Vinylimidazole-Based Asymmetric Ion Pair Comonomers: Synthesis, Polymerization Studies and Formation of Ionically Crosslinked PMMA

Satyasankar Jana,[1] Vivek Arjunan Vasantha,[1] Ludger Paul Stubbs,[1] Anbanandam Parthiban,[1] and Julius G. Vancso[1,2]

[1]Institute of Chemical and Engineering Sciences (ICES), Agency for Science, Technology and Research (A*STAR), 1 Pesek Road, Jurong Island, Singapore 627833, Singapore
[2]MESA+ Research Institute for Nanotechnology, Faculty of Science and Technology, University of Twente, P.O. Box 217, 7500, AE Enschede, The Netherlands
Correspondence to: S. Jana (E-mail: satyasankar_jana@ices.a-star.edu.sg) or A. Parthiban (E-mail: a_parthiban@ices.a-star.edu.sg)

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ABSTRACT: Vinylimidazole-based asymmetric ion pair comonomers (**IPCs**) which are free from nonpolymerizable counter ions have been synthesized, characterized and polymerized by free radical polymerization (FRP), atom transfer radical polymerization (ATRP), and reversible addition-fragmentation chain transfer (RAFT) mediated polymerizations in solution and by dispersion polymerization in water. The asymmetric nature of **IPCs** is due to the fact that cationic component of these **IPCs** is derived from vinylimidazole (VIm) and anionic component is derived from either styrenesulfonate (SS) or 2-acrylamido-2-methyl-1-propanesulfonate. Although under ATRP, conversions are either very low or negligible, FRP and RAFT produces polymers with high to moderate monomer conversions but with different solubility characteristics. This investigation provides insight to the polymerization behavior of each component of the asymmetric **IPCs** and also its effects on composition and solubility characteristics of the resulting polymers. The **IPCs** studied here are high temperature ionic liquid and thus the polymers synthesized from these **IPCs** are highly ionic in nature and possess very strong intermolecular interactions which makes some of these **IPC** based polymers completely insoluble in organic and aqueous solvents. This highly ionic interaction is exploited to synthesize ionically crosslinked PMMA. MMA on copolymerization with 5–6 mol % of **IPC** yielded copolymer which is insoluble in common organic solvents like THF, DMF, etc., unlike homo PMMA. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 3260–3273

KEYWORDS: ATRP; copolymrization; ion pair comonomer; ionic liquid; polyampholyte; reversible addition-fragmentation chain transfer (RAFT); styrenesulfonate; vinylimidazole

INTRODUCTION Ion pair comonomers (**IPC**s) are salts, made up of both polymerizable cationic and anionic units and are useful for the synthesis of ampholytic polymers or polyampholytes. Polyampholytes[1–3] are different from zwitterionic polymers.[4,5] In the case of polyampholytes, counterions belong to different repeating unit of the polymer chain, whereas the counter ions in zwitterionic polymers belong to the same repeating unit. Generally, polymerization of **IPC**s composed of cationic and anionic components of similar reactivity produces charge neutral polyampholytes, which have shown exceptional behavior with respect to their solubility, viscosity, and so forth.[1–3] Such polyampholytes are potential materials for protein separation, binding metal ions to separate it from crude oil in petroleum industry, and so forth[2] and could be an alternative to zwitterionic polymers. Polyampholytes which are synthesized from **IPC**, have been recently reported to exhibit anti-biofouling characteristics.[6] The earliest synthesis and polymerization of **IPC**s were reported by Salamone et al.[7–10] To date, the **IPC**s that have been studied well and available in the literature are (meth)acrylamide-(meth)acrylamide,[8,9] (meth)acrylate-(meth)acrylate,[6,9–11] and 4-vinylpyridine-styrenesulfonate[7] based systems. We hereby report the synthesis, characterization and polymerization behavior of vinylimidazole (VIm) based asymmetric **IPC**s. We have chosen 1-vinylimidazole (VIm) as a cationic component for the **IPCs** due to the significant interest in VIm based poly(ionic liquids) (PILs) for many applications[12–18] which include highly conductive polymers, use as solvents for inorganic matrixes like graphene and carbon nanotubes, chromatographic separations, enhanced CO_2 absorption, and so forth. Similarly, sulfonate-based component was chosen as the anionic component of **IPC**s because

Additional Supporting Information may be found in the online version of this article.

of its wider application as polyelectrolyte, surfactant and also in ion exchange resins. The polymerization behavior of these **IPCs** was investigated in detail by free radical polymerization (FRP), atom transfer radical polymerization (ATRP), and reversible addition-fragmentation chain transfer (RAFT) mediated polymerizations. Controlled radical polymerization techniques were used here as the polymerization techniques like ATRP,[19,20] single-electron transfer living radical polymerization (SET-LRP),[21] and RAFT[20,22] can be expected to provide greater control over the structure of the polymers synthesized and also for the purpose of verifying the suitability of these techniques for surface initiated polymerizations[23] of asymmetric **IPCs**. Aqueous dispersion polymerization using free radical initiators was also used to produce copolymers. Finally, the highly ionic interactions of these **IPC**-based copolymers have been exploited to synthesize ionically crosslinked PMMA. Such copolymers of PMMA even with 5–6 mol % **IPC** content yielded insoluble polymers. The swelling studies of these copolymers which are crosslinked by ionic interactions are also described herein.

EXPERIMENTAL

Materials and Characterizations

All chemicals including RAFT agents were purchased from Sigma-Aldrich and Alfa Aesar. 2,2′-Azobisisobutyronitrile (AIBN) was obtained from HalloChem Pharm Co. AIBN was purified by recrystallization from absolute alcohol. Spectra/Por regenerated cellulose membrane tubing for dialysis (MWCO 1000 and 3500) was bought from Spectrum Labs.

NMR spectra were recorded on a 400 MHz Bruker UltraShield AVANCE 400SB spectrometer. Elemental microanalysis was performed using Eurovector E300 elemental analyzer. Thermogravimetric analysis (TGA) was performed under N_2 atmosphere at a heating rate of 10 °C/min using SDT-2960T TA instruments. The differential scanning calorimetry (DSC) was performed using Perkin Elmer Pyris Diamond Hyper DSC instruments at a heating rate of 10 °C/min under N_2. The aqueous GPC system was equipped with a Delta 600 HPLC pump, a 600 controller, a 717 plus autosampler, a 2487 dual absorbance detector, and a 2414 refractive-index detector, all from Waters. The following GPC columns were arranged in series: Ultrahydragel guard, and Ultrahydragel 120 (7.8 mm ID × 300 mm) and an Ultrahydragel Linear (7.8 mm ID × 300 mm). The eluant (0.1 M $NaNO_3$ in deionized water) flow rate was 0.7 mL/min and the columns were maintained at 30 °C. The results were obtained using polyethylene oxide (PEO) and polyethylene glycol (PEG) calibrations.

Synthesis of Vinylimidazole (VIm) Based IPCs

Synthesis of IPC1

This novel comonomer was synthesized in a two-step procedure as given below and stored in freezer before use.

Step I: Excess 1-bromohexane (21.048 g, 127.5 mmol) was added to a solution of 1-vinylimidazole (VIm, 10 g, 106.25 mmol) in dry tetrahydrofuran (100 mL) in a round bottom flask fitted with condenser and the mixture was heated at 60 °C for 48 h. The mixture was cooled down to room temperature, and the bottom layer was separated out and washed with THF further (2 × 25 mL). The brownish liquid product 3-hexyl-1-vinylimidazolium bromide (C_6VImBr) was then dried in a vacuum oven. Yield 14.22 g (51.63%). ^{1}H NMR (400 MHz, d_4-MeOD, δ): 0.92 (t, 3H, —CH_3), 1.34–1.41 (m, 6H, 3×CH_2), 1.94 (t, 2H, CH_2), 4.28 (t, 2H, N—CH_2), 5.45 (d, 1H, vinyl CH_2), 5.96 (d, 1H, vinyl CH_2), 7.28 (t, 1H, vinyl C*H*), 7.79 (s, 1H, imidazole N—C*H*), 8.02 (s, 1H, imidazole C*H*—N^+), 9.3 (s, reduced intensity, imidazole N—C*H*—N^+). ^{13}C NMR (400 MHz, d_4-MeOD, δ): 14.29, 23.49, 26.96, 30.92, 32.28, 51.28, 109.96, 120.79, 124.45, 129.83.

