

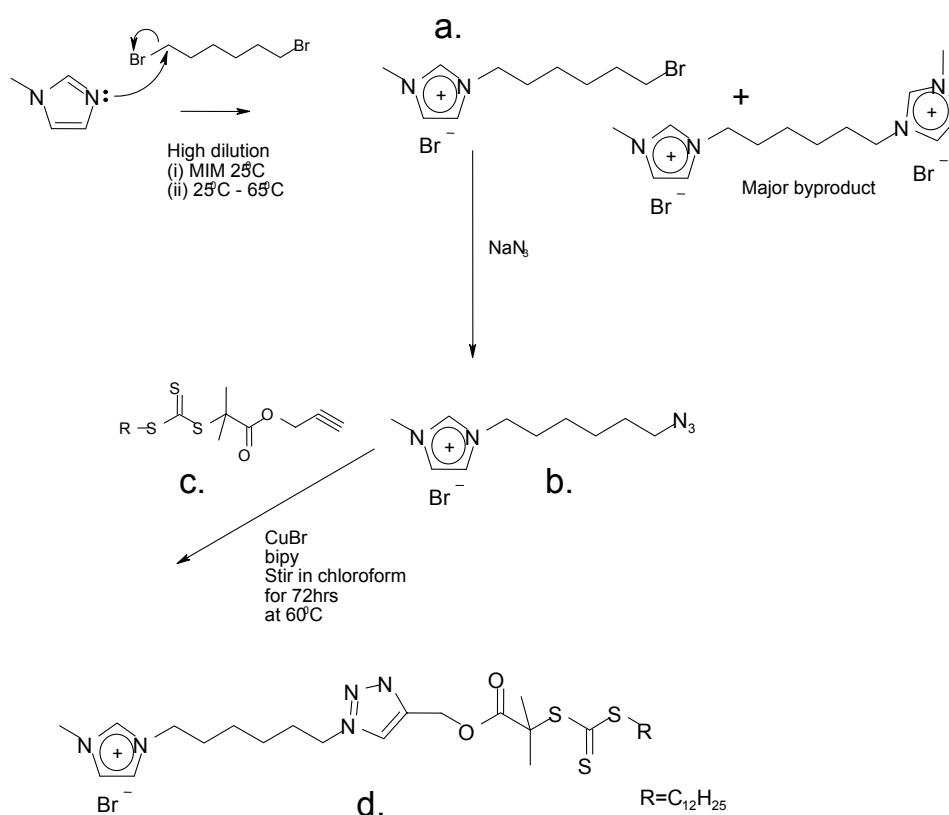
Supporting Information

RAFT-Functional Ionic Liquids: Towards Understanding Controlled Free Radical Polymerisation in Ionic Liquids

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1. Synthesis of RTIL-tethered RAFT agent.

The general procedure for the synthesis of the RTIL-tethered RAFT agent is summarised in Scheme S1.



a. Synthesis of 3-(6-bromohexyl)-1-methyl imidazolium bromide.

1,6-dibromohexane (42.47 mL, 107 mmol) was dissolved in 100 mL dry dichloromethane in a 250 mL round-bottom flask. 7.33 mL of dry 1-methyl imidazole (86 mmol) was added dropwise to the mixture with stirring over a period of 1 hour. The reaction mixture was heated to 70 °C for 72 hours under reflux. The white precipitate that was formed was filtered and the product was purified by column chromatography (7:1 mixture of dichloromethane:methanol). The major unwanted byproduct was the bis-imidazolium species which lead to a low overall yield of 6.022 g (20.1 %). δ_{H} (300 MHz; CDCl₃) 0.9-1.8 (8H, br m,

NCH₂CH₂CH₂CH₂CH₂CH₂Br), 3.21 (2H, t, CH₂Br), 3.99 (3H, t, CH₃N), 4.27 (2H, t, NCH₂-), 7.39-7.45 (2H, m, -N-CH-CH-N-), 10.9 (1H, s, -NCHN-).

