded in methanol-d_4 by gradually adding D_2O into the NMR tube (Figure 5). D_2O being selective for the PIL block only, this provoked a progressive decrease—until complete disappearance—of the intensity of protons of PMMA blocks, as a result of their aggregation in the core of micelles.

Next, the ionic responsiveness of PILs and related DHBCs was investigated. Bromide (Br^-) being the counteranion in these IL-based (co)polymers, all these compounds were highly soluble in water. As emphasized above, solubility of PILs can be finely tuned by simply changing the counteranion.[25,38] Anion exchange was first experimented on RAFT-derived homopolymers (PILs) using excess of $Li^+{}^-N(SO_2CF_3)_2$, as illustrated in Scheme 3. Addition of this salt onto water PIL solutions resulted in the formation of a precipitate that was subsequently washed with water to remove the excess of salts. The corresponding PILs, noted PIL-$\mathbf{1}^+$ $^-N(SO_2CF_3)_2$, PIL-$\mathbf{2}^+$ $^-N(SO_2CF_3)_2$, and PIL-$\mathbf{3}^+$ –$N(SO_2CF_3)$, were all soluble in acetone, allowing their characterization by ^{1}H NMR in acetone-d_6, as shown in Figure 6. Of particular interest, the $^-N(SO_2CF_3)$ counteranion in these PILs could be readily exchanged back to bromide by a simple stirring with LiBr in acetone solution. In this way, PIL-$\mathbf{1}^+$ –$N(SO_2CF_3)_2$, PIL-$\mathbf{2}^+$ $^-N(SO_2CF_3)_2$, and PIL-$\mathbf{3}^+$ $^-N(SO_2CF_3)$ were transformed back into their precursors, PIL-**1**, PIL-**2**, and PIL-**3**, respectively. This demonstrates the true reversibility of the salt-responsiveness of RAFT-derived PILs. In all these experiments, a large excess of salt was employed to drive the anion exchange reactions to completion, which could be verified by ^{1}H NMR and IR spectroscopy, as already reported.[37]

This anion exchange from Br^- to $^-N(SO_2CF_3)_2$ was also accomplished on IL-based DHBCs by adding the same $Li^+{}^-N(SO_2CF_3)$ salt in excess, for instance, into a water solution of PIL-**1**-*b*-PAm DHBC (Scheme 3). In contrast to the case of homopolymers, however, the corresponding diblock copolymer, noted PIL-$\mathbf{1}^+$ $^-N(SO_2CF_3)_2$-*b*-PAm, remained entirely water-soluble after anion exchange although the solution turned slightly blue. This strongly supports the formation of micelle-like structures with PIL-$\mathbf{1}^+$ $^-N(SO_2CF_3)_2$ blocks at the core surrounded by a PAm corona. Since PIL-$\mathbf{1}^+$ $^-N(SO_2CF_3)_2$ is insoluble in water, the formation of a clear homogeneous water solution of PIL-$\mathbf{1}^+$ $^-N(SO_2CF_3)_2$-*b*-PAm also suggests that this amphiphilic block copolymer is free of PIL-$\mathbf{1}^+$ $^-N(SO_2CF_3)_2$ homopolymer. This is another piece of evidence for the existence of a pure diblock copolymer. Figure 7 shows the monitoring by ^{1}H NMR spectroscopy of the water solution of PIL-**1**-*b*-

PAm before and after anion exchange. The disappearance of the signals due to the resonance of the PIL block in D_2O is indicative of the formation of PIL-**1**$^+$ $^-$N(SO_2CF_3)$_2$-*b*-PAm after anion exchange and of its self-assembly in a micellar structure. Submitted to a same anion exchange, from Br^- to $^-N(SO_2CF_3)_2$, the other DHBCs described above also showed micellar aggregation; for instance PIL-**2**-PMAA, whose ^{1}H NMR monitoring before and after anion exchange is displayed in Figure 8. We thus provide the very first examples of IL-based DHBCs exhibiting truly anion-sensitive micellization.[62]