Step II: Aqueous solution (50 mL) of 3-hexyl-1-vinylimidazolium bromide (C_6VImBr, 14.22 g, 54.9 mmol) was added to an aqueous solution (100 mL) of sodium 4-styrenesulfonate (SSS, 13.575 g, 65.04 mmol) and the homogeneous mixture was stirred at room temperature overnight. The ion pair monomer product was extracted from this homogeneous solution using $CHCl_3$ (3 × 75 mL). The chloroform phase was then dried over anhydrous $MgSO_4$ and removed in a rotary evaporator followed by drying in a vacuum oven at room temperature finally to yield white powder which was stored in a freezer before use. Yield 19.5 g, 98%. The product was soluble in MeOH, $CHCl_3$, acetone, THF, DMF, CAN and insoluble in toluene and water. ^{1}H NMR (400 MHz, d_4-MeOD, δ): 0.92 (t, 3H, —CH_3), 1.33–1.36 (m, 6H, 3×CH_2), 1.89 (t, 2H, CH_2), 4.22 (t, 2H, N—CH_2), 5.32 (d, 1H, styrene vinyl CH_2), 5.42 (d, 1H, imidazole vinyl CH_2), 5.83–5.92 (m, 2H, vinyl CH_2 of imidazole and styrene), 6.73–6.80 (m, 1H, styrene vinyl C*H*), 7.19–7.25 (m, 1H, imidazole vinyl C*H*), 7.48 (d, 2H, styrene aromatic C*H*), 7.73 (d, 1H, imidazole N—C*H*), 7.78 (d, 2H, styrene aromatic C*H*), 7.97 (d, 1H, imidazole C*H*—N^+), 9.29 (s, reduced intensity, imidazole N—C*H*—N^+). ^{13}C NMR (400 MHz, d_4-MeOD, δ): 14.30, 23.48, 26.95, 30.89, 32.27, 51.23, 109.86, 115.90, 120.71, 124.40, 127.07, 127.28, 129.81, 137.27, 140.88, 145.67. Anal. calcd. For $C_{19}H_{26}N_2O_3S$: C 62.96, H 7.33, N 7.73, S 8.85, O 13.24%; Found: C 62.26, H 7.10, N 7.62, S 8.41, O 12.91%.

Synthesis of IPC2

This novel comonomer was synthesized by a modified method of Qiu et al.[24] in a two-step procedure as given below and stored in freezer before use.

Step I: Excess 1-bromohexadecane (38.93 g, 127.5 mmol) was added to a solution of 1-vinylimidazole (VIm, 8 g, 85 mmol) in dry THF (80 mL) in a round bottom flask fitted with condenser and the solution was heated at 60 °C for 48 h. The homogeneous solution was then concentrated to ~50 mL and the product was precipitated from excess ether (120 mL). The white product 3-hexadecyl-1-vinylimidazolium bromide (C_{16}VImBr) was then dried in a vacuum oven at room temperature to produce white powder. Yield 15.25 g, 45%. ^{1}H NMR (400 MHz, d_4-MeOD, δ): 0.91 (t, 3H, —CH_3), 1.30-1.39 (m, 26H, 13×CH_2), 1.94 (t, 2H, CH_2), 4.28 (t, 2H, N—CH_2), 5.47 (d, 1H, vinyl CH_2), 5.96 (d, 1H, vinyl CH_2), 7.28 (t, 1H, vinyl C*H*), 7.79 (s, 1H, imidazole N—C*H*—N^+),

8.02 (s, 1H, imidazole C*H*—N^+), 9.3 (s, 1H, imidazole N—C*H*—N^+). ^{13}C NMR (400 MHz, d_4-MeOD, δ): 14.45, 23.74, 27.29, 27.29, 30.11, 30.96, 33.08, 51.28, 109.95, 120.78, 124.44, 129.82.

Step II: Methanolic solution (15 mL) of 3-hexadecyl-1-vinylimidazolium bromide (C_{16}VImBr, 10 g, 25 mmol) was added dropwise to an aqueous solution (100 mL) of SSS (6.194 g, 30 mmol) and stirred at room temperature. Precipitation was observed immediately and the reaction mixture was stirred overnight. **IPC2** was collected by filtration followed by drying in a vacuum oven at room temperature to yield white powder which was stored in a freezer before use. Yield 11.91 g, 95%. The product was soluble in MeOH, $CHCl_3$, acetone, insoluble in water, THF and partially soluble in DMF and ACN. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.86 (t, 3H, -C*H*$_3$), 1.19-1.24 (m, 26H, 13×C*H*$_2$), 1.77 (t, 2H, C*H*$_2$), 4.20 (t, 2H, N—C*H*$_2$), 5.24-5.27 (m, 2H, 2×vinyl CHC*H*$_2$ of vinylimidazole and styrene units), 5.72-5.86 (dd, 2H, imidazole and styrene vinyl C*H*$_2$), 6.64-6.71 (m, 1H, styrene vinyl C*H*), 7.30-7.34 (t, 1H, imidazole vinyl C*H*) 7.37-7.39 (m, 3H, styrene 2×C*H* and imidazole NC*H*), 7.69 (s, 1H, imidazole C*H*—N^+), 7.82-7.84 (d, 2H, styrene 2×C*H*), 10.24 (s, 1H, imidazole N—C*H*—N^+). ^{13}C NMR (400 MHz, $CDCl_3$, δ): 14.11, 22.68, 26.21, 28.99-30.12, 31.91, 50.39, 109.34, 115.11, 118.92, 122.47, 125.96, 126.29, 128.54, 136.13, 136.56. Anal. calcd. For $C_{29}H_{46}N_2O_3S$: C 69.28, H 9.22, N 5.57, S 6.38, O 9.55%, Found: C 69.09, H 9.18, N 5.52, S 6.35, O 9.40%.

Synthesis of IPC3

This was synthesized by a modified method of Qiu et al.[24] where 1-vinylimidazole (VIm, 2.001 g, 21.269 mmol) was added to a dispersion of equimolar amount of 2-acrylamido-2-methyl-1-propanesulfonic acid (4.408 g, 21.269 mmol) in methanol (20 mL). A homogeneous solution was formed after stirring for a while. The clear solution was stirred further for 4 h at room temperature and finally methanol was removed in a rotary evaporator followed by high vacuum oven to yield a clear viscous liquid. The product was stored in freezer before use which finally produced white waxy solid. Yield 6.41g, ~100%. The product was soluble in methanol, water, partially soluble in chloroform and ethanol and insoluble in ACN. ^{1}H NMR (400 MHz, d_4-MeOD, δ): 1.57 (s, 6H, acrylamide 2×C*H*$_3$), 3.21 (s, 2H, acrylamide C*H*$_2$S), 5.44 (d, 1H, imidazole vinyl C*H*$_2$), 5.57 (d, 1H, acrylamide vinyl C*H*$_2$), 5.92 (d, 1H, imidazole vinyl C*H*$_2$), 6.08-6.23 (m, 2H, acrylamide vinyl C*H* and C*H*$_2$), 7.32 (m, imidazole vinyl C*H*), 7.66 (s, 1H, imidazole NC*H*), 8.01(s, 1H, imidazole C*H*NH^+), 9.19 (s, 1H, imidazole NC*H* NH^+). ^{13}C NMR (400 MHz, d_4-MeOD, δ): 27.01, 53.48, 60.28, 109.19, 120.19, 121.97, 125.56, 129.91, 133.58, 135.87, 167.47. Anal. calcd. For $C_{12}H_{19}N_3O_4S$: C 47.83, H 6.35, N 13.94, S 10.64, O 21.24%; Found C 45.21, H 6.35, N 12.97, S 10.22, O 22.58%.

Synthesis of Polymers

Representative FRP of IPC1

Monomer (**IPC1**, 0.5 g, 1.379 mmol), 2,2′-azobisisobutyronitrile (AIBN, 4.52 mg, 0.028 mmol) and DMF (six drops, as internal standard) were dissolved in methanol (1.5 mL) and transferred to a 25 mL Schlenk tube (**IPC1**:AIBN = 50:1). The solution was then degassed with three freeze-pump-thaw cycles using N_2 and then heated on an oil bath at 70 °C for 20 h. Aliquots were collected to periodically to determine the monomer conversion by ^{1}H NMR spectroscopy. The reaction became heterogeneous in after 2 h. Finally the reaction was stopped by cooling to room temperature followed by addition of excess chloroform to the reaction mixture. The white powdery polymer **CP1** was filtered off and dried in a vacuum oven at 50 °C overnight to yield 0.475 g (95%) polymer measured gravimetrically.

Representative ATRP of IPC1

Monomer (**IPC1**, 0.5 g, 1.379 mmol), ethyl-2-bromoisobutyrate (EBiB, 5.38 mg, 0.028 mmol), *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA, 9.56 mg, 0.055 mmol) and DMF (six drops, as internal standard) were dissolved in methanol (1.5 mL). Separately a 25 mL Schlenk tube was charged with CuBr (3.96 mg, 0.028 mmol) and purged with N_2. The earlier solution was then added to the Schlenk tube and cooled immediately in a liquid N_2 bath. The content (**IPC1**:EBiB:CuBr:PMDETA = 50:1:1:2) was degassed with three freeze-pump-thaw cycles using N_2 gas and then heated on an oil bath at 70 °C for 44 h. Aliquots were withdrawn from the reaction mixture periodically to determine the monomer conversion.

Representative RAFT Polymerization of IPC1

A solution monomer (**IPC1**, 0.5 g, 1.379 mmol), 2-cyano-2-propyl benzodithioate (CPBD, 6.1 mg, 0.028 mmol), AIBN (1.4 mg, 0.008 mmol) and DMF (six drops, as internal standard) in methanol (1.5 mL) was transferred to a 25 mL Schlenk tube. The content (**IPC1**:CPBD:AIBN = 50:1:0.3) was then degassed with three freeze-pump-thaw cycles using N_2 gas and then heated on an oil bath at 70 °C for 44 h. Aliquots were withdrawn from the reaction mixture periodically to determine the monomer conversion by 1H NMR spectroscopy. Finally the reaction was stopped by cooling to room temperature followed by precipitation of polymer from excess ether. The light pink powdery polymer **CP3** was filtered off and dried in vacuum oven at 50 °C overnight. Yield 350 mg (70%).