b. Synthesis of 3-(6-azidohexyl)-1-methyl imidazolium bromide

6g 3-(6-bromohexyl)-1-methyl imidazolium bromide (18.4 mmol) was dissolved in 80 mL deionised water and added to a 250 mL round-bottom flask. 1.625 g NaN₃ (25 mmol) was dissolved in water and added to the flask. The reaction mixture was heated to 60 °C and stirred for 24 hours. The resulting mixture was washed with diethylether (3 times) and extracted into DCM. The product was recovered after solvent removal under vacuum. 3-(6-azidohexyl)-1-methyl imidazolium bromide was recovered as a viscous liquid in 90 % yield (4.78 g). δ_H (300 MHz; CDCl₃) 0.9-1.8 (8H, br m, NCH₂CH₂CH₂CH₂CH₂CH₂Br), 2.82 (2H, t, CH₂N₃), 3.99 (3H, t, CH₃N), 4.27 (2H, t, NCH₂-), 7.39-7.45 (2H, m, -N-CH-CH-N-), 10.9 (1H, s, -NCHN-).

c. Synthesis of alkyne terminated CTA (c)

S-1-dodecyl-S'-(α,α'-dimethyl-α''-acetic acid)trithiocarbonate (CTA2) was synthesised according to the method of Shea et al.¹ Thus, the alkyne-terminated CTA was synthesised as follows²: 1 g CTA(2) (2.73 mmol), 0.783g N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) (4.095 mmol), 0.5 g 4-dimethylaminopyridine (DMAP) (8.9 mmol) and 10 mL dichloromethane was stirred in a round bottom flask under nitrogen. 0.5 mL propargyl alcohol was then added to the mixture and stirred overnight at room temperature. The product was then washed with acidic water, water and brine, three times each. The product was dried with MgSO₄, filtered, evaporated and then dried under vacuum for 24 hours. The resulting compound was a low melting yellow solid. δ_H (300 MHz; CDCl₃) 0.87 (3H, t, CH₂CH₃), 1.2-1.4 (20H, m, CH₂CH₂), 1.65 (6H, s, C(CH₃)), 2.5 (1H, s, CHC), 3.25 (2H, t, CH₂S), 4.7 (2H, s, CH₂C).

d. Synthesis of RTIL-tethered RAFT agent (d)

357 mg 3-(6-azidohexyl)-1-methyl imidazolium bromide (1.24 mmol), 500 mg CTA(c) (1.24 mmol) and 34 mg CuBr (0.24 mmol) were added to a 10 mL test tube. 5 mL chloroform was added to the vessel. The test tube was sealed with a pressure septum and inserted into a CEM microwave for irradiation (CEM Discovery). The experiment was run at a microwave power of 150 Watts for 60 minutes during which time the temperature was kept constant at 80 °C via suitable pulsing of the microwave power and cooling by constant air flow at 5 bar.

The resulting mixture was purified by column chromatography on silica gel using 3:1 solvent mixture of dichloromethane:methanol (R_f = 0.7). The resulting product was isolated in 42 % yield as a viscous yellow oil. δ_H (300 MHz; CD₃OD) 0.91 (3H, t, CH₂CH₃), 1.2-1.4 (22H, br m, -CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃ + -CH₂CH₂CH₂CH₂N), 1.67 (2H, q, SCH₂CH₂), 1.69 (6H, s, C(CH₃)₂), 1.9(4H, m, NCH₂CH₂CH₂CH₂CH₂CH₂N), 3.25 (2H, t, SCH₂), 3.96 (3H, s, CH₃N), 4.24 (2H, t, CH₂CH₂N), 4.43 (2H, 2, N-CH₂), 5.22 (2H, s, CH₂O), 7.6-7.65 (2H, m, -NCHCHN), 7.75 (1H, s, NCHCNC), 9.0 (NCHN). ESI-MS m/z: 610.325 (M⁺, 100 %), 611.329 (37.2), 612.324 (19.3), 613.327 (4.8), 614.325 (1.0).

2. RAFT polymerisation procedure.

A typical RAFT mediated reaction targeting a polymer molecular weight of 25 kDa using $[C_4MIM][PF_6]$ as solvent is as follows: 1 mL methyl methacrylate (0.94 g, 9.4 mmol), 9 mL $[C_4MIM][PF_6]$, 13.38 mg CTA2 (0.0376 mmol) and 2 mg AIBN (.0075 mmol) were added to a 25 mL round-bottom flask and subject to three freeze-pump-thaw cycles. The reaction was then conducted under a blanket of nitrogen gas at 65 °C for 24 hours.