Further investigations by dynamic light scattering (DLS) revealed that the size of the aggregates formed in water after complete exchange varied dramatically from one sample to the other (see ESI; the thorough investigation of self-assembly of IL-based DHBCs will be discussed in a forthcoming publication). The hydrodynamic radius is 17 nm for PMAA-*b*-PIL-**2**$^+$ $^-$N(SO_2CF_3)$_2$ and 86 nm for PMAA-*b*-PIL-**3**$^+$ $^-$N(SO_2CF_3)$_2$, indicating the formation of two different morphologies. It is very likely that ionic liquid monomer units resulting from IL-**2** brought about the formation of spherical micelles (17 nm) whereas those originating from IL-**3** with their large size substituent resulted in the formation of bigger aggregates whose morphology is currently under investigation.

Finally, the substitution process of $^-N(SO_2CF_3)_2$ for Br^- was monitored by DLS on two samples: PMAA-*b*-PIL-**2** and PMAA-*b*-PIL-**3**. It was observed that anion exchange led to the formation of micellar aggregates whose size varied as a function of the amount of Li$N(SO_2CF_3)_2$ added. For instance, different amounts (2, 40 μL etc.) of Li$N(SO_2CF_3)_2$ solution (stock solution in water of 5 g/L) were added at regular intervals onto a 2 mL of PMAA-*b*-PIL-**3** aqueous solution (c =1 g/L). As monitored by DLS (Figure 9), a progressive transition from unimers to micellar aggregates of increasing size was noted with the addition of Li$N(SO_2CF_3)_2$. The solution also turned slight blue when adding Li$N(SO_2CF_3)_2$, along with the observed increase of the hydrodynamic radius (Figure 9b). In this case, the anion exchange reactions occur readily. In other words, these IL-based DHBCs behaved as efficient sensors of $^-N(SO_2CF_3)_2$ anions under very dilute conditions.

The PMAA-*b*-PIL-**3**$^+$ $^-$N(SO_2CF_3)$_2$-based micelles formed in water were then subjected to anion exchange in an attempt to disrupt these micellar aggregates. LiBr was thus added with a view of substituting Br^- for $^-N(SO_2CF_3)_2$ and using this process as sensor for bromide anion. However, the anion exchange from $^-N(SO_2CF_3)_2$ to Br^- occurred slowly and required a large excess of LiBr to attain completion, unlike the reverse process. Though anion exchanges are reversible in these DHBCs, that of Br^- at the expense of $^-N(SO_2CF_3)_2$ is hindered by the micellar structure of the copolymers in water which requires a large excess of LiBr for anion exchange to occur.

Conclusion

Ionic liquid monomers could be successfully polymerized and sequentially copolymerized with methacrylic acid or acrylamide in the presence of a RAFT agent and a radical source. Ionic liquid homopolymers as well as double hydrophilic block copolymers consisting of ionic liquid blocks could be obtained under living/controlled conditions. The solution properties of these DHBCs could be further manipulated, for instance, by chemical modification of the hydrophilic poly(methacrylic acid) block into a hydrophobic poly(methyl methacrylate acid) one. More interestingly, the anion sensitivity of these DHBCs, that is the change of solubility in water as a function of the counteranion associated with the ionic liquid block was found to occur reversibly. Thus, either soluble unimers with Br^- as anion or micellar aggregates of varying size with $^-N(SO_2CF_3)_2$ as counteranion were observed in water. The anion exchange occurs reversibly and could even be used as a sensing method to detect minute concentrations of $^-N(SO_2CF_3)_2$. The morphology of the structures formed by self-assembly in solution of IL-based DHBCs will be the topic of a forthcoming publication.

Acknowledgment. We thank Euskadi and Aquitaine regions and CNRS for the financial support.

Supporting Information Available: Figures illustrating the anion exchange reactions and intensity autocorrelation function and CONTIN plots for PMAA-*b*-P(IL-**2**)$^+$ $^-$N(SO_2CF_3)$_2$ [R_h = 17 nm] and PMAA-*b*-P(IL-**3**)$^+$ $^-$N(SO_2CF_3)$_2$[R_h = 86 nm] (3 pages). This information is available free of charge via the Internet at http://pubs.acs.org.

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