A part of polymer sample (150 mg) was dissolved in 0.2 M NaBr (5 mL) and dialyzed against distilled water using MWCO 3.5 K dialysis tubing at 50 °C for 2 days. Polymer from aqueous solution was finally collected by removing water using high vacuum rotary evaporator at 60 °C followed by drying the sample in high vacuum oven at 60 °C overnight. Final polymer weight was ~130 mg).

Representative Dispersion Polymerization of IPC2 in Water

Monomer (**IPC2**, 0.5 g, 9.95×10^{-4} mol) was dispersed in water (15 mL) in a 50 mL round bottom flask and the mixture was purged with N_2 for 20 min. Then the dispersion was heated to 70 °C on an oil bath to produce cloudy (and foamy) solution. Aqueous solution of ammonium persulfate

(APS, 3.4 mg, N_2 purged) was added and the polymerization was continued for 4h. Polymer started precipitating after a few minutes of the addition of APS. Finally the precipitated polymer **CP11** was filtered and dried in a vacuum oven to yield white powder (yield 70%). The product was insoluble in THF, DMF, ACN, acetone, toluene, 2,2,2-trifluoro ethanol (TFE) and formamide.

Dispersion Copolymerization of MMA with IPC1 in Water

Monomer (**IPC1**, 0.1 g, 2.758×10^{-4} mol, 2.86 mol % of total monomer) was dispersed in water (10 mL) in a 50 mL round bottom flask and the mixture was purged with N_2 for 20 min. The dispersion was heated to 70 °C on an oil bath to produce cloudy solution. Then the N_2 purged methyl methacrylate (MMA) (1 mL, 0.936 g, 9.348×10^{-3} mol, 97.14 mol %) was added and stirred at 500 rpm for 10 min. Aqueous solution of ammonium persulfate (APS, 10.67 mg, N_2 purged, 0.5 mol % relative to monomers) was added and the polymerization was continued. Polymer started precipitating after a few minutes of the addition of APS and the reaction was stopped after 4h. Finally the precipitated polymer **CP12** was filtered and dried in a vacuum oven to yield white powder (yield 600 mg, 58%). The product was insoluble in THF, $CHCl_3$, ACN, acetone, toluene, swelled in DMF but soluble in 2,2,2-trifluoro ethanol (TFE), 1,1,1,3,3,3-hexafluoroisopropanol (HFiP) and 10% LiTFSI and $LiPF_6$ solution of DMF quickly. Found: C 59.27, H 7.78, N 1.45, S 1.64% (**IPC1** unit content in copolymer was ~5.5 mol %).

Sample Preparation and Swelling Studies of CP12

CP12 (50 mg) was dissolved in 1 mL TFE. A part of this solution was used to fill a disc shape Teflon die which when dried (at room temperature for 24 h and then in oven at 50 °C for 5 h) produced a disc shape polymer sample of 12 mm diameter and ~ 1 mm thickness (weight 19.8 mg). This disc was then added THF (2 mL) in a glass vial, stirred occasionally and kept aside for 3 days. Finally the disc sample was taken out and diameter and weight was measure before drying (diameter 15 mm, wt 40 mg) and after drying (diameter 12 mm, wt 19 mg, weight loss = 4%) of swelled disc. For comparison a disc of pure poly(MMA) of similar size was produced and solubility behavior in THF was studied.

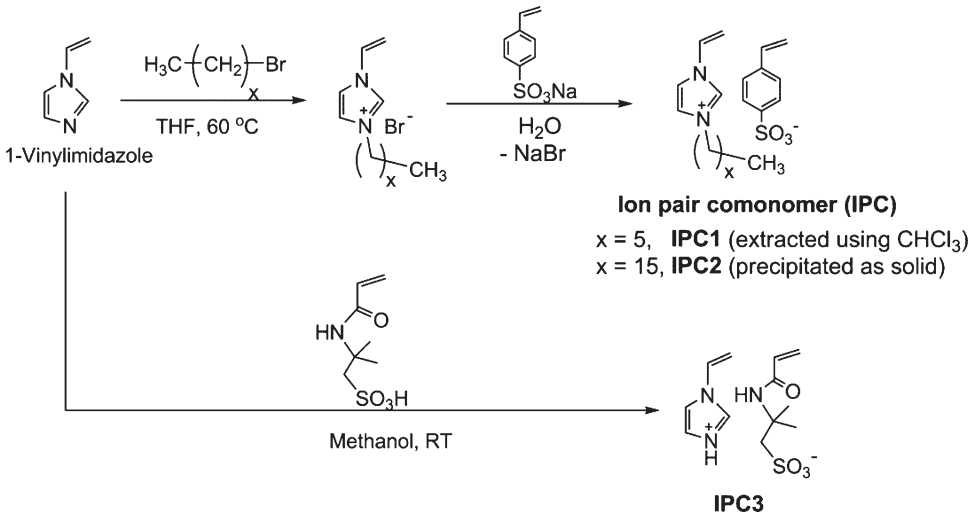
Synthesis of Polymer Network Between Poly(C_6VImBr) and Poly(*SSS*)

At first 3-hexyl-1-vinylimidazolium bromide (C_6VImBr, 1 g, 3.858 mmol) was polymerized by AIBN (12.67 mg, 0.077 mmol) under N_2 at 70 °C in MeOH for 48 h. Polymer was precipitated out from ether and dried in oven to yield 0.8 g of poly(C_6VImBr). Next, SSS (5 g, 24.25 mmol) was polymerized in water under N_2 at 70 °C for 5.5 h using APS initiator (111 mg, 0.486 mmol). Poly(SSS) (4.8 g) was precipitated out from acetone and dried in oven. Then, a solution of poly(C_6VImBr) (108 mg, mmol, 0.417 mmol respect to repeat unit) in 2:1 MeOH/water (5 mL) was added slowly to a aqueous solution (20 mL) of poly(SSS) (85.92 mg, 0.417 mmol respect to repeat unit) at room temperature and stirred for 2 h before heating at 90 °C for 2 h. The white precipitate product was collected by centrifuging the mixture followed by drying in vacuum oven. Yield 120 mg (80%). Found: C 57.8, H 7.26, N 8.48, S 7.58, O 17.92%.

RESULTS AND DISCUSSION

Synthesis and Characterization of IPCs

Vinylimidazole-based **IPCs**, **IPC1** and **IPC2**, were synthesized by a two-step process and **IPC3** was synthesized by a one-step process as shown in Scheme 1. For the synthesis of novel **IPC1** (Fig. 1), at first, 3-hexyl-1-vinylimidazolium bromide (C_6VImBr) was synthesized by the quaternization of 1-vinylimidazole (VIm) with 1-hexyl bromide. Mixing of this aqueous salt solution with the aqueous solution of SSS produced a homogeneous solution. However, the product **IPC1** was extracted from the aqueous solution using $CHCl_3$. The salt formed as a byproduct, viz., NaBr remained in the aqueous solution. On removal of the organic phase, **IPC1** was obtained as a fine white powder. The presence of equimolar quantities of components, that is, 3-hexyl-1-vinylimidazolium



SCHEME 1 Synthesis of different **IPC**s.

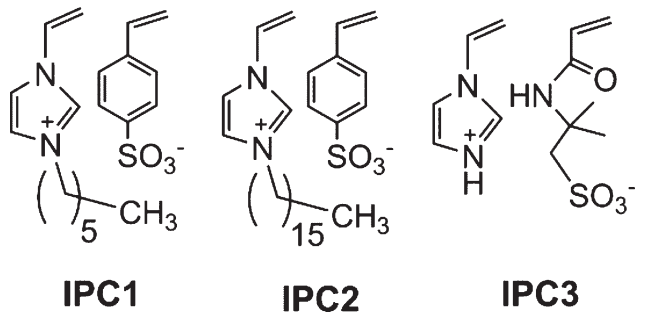


FIGURE 1 IPCs used for this study.

(C_6VIm) cation and 4-styrenesulfonate (SS) anion in **IPC1** was confirmed by NMR spectroscopy (Fig. 2) and elemental microanalysis. The characteristic vinyl $=C-H$ resonances were observed at 5.43, 5.89, and 7.23 ppm for C_6VIm cation and at 5.34, 5.89, and 6.78 ppm for SS anion in nearly 1:1 ratio in the ^{1}H NMR spectrum of **IPC1** along with all other expected signals (Fig. 2). The reduced intensity of $N^+=CH-N$ proton at 9.29 ppm of C_6VIm cation of **IPC1** (Fig. 2) was due to the acidic nature of this proton and possible deuterium exchange of this proton with the NMR solvent, that is, CD_3OD. Higher intensity of $N^+=CH-N$ proton of VIm cation was observed in lesser or nonexchangeable solvents like $CDCl_3$ (see Supporting Information Fig. S1). ^{13}C NMR spectrum of this comonomer showed the expected signals (Fig. 2).