The resulting polymer/monomer was extracted from the ionic liquid using toluene and then precipitated into hexane. The resulting solid was then dried under vacuum for 24 hours followed by characterisation using NMR and GPC.

3. Chemicals and solvents

2,2-azobisisobutyronitrile (AIBN) was obtained from WAKO and recrystallised from methanol three times prior to use. Methyl methacrylate, Copper bromide, propargyl alcohol, N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC), 4-dimethylaminopyridine (DMAP), Sodium azide, diethylether and 1-methyl imidazole were purchased from Sigma Aldrich and used as received. RTILs were synthesised using optimised literature methods.

4. Kinetic details of polymerisation

The kinetics of polymerisation was followed for a number of the reactions. The conversion vs time and kinetic plots for free RAFT agent (both CTA1 and CTA2) in $[C_4MIM][NTf_2]$ (RAFT:AIBN = 1:1) and for CTA3 in $[C_4MIM][PF_6]$ (RAFT:AIBN = 1:0.5) is shown below.

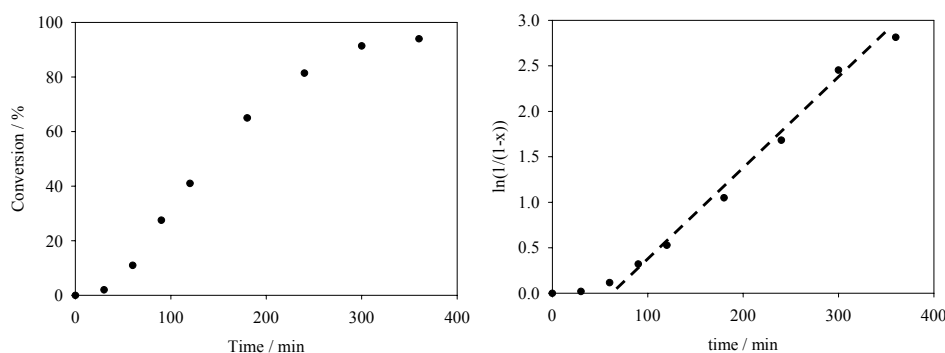


Figure S1. Conversion vs Time (left) and kinetic plot (right) showing pseudo first order kinetics exist for polymerisation of MMA in $[C_4MIM][NTf_2]$ using CTA1. The inhibition period is characteristic of polymerisations involving dithiobenzoates. RAFT:AIBN = 1:1. Conversion monitored by 1H NMR spectroscopy.

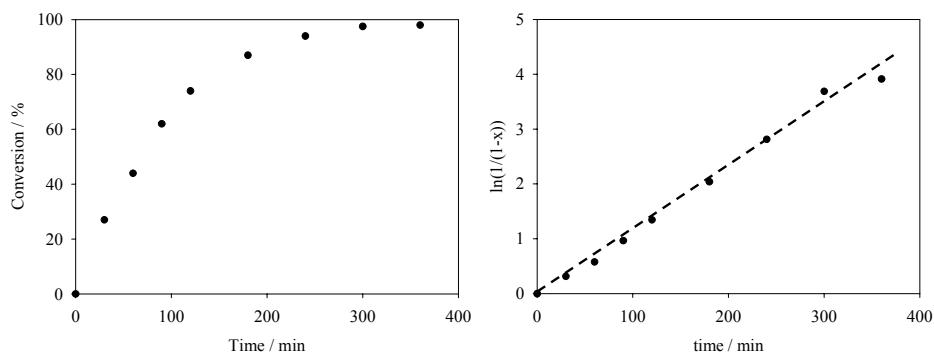


Figure S2. Conversion vs Time (left) and kinetic plot (right) showing pseudo first order kinetics exist for polymerisation of MMA in $[C_4MIM][NTf_2]$ using CTA2. RAFT:AIBN = 1:1. Conversion monitored by 1H NMR spectroscopy.