Similarly, 3-hexadecyl-1-vinylimidazolium bromide (C_{16}VImBr) was synthesized by the quarternization of VIm with 1-hexadecyl bromide (Scheme 1). Interestingly, mixing of the aqueous solution of both 3-hexdecayl-1-vinyl imidazolium bromide (C_{16}VImBr) and SSS instantly produced a white precipitate of **IPC2** (Fig. 1 and Scheme 1). Again the presence of equimolar quantities of components, that is, 3-hexadecyl-1-vinylimidazolium (C_{16}VIm) cation and SS anion in **IPC2** was confirmed by NMR spectroscopy and elemental microanalysis. The signals corresponding to $C-H$ resonances of C_{16}VIm cation shifted upfield in ^{1}H NMR spectra when the bromide (Br^-) counter anion of C_{16}VImBr was replaced by the 4-styrenesulfonate

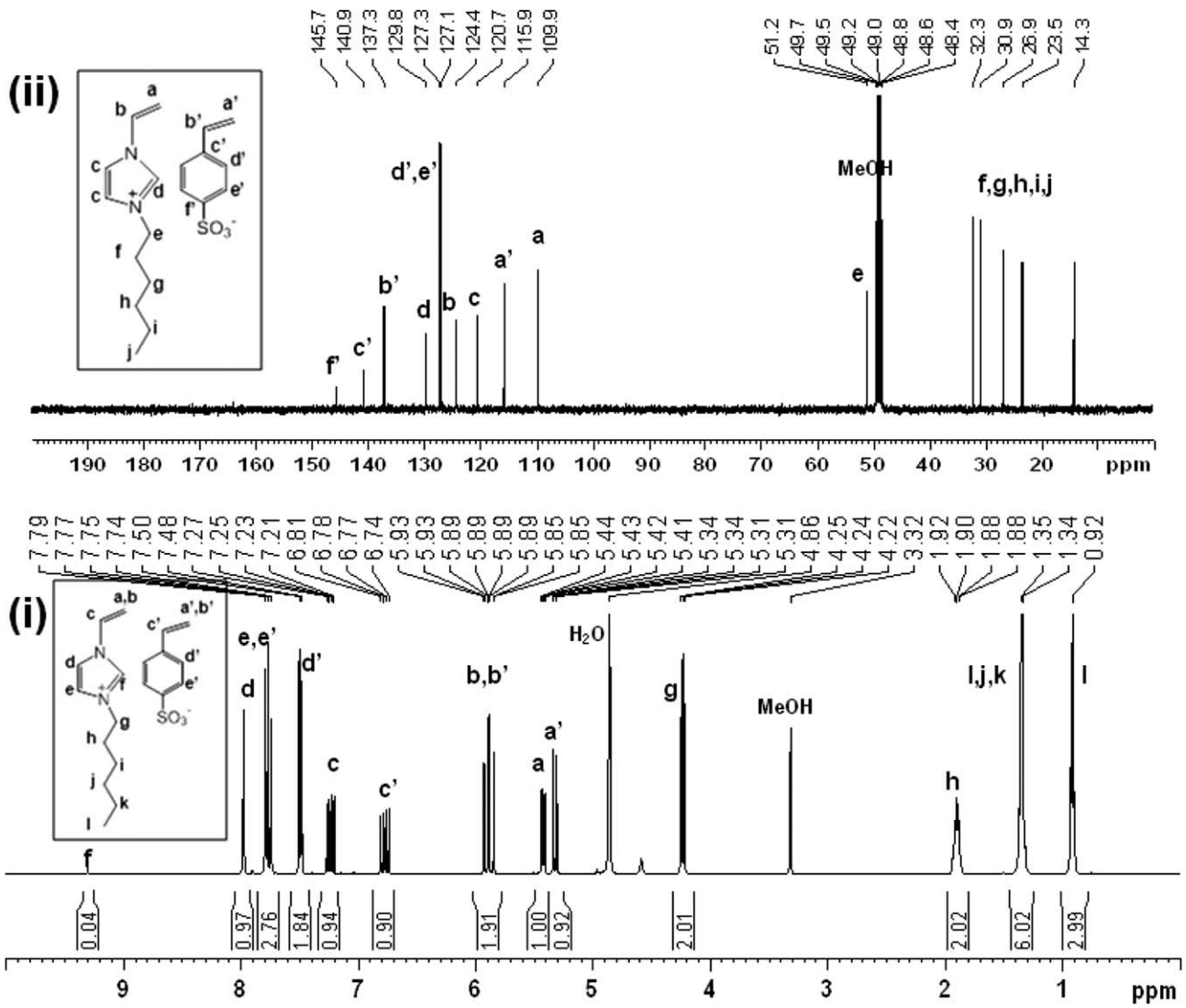


FIGURE 2 (i) ^{1}H NMR and (ii) ^{13}C NMR spectra of **IPC1** (in CD_3OD).

(SS) counter anion to produce **IPC2** as seen in Supporting Information Figure S2 due to the change in interaction between cation and anion.

The other comonomer **IPC3** (Fig. 1), was synthesized by mixing methanolic solution of VIm with an equimolar methanolic dispersion of 2-acrylamido-2-methyl-1-propanesulfonic acid (Scheme 1). The resulting solution was homogeneous and yielded **IPC3** as colorless, highly viscous mass on removal of methanol under vacuum. The product was finally transformed to a waxy solid on storing in a freezer. **IPC3** was not simply a physical mixture of VIm and 2-acrylamido-2-methyl-1-propanesulfonic acid. Instead it was in ionic form as confirmed by ^{1}H NMR spectroscopy (Fig. 3). The ^{1}H NMR signals corresponding to C—*H* resonances of VIm appearing at 4.97, 5.50, 7.14, 7.48, and 7.90 ppm were shifted downfield to 5.47, 5.97, 7.32, 7.67, and 8.02 ppm, respectively, and the largest shift was observed for the N^+=C*H*—N proton from 7.04 to 9.21 ppm confirming the protonation of VIm unit to produce VImH cation. However, proton signals of 2-acrylamido-2-methyl-1-propanesulfonate anion did not shift due to its nonconjugated nature.

Ionic Liquid Behavior of IPCs

The ion pair comonomers **IPC1–3**, have also been studied by DSC under N_2 atmosphere. **IPCs**, **IPC1–3**, were found to be high temperature ionic liquids with melting temperatures (T_m) of 69.7 °C, 94.6 °C, and 111.9 °C, respectively. Heating of representative **IPC2** in DSC from 20 °C to 270 °C showed (Fig. 4) one endothermic transition corresponding to the melting of **IPC2** and two exothermic transitions due to polymerizations. Any exothermic transition corresponding to solidification or crystallization was not observed in the cooling cycle during this experiment. This was due to the polymerization of the comonomer during the heating cycle (owing to heating to high temperature). However, both solid-to-liquid and liquid-to-solid transitions of **IPC2** were observed during heating and cooling cycles, respectively, when the DSC experiment was performed from 20 °C to 110 °C thereby avoiding the polymerization (Fig. 4).

Polymerization of IPCs

Polymerization of **IPC1–3** by FRP, ATRP, and RAFT-mediated polymerization were performed (targeted degree of polymerization

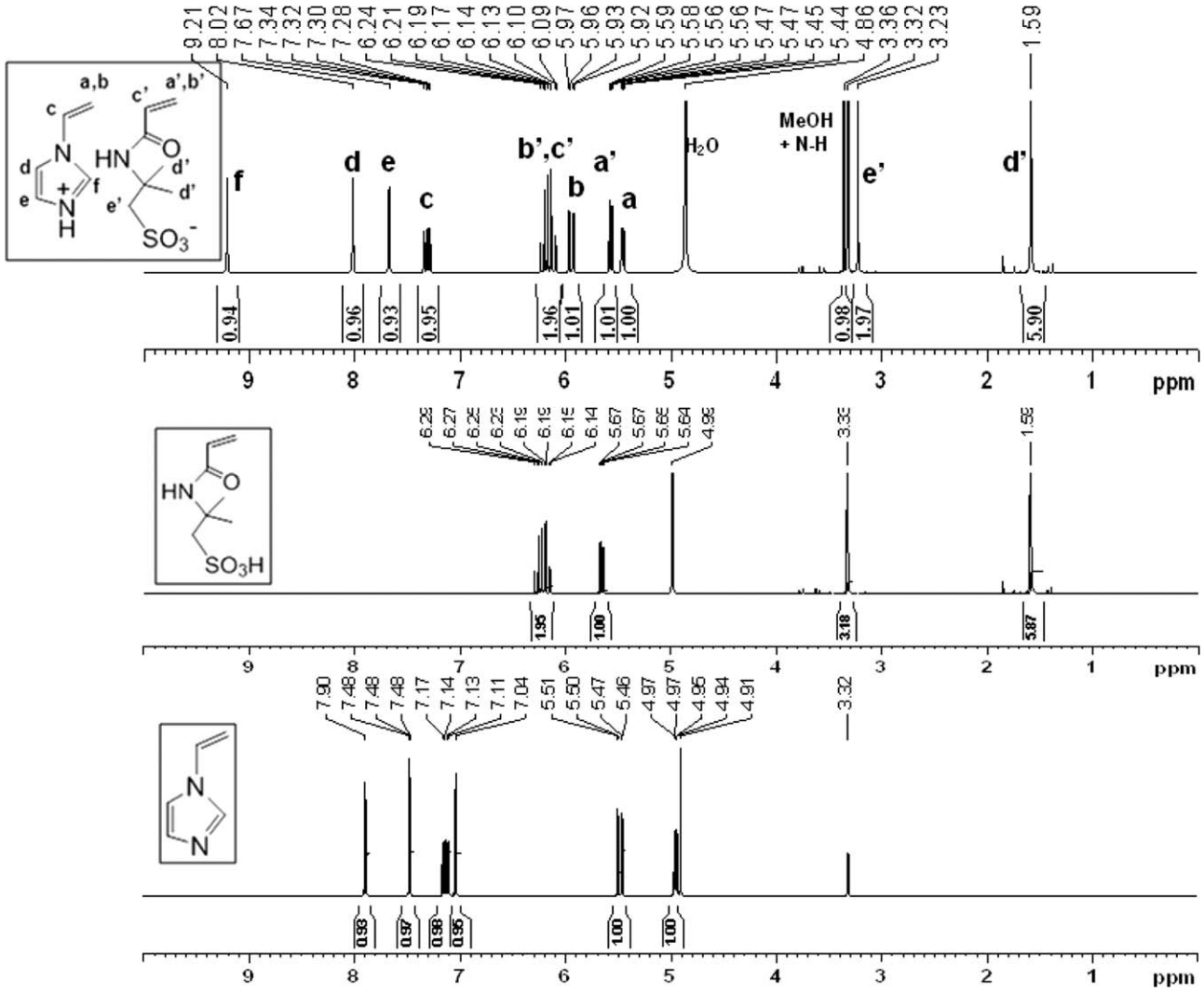


FIGURE 3 Overlay ^{1}H NMR spectra of **IPC3** and its precursors (in CD_3OD).

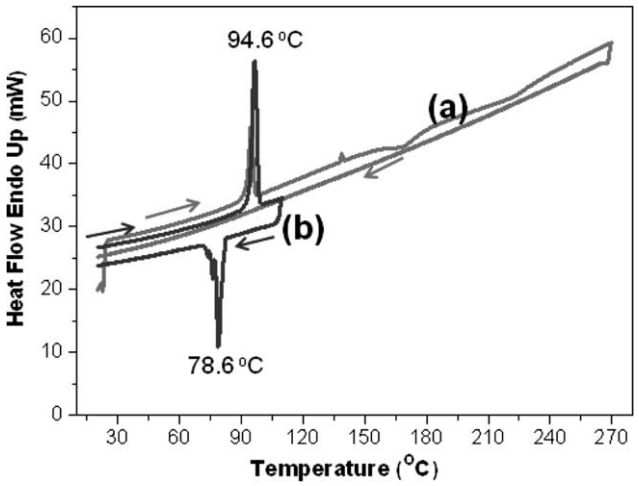


FIGURE 4 Overlay DSC plots of **IPC2** for different heating-cooling cycles: (a) 20–270 °C and (b) 20–110 °C.

was 50) in methanol and the time dependent conversions of individual ionic unit of **IPCs** were determined by ^{1}H NMR spectroscopic analysis using either $CDCl_3$ or preferably CD_3OD as solvent. Controlled radical polymerization techniques were used here as the polymerization techniques like ATRP,[19,20] SET-LRP,[21] and RAFT[20,22] can be expected to provide greater control over structure of polymers synthesized and also for the purpose of verifying the suitability of these techniques for surface initiated polymerizations[23] of **IPCs**.

The FRP of **IPC1** using 2,2′-azobisisobutyronitrile (AIBN) as initiator was heterogeneous and yielded a powdery white copolymer (**CP1** in Table 1). Both the final monomer conversion and polymer yield were high (∼95%). Characterization of this copolymer was difficult because of the insolubility of **CP1** in all common organic solvents tested including highly polar solvents like 2,2,2-trifluoroethanol (TFE) and formamide as well as in different aqueous solutions (Table 1). The highly insoluble nature of copolymer was most probably due to the prevalence of very strong intermolecular interactions of cationic and anionic pendant groups of **CP1**.

Both monomer conversion and copolymer yield from the ATRP of **IPC1** using traditional ethyl-2-bromoisobutyrate (EBiB) initiator, CuBr catalyst and *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA) ligand were low (below 12%, **CP2** in Table 1). The polymerization reaction was homogeneous, and the resultant polymer was difficult to isolate in pure form. Hence, characterization by GPC was not possible. This was no surprise as no successful ATRP or SET-LRP has been reported in the literature even for the parent 3-hexyl-1-vinylimidazolium (C_6VIm) based monomers most probably because of the catalyst poising by the VIm moiety. However moderate conversions and yield were observed in the RAFT-mediated polymerization of this comonomer (Scheme 2 and Table 1) using AIBN as initiator and 2-cyano-2-propyl benzodithioate (CPBD) as chain transfer agent. The rate of polymerization was slower than FRP as expected, and the reaction was homogeneous throughout the course of polymerization. Finally, the copolymer was separated by precipitating in ether to produce pink powder (Supporting Information Fig. S3). Interestingly, unlike **CP1** formed by FRP of **IPC1**, the copolymer **CP3** produced by RAFT from **IPC1** was soluble in some common organic solvents including methanol and also in 0.1 N aqueous solution of $NaNO_3$ (Table 1). Thus, it was possible to characterize **CP3** by aqueous GPC [Fig. 5(a)] and also by NMR spectroscopy. Although **IPC1** composed of equimolar mixture of 1:1 3-hexyl-1-vinylimidazolium (C_6VIm) cation and styrenesulfonate (SS) anion, the copolymer **CP3**, was formed by 37% and 79% of conversion of cations and anions, respectively. This was possibly due to the difference in chain transfer and reinitiation capability of polymer chains ending with C_6VIm based repeat unit in comparison to the chain end terminating with SS based repeat unit. However, this has created a charge imbalance within the polymer chain and therefore the negative charge of about 42% excess anionic SS unit was to be neutralized by the nonpolymerized or monomeric C_6VIm cations. This was indeed observed in the ^{1}H NMR spectrum of **CP3**. Repeated dialysis of copolymer **CP3** even in the presence of NaBr as well as at higher temperatures (50 °C) did not remove monomeric C_6VIm cations completely from the polymer as was observed in the ^{1}H NMR spectrum of dialyzed copolymer (Fig. 6). This may be due to the higher affinity of anionic SS derived repeat units to C_6VIm cations over the inorganic Na^+ cations.

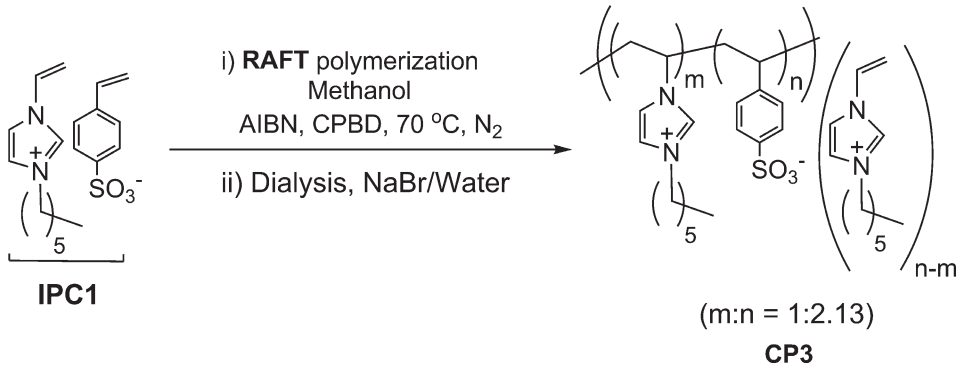
The improved solubility of **CP3** may be attributed to various factors such as greater control over the polymer structure caused by RAFT polymerization, due to the weaker interchain interactions among the inherently charge imbalanced polymer chains and because of the presence of monomeric C_6VIm cations to the polymer chains (Scheme 2) through ionic interactions, and so forth. The gel permeation chromatogram of **CP3** was monomodal, molecular weight ($M_{n,GPC}$) of the copolymer matched fairly well with the theoretically estimated molecular weight ($M_{n,Theo}$) and the polydispersity index (PDI) was also narrow (1.23) [Fig. 5(a) and Table 1].