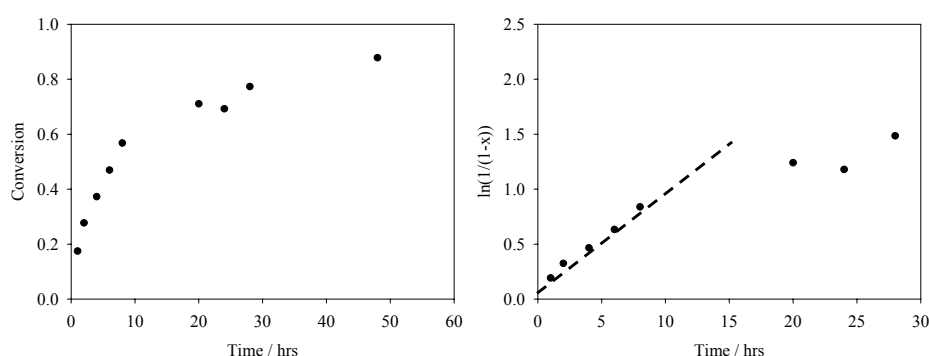


Figure S3. Conversion vs Time (left) and kinetic plot (right) showing pseudo first order kinetics exist for polymerisation of MMA in $[C_4MIM][PF_6]$ using CTA3 up to about 70 % conversion. RAFT:AIBN = 1:0.5. Conversion monitored by Raman Spectroscopy.

5. Chain extension experiments

Chain extension experiments were carried out on a number of homopolymers formed in various ionic liquids. In all cases, the PMMA homopolymer was chain extended with styrene in a single ionic liquid (styrene + additional AIBN was added). While a narrow PDI was generally retained during polymerisation with CTA1, homopolymerisation and subsequent chain extension using CTA3 in $[C_4MIM][PF_6]$ exhibited relatively broad PDIs (ie. 1.5). In both cases, M_n and peak molecular weight (M_p) both increased and unimodal peaks were observed suggesting successful chain extension. GPC data show that the chains are living and details are provided below:

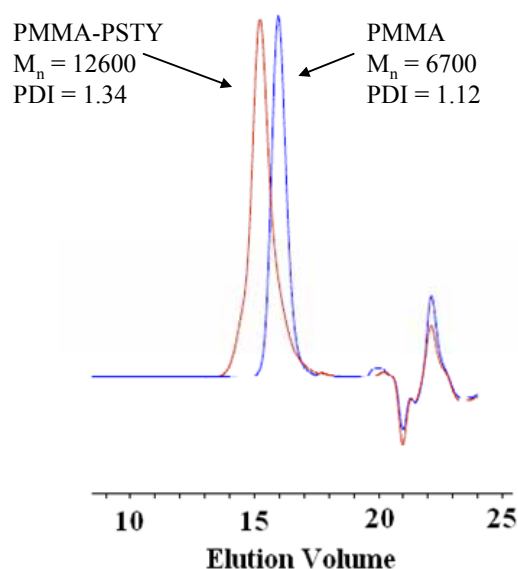


Figure S4. GPC trace and molecular weight details for PMMA formed in $[C_4MIM][NTf_2]$ using CTA1 and the subsequent trace after chain extension with styrene.

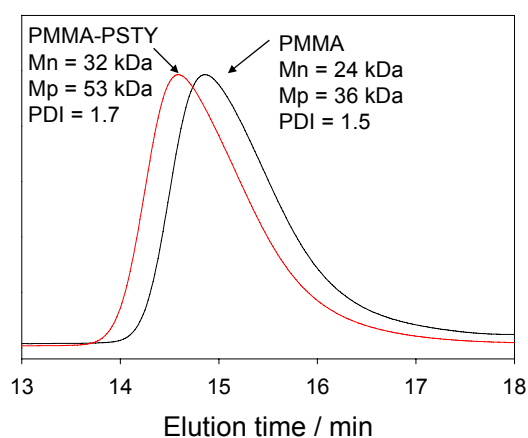


Figure S5. GPC trace and molecular weight details for PMMA formed in $[C_4MIM][PF_6]$ using CTA3 (12 hrs reaction, 70 % conversion, $M_n = 24$ kDa, $M_p = 36$ kDa, PDI = 1.5) and the subsequent trace following chain extension with styrene ($M_n = 32$ kDa, $M_p = 53$ kDa, PDI = 1.7).

References.

- (1) J. T. Lai, D. Filla, R. Shea, *Macromolecules* 2002, **35**, 6754.
- (2) R. Ranjan, W. J. Brittain, *Macromol. Rapid Commun.* 2007, **28**, 20.