Monomer conversion in FRP of **IPC2** was high (>85%), and the corresponding polymer was completely insoluble (**CP4** in Table 1). Several of our attempts to make soluble copolymer by FRP of **IPC2** by using different polymerization solvents like *N,N*-dimethylformamide (DMF), 1,2-dichloroethane, ethanol, or by dispersion polymerization in water did not succeed. ATRP of **IPC2** even at higher temperature failed to produce any polymer (Table 1) again possibly due to the catalyst poisoning by the VIm moiety as well as poor reactivity of Vim under ATRP. Again no successful ATRP or SET-LRP has been reported in the literature for its parent monomer consisting of 3-hexadecyl-1-vinylimidazolium (C_{16}VIm) species. RAFT-mediated polymerization of **IPC2** was, however, homogeneous and yielded pink-colored copolymer with high conversions when precipitated from excess MeOH at room temperature. The conversion of C_{16}VIm cation and SS anion were not same. As previously noted for the RAFT polymerization of **IPC1**, the charge imbalance in the polymer of **IPC2**, although low, was nevertheless noticed. The conversions of C_{16}VIm and SS ions

TABLE 1 Polymerization Results of Ion Pair Comonomers, **IPC1–3**

Comonomer	Copolymer Code	Process[a]	Status of Polymerization	Time (h) Dependant % Conversion[b] of VIm Cation/SS Anion	Copolymer Yield[c] (%)	Solubility[d]	$M_{n,GPC}$ (g/mol) (PDI)
IPC1	**CP1**	FRP	Precipitation	2 h: 50.5/61.9 20 h: 93.4/99.5	95	Insoluble	NA
	CP2	ATRP	Solution	2 h: Neg/Neg[e] 20 h: 2.3/11.0 44 h: 2.4/11.2	NA	NA	NA
	CP3	RAFT	Solution	2 h: Neg/Neg 20 h: 22.5/58.3 44 h: 37.1/79.0	70	MeOH, $HCONH_2$, TFE and 0.1 M $NaNO_3$ in H_2O	8,680[f] (1.23)
IPC2	**CP4**	FRP	Precipitation	2 h: 22.5/33.0 20 h: 85.9/99.3	87	Insoluble	NA
	CP5	ATRP	Solution	2 h: Neg/ Neg 20 h: Neg/ Neg 44 h: Neg/ Neg	NA	NA	NA
	CP6	RAFT	Solution	2 h: 4.5/7.9 20 h: 58.4/74.7 44 h: 64.8/84.0	75	$CHCl_3$/MeOH, THF/MeOH, DMF/MeOH, mixtures, TFE	NA
IPC3	**CP7**	FRP	Solution	2 h: 44.4/61.6 7 h: 77.9/98.5	74.0	MeOH, H_2O and 0.1 M $NaNO_3$ in H_2O	38,860 (2.18)
	CP8	ATRP	Solution	NA[g]	NA	NA	NA
	CP9	RAFT	Solution	2 h: 5.4/7.7 19 h: 25.3/49.8 44 h: 29.9/59.1	42.5	MeOH, H_2O and 0.1 M $NaNO_3$ in H_2O	11,100[h] (1.28)

[a] All polymerizations were performed under N_2 in MeOH and at 70 °C except the **CP5,** which was performed in 3:1 MeOH/DMF and at 80 °C. For FRP **IPC**: AIBN = 50:1, for ATRP **IPC**:EBiB:CuBr:PMDETA= 50:1:1:2, for RAFT **IPC**:CPDB:AIBN = 50:1:0.3; (AIBN = 2,2′-azobisisobutyronitrile, EBiB = ethyl-2-bromoisobutyrate; PMDETA = *N,N,N′,N″,N″*-pentamethyl-diethylenetriamine; CPBD = 2-cyano-2-propyl benzodithioate).
[b] Determined by ^1H NMR.
[c] Determined by gravimetry, after completion of polymerization.
[d] Solvents used for solubility tests were $CHCl_3$, ACN, THF, DMF, acetone, MeOH, H_2O, 0.1 M $NaNO_3$ in H_2O, TFE, and $HCONH_2$.
[e] Neg = negligible.
[f] $M_{n,Theo}$ = 10,780 g/mol.
[g] Could not be determined.
[h] $M_{n,Theo}$ = 7,740 g/mol.



SCHEME 2 Synthesis of **CP3** by RAFT polymerization of **IPC1** (RAFT agent derived end functional groups have been omitted for simplicity).

were 64.8% and 84%, respectively. The copolymer **CP6** showed surprising solubility behavior. **CP6** was insoluble in DMF, THF, $CHCl_3$, and MeOH. However, it was soluble in mixture of DMF/MeOH, THF/MeOH, and $CHCl_3$/MeOH. The improved solubility of **CP6** over **CP4** was most probably attributed to both controlled nature of the polymer structure and the ionically attached monomeric C_{16}VIm cations to the polymer chains to neutralize the excessive negative charge present in the polymer chain. The presence of ionically attached, nonpolymerized C_{16}VIm cations to the copolymer chain was again observed in the ^{1}H NMR spectrum of dialyzed **CP6.** The copolymer **CP6** was dissolved in a mixture of $CDCl_3$ and CD_3OD for NMR spectroscopic analysis. The molecular weight of copolymer **CP6** could not be determined due to the insolubility of **CP6** in a suitable solvent which is used in GPC as eluant.

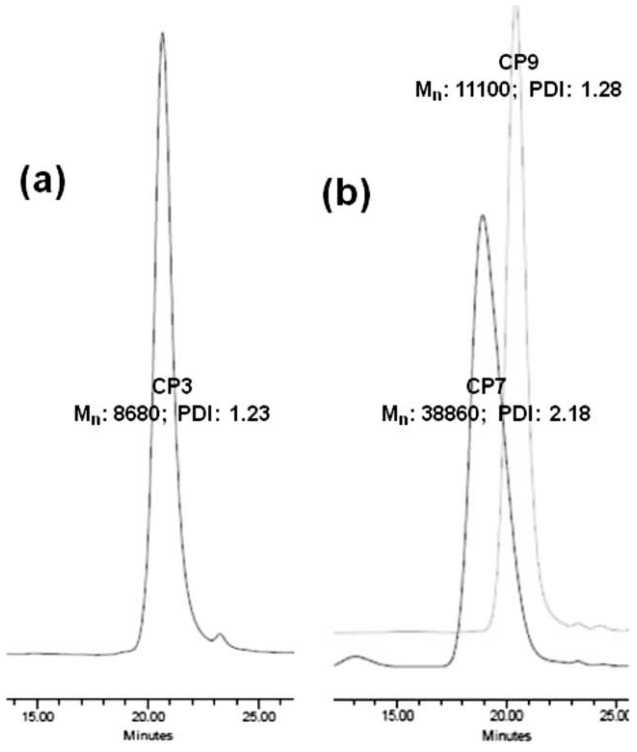


FIGURE 5 Aqueous GPC chromatogram of (a) **CP3** and (b) overlay chromatograms of **CP7** (red) and **CP9** (green).

Vinylimidazole (VIm) and acrylamide-based asymmetric comonomer **IPC3** (Fig. 1) was polymerized in the same way as described before for **IPC1** and **IPC2** (Table 1). However, FRP of **IPC3** in MeOH proceeded homogeneously. The monomer conversions were high but unequal. The copolymer **CP7** was soluble in a range of solvents and hence was characterized by ^{1}H NMR spectroscopy (Supporting Information Fig. S4) as well as GPC analysis [Fig. 5(b)].

The dialyzed product of this copolymer still revealed the presence of some monomer, VImH cations ionically bonded with the copolymer to neutralize the excessive anions derived from acrylamide comonomer of **IPC3**. It may be noted here that unlike copolymers **CP1**, **CP4**, and **CP7** exists in its protic form and thus exhibits different solubility characteristics.

Similar to **IPC1** and **IPC2**, **IPC3** also could not be polymerized under ATRP. The lack of polymerization under ATRP may be due to the presence of exchangeable protons in the polymerization system. It is well known that acidic monomers cannot be directly polymerized under ATRP. However, RAFT-mediated polymerization of **IPC3** proceeded with moderate conversions and yield. The molecular weight of the colored (Supporting Information Fig. S3) copolymer **CP9** matched fairly well with the theoretically estimated value and the PDI was narrower than the polymer obtained by FRP (i.e., **CP7**) [Fig. 5(b) and Table 1].

One common feature of all **IPC**s during polymerization has been that conversion of anionic comonomer of the ion pair monomer was invariably higher. This is most likely due to α, β-unsaturated (i.e., conjugated) nature of anionic comonomer because of which its reactivity is far greater than that of the cationic counterpart derived from VIm.

Thermal Properties of IPCs and CP1

Thermal stability of all asymmetric **IPCs**, **IPC1–3**, and a representative copolymer produced from **IPC1** by FRP, that is, **CP1** were determined by TGA under nitrogen atmosphere

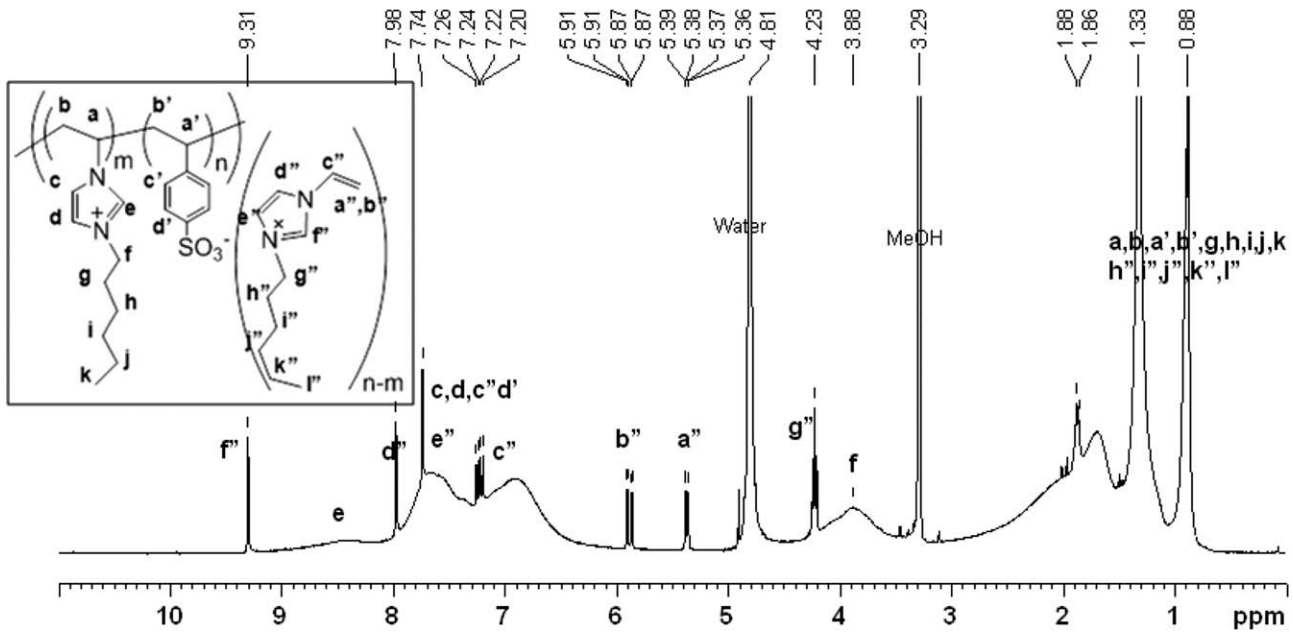


FIGURE 6 ^{1}H NMR spectrum of **CP3** in CD_3OD after dialysis.

(Fig. 7). In general, due to the hygroscopic nature of these comonomers and polymer, weight loss was invariably observed below 100 °C. Comonomers **IPC1** and **IPC2**, which were made of C_6VIm or C_{16}VIm and SS ions, respectively, were stable up to 300 °C. However, **IPC3**, which was obtained by combining VImH and acrylamide-based ions, was stable only up to 200 °C. The residual weight for all the materials analyzed was 8%–10%, which is most probably due to the char formation of heteroatom containing materials.

Intra- versus Intermolecular Interactions in Copolymer Produced by FRP of IPCs and their Solubility Behavior

Based on electrostatic interactions, ionic interactions of copolymers synthesized from **IPCs** can be expected to be of intra chain and inter chain in nature (Scenario **A** and **B**, respectively, of Scheme 3) or more probably mixed interactions (Scenario **C** of Scheme 3). The formation of partially neutralized copolymers as confirmed by monomer conversion as well as NMR spectroscopic analysis clearly points to the prevalence of structure proposed in Scenario **C** as for Scenario **B** to prevail, equal conversion of **IPCs** is a prerequisite. This scenario here is unique caused by the unusual reactivity of vinyl monomers which are the components of **IPCs** unlike previously reported polyampholytes[6,8–11] synthesized from symmetrical **IPCs** with similar reactivity.

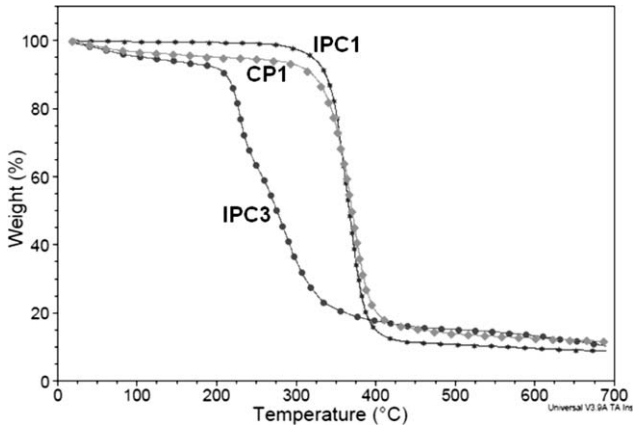
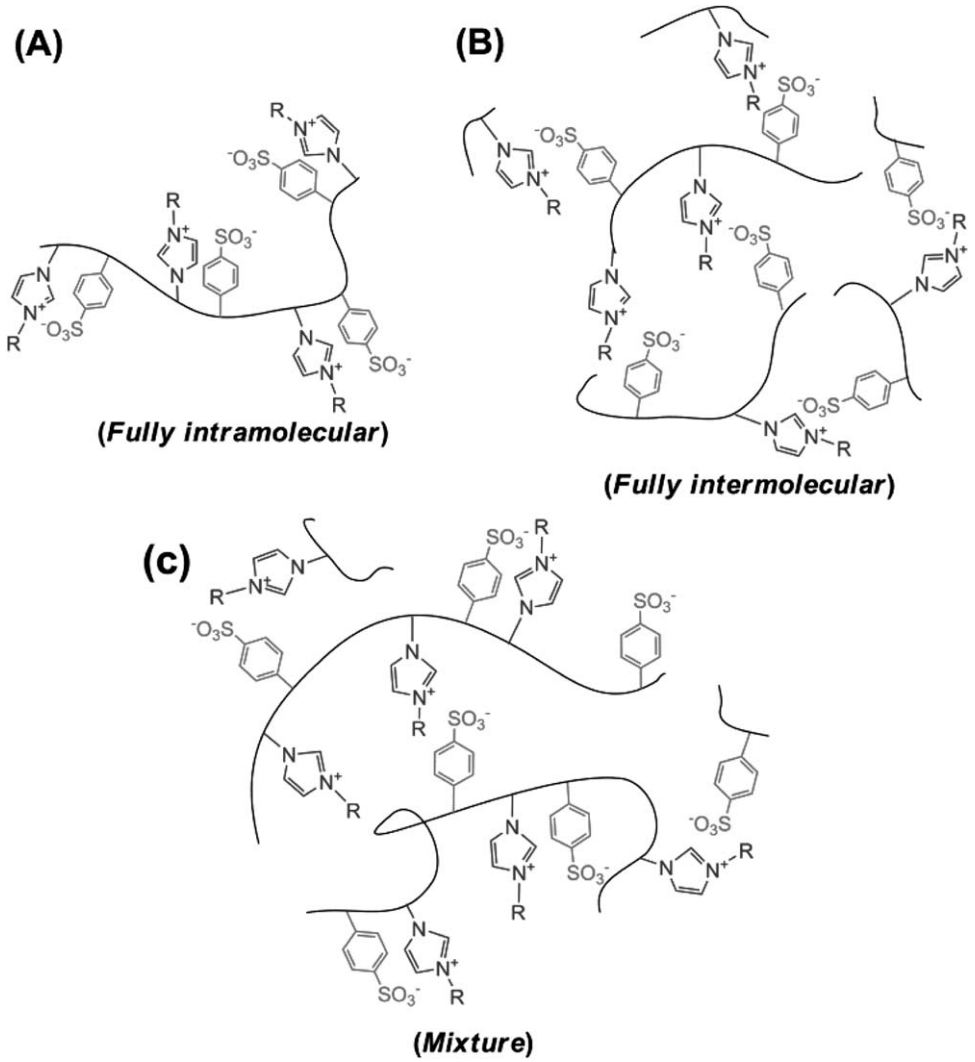


FIGURE 7 TGA of **IPC1**, **IPC3**, and **CP1**.

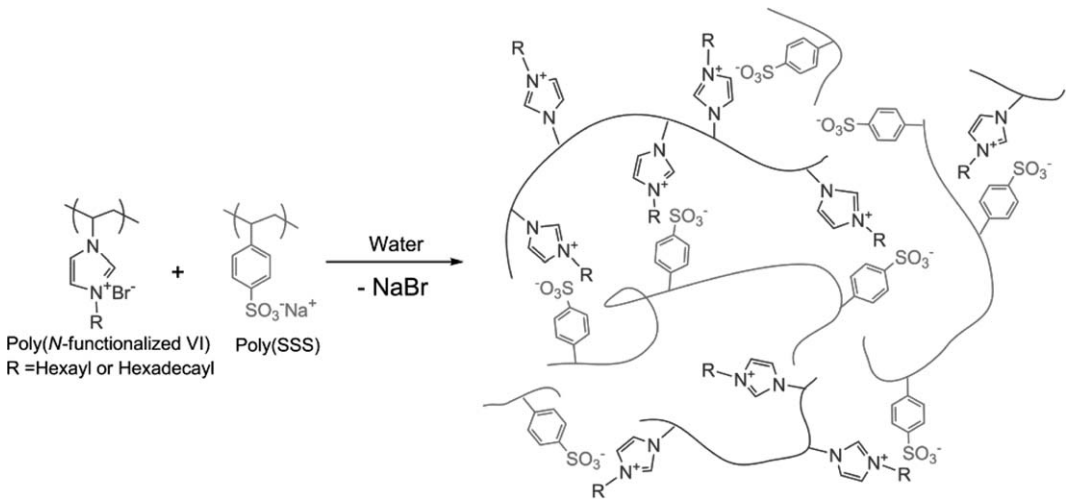
The insoluble nature of copolymers obtained by FRP of **IPC1** and **IPC2** (i.e., **CP1** and **CP4**, respectively, in Table 1) even in very polar organic solvents as well as in concentrated salt solutions supports the strong interchain interaction, although may not be 100%, combined with the formation of high molecular weight polymers. The lack of solubilizing behavior of these polymers due to interchain interactions was partially supported by the synthesis of fully inter chain ionically crosslinked polymer prepared according to Scheme 4. The homopolymers of C_6VImBr and SSS were mixed in equimolar quantities to instantly produce highly insoluble network copolymer of poly(C_6VIm) and poly(SS) (Scheme 4).

Dispersion Polymerization of IPCs and Preparation of Ionically Crosslinked PMMA

IPC1 and **IPC2** were insoluble in water at room temperature but were sparingly soluble at high temperatures. The cloudy and foaming solution of these comonomers was polymerized using ammonium persulfate (APS) initiator to observe any effect on the solubility of polymer produced. Due to the foaming nature **IPCs** it can be considered as polymerizable surfactants (Supporting Information Fig. S5). However, during the course of polymerization the polymer was precipitated out as white solid from the reaction mixture. The polymers thus formed, **CP10** and **CP11** (Table 2), were



SCHEME 3 Possible polymerization products of **IPCs**.



SCHEME 4 Interchain ionic crosslinking.

TABLE 2 Dispersion Copolymerization of **IPCs**

Comonomer	Code	Polymer Yield[a] (%)	Solubility of Polymer[b]
IPC1	**CP10**	72	Insoluble
IPC2	**CP11**	70	Insoluble
IPC1 and **MMA**	**CP12**	58	Insoluble in THF, acetone, $CHCl_3$, swelled in DMF, soluble in TFE and in DMF containing Li+ salts.

All polymerizations were performed in water under N_2 and at 70 °C for 4 h using ammonium persulfate (APS) initiator with monomer:initiator 50:1 ratio.

[a] Determined gravimetrically.
[b] Solvents used for the solubility tests were $CHCl_3$, ACN, THF, DMF, acetone, MeOH, H_2O, 20% NaCl in H_2O, TFE.

insoluble in all solvents tested which was similar to the solubility behavior of copolymer **CP1** and **CP2** discussed before.

The strong inter chain interaction of copolymer produced from **IPC1** was exploited to synthesize ionically crosslinked PMMA by copolymerizing MMA with small quantity of **IPC1.** The interaction between C_6Vim cations and SS anions derived from two or more polymer chains can be expected to result in network formation. This kind of ionically crosslinked materials were reported previously to have different physical properties, for example, stiffness, fatigue strength, fracture behavior, and so forth, in comparison to their linear analogs such as PMMA,[25(a)] PS[25(b)], and so forth. Therefore, a small quantity of **IPC1** (2.86 mol %) was copolymerized with excess MMA (97.14 mol %) in water by dispersion polymerization technique using APS initiator (Fig. 8). The white powdery copolymer **CP12** contained about 5.5 mol % of **IPC1** as determined by nitrogen content in elemental analysis and was mainly composed of MMA (~94.5 mol %). Unlike the homopolymer PMMA, this copolymer **CP12** [poly (MMA-*co*-**IPC1**)] was insoluble in THF, acetone, $CHCl_3$, and only swelled in DMF. It may be noted that swelling is a

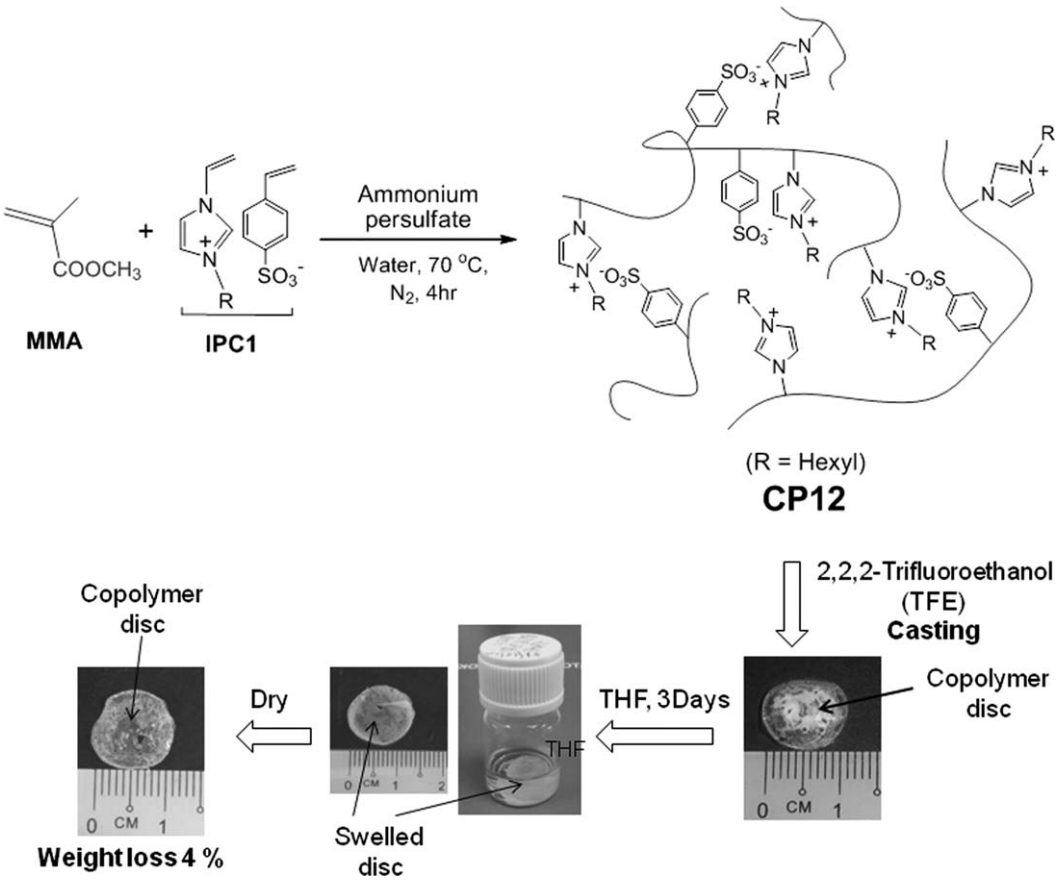


FIGURE 8 Synthesis of ionically crosslinked PMMA, that is, **CP12** by aqueous dispersion polymerization and swelling study (in THF) of a disc shape sample produced using the copolymer.

tendency commonly associated with networked polymers. However, this copolymer was soluble in 10% lithium salt (like LITFSI or $LiBF_4$) solution of DMF or DMSO. Copolymer **CP12** was also soluble in strongly H-bonding solvents like 2,2,2-tifluoroethanol (TFE) and 1,1,13,3,3-hexafluoro isopropanol (HFiP). This unusual solubility behavior of this copolymer mainly composed of MMA is most likely due to the intermolecular ionic interactions as depicted below (Fig. 8). The solubility behavior in salt solutions as well as strongly H-bonding solvents further confirm the existence of weakly networked structures where the network junctions are noncovalent in nature and thus can be disrupted by ionic as well as H-bonding interactions. The disruption of ionic interaction occurs due to the effective solvation of ions by these solvents. Several other experiments confirmed that poly(MMA-*co*-**IPC1**) with < 3 mol % of **IPC1** content was insoluble in THF and $CHCl_3$ but soluble in DMF. However, poly(MMA-*co*-**IPC1**) with 20 mol % of **IPC1** content was insoluble in all organic solvent including TFE and HFiP.

This ionically crosslinked PMMA, **CP12** was used for swelling studies. A sample of **CP12** in the form of a disc (Fig. 8) remained undissolved in THF; however, it swelled $\sim$ 25% over 3 days. A PMMA disc of similar dimension dissolved in less than 2 min in THF. On drying of the swollen disc, it shrunk back to its original shape and dimension with barely 4% of weight loss but with improved flexibility indicating that the solvent was retained in the voids of networked polymer which also plasticized the disc. This also confirms that the sample was truly a copolymer, that is, poly(MMA-*co*-**IPC1**) and not a physical mixture of homopolymer of PMMA and poly(**IPC1**). It is quite likely that the **IPC** acts as a divinyl monomer like divinyl benzene, ethylene glycol di(meth)acrylate, and so forth, in the copolymerization with MMA through the ionic interaction.

CONCLUSIONS

The asymmetric nature of **IPC**s were reflected in their polymerization behavior where the incorporation of styrenesulfonate (*SS*) or acrylamide-based anions exceeded the incorporation of vinylimidazole (VIm) cations in all kinds of radical polymerization methods studied. In general, ATRP of these monomers were very sluggish or negligibly small and completely prohibited in the case of **IPC2,** whereas RAFT-mediated polymerization of all of these comonomers produced relatively well controlled polymers with improved solubility. The FRP polymer of high temperature ionic liquid C_nVIm-*SS* based **IPC1** and **IPC2** were poorly soluble due to the strong intermolecular interactions. This strong interactive nature of VIm-*SS* based copolymers was exploited to produce ionically crosslinked PMMA. In future, we plan to apply this type of ionic crosslinking for other copolymer networks with special interest on reversible crosslinking as reported recently by Sun et al.[26] The synthetic methodology used here for the synthesis of **IPCs** and copolymers are potential for applications like polyelectrolytes, antifouling materials, layer by layer deposition techniques, and many others similar to poly(ionic liquids).

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