

Supporting Information

For

The Influence of Domain Segregation in Ionic Liquids upon Controlled Polymerisation Mechanisms: RAFT Polymerisation

*Simon Puttick, Adrienne L. Davis, Kevin Butler, Derek J. Irvine, Peter Licence and
Kristofer J. Thurecht*

Synthesis and characterisation of materials:

2-Cyano prop-2-yl dithiobenzoate (CPDB) RAFT Agent

Carbon disulfide (1 mL, 0.017 moles) was added drop-wise via cannula to a solution of phenyl magnesium bromide (1.8 mL, 0.01 moles solution in dry THF) and the reaction stirred under a dry argon atmosphere at room temperature for 3 hours. The THF was removed under vacuum and the resulting viscous red oil was dissolved in a dilute potassium carbonate solution (100 mL). The resulting mixture was filtered and washed with diethyl ether (3 x 50 mL). To the stirred solution iodine (10.42 mL, 0.054 moles 0.96 N solution) was added drop-wise causing a pink precipitate to form. A few crystals of sodium thiosulfate were added to eliminate any excess iodine. The mixture was washed and the product extracted with dichloromethane. The solution was subsequently dried over sodium sulphate and the dichloromethane evaporated to yield the product as a pink powder (**1**). AIBN (0.57 g, 0.0035 moles) and product **1** (1.06 g, 0.0035 moles) were dissolved in dry ethyl acetate. The solution was degassed by three freeze, pump thaw cycles and heated to reflux (85 °C) for 16 hours under an argon atmosphere. The solvent was subsequently removed and the product purified by column chromatography using a 7 : 3 hexane : diethyl ether eluent. The product eluted as the first fraction. Fractions containing the pure product were combined and the eluent removed under vacuum to yield a viscous red oil (185 mg, 8.3×10^{-4} moles, 24 %).

$^1\text{H NMR}$ (400.13 MHz, CDCl_3) δ = 7.96 - 7.90 (m, 2 H), 7.60 - 7.54 (m, 1 H), 7.44 - 7.37 (m, 2 H), 1.95 (s, 6 H)

$^{13}\text{C NMR}$ (100.61 MHz, CDCl_3) δ = 223.1, 144.5, 132.9, 128.5, 126.6, 119.9, 41.7, 26.5

m/z [(H)(C₁₁H₁₁NS₂)⁺]: 222 (100 %), 223 (16 %), 224 (9 %)

[(Na)(C₁₁H₁₁NS₂)⁺]: 244 (56 %), 245 (7 %), 246 (5 %)

CHN Predicted: C = 59.73 %, H = 4.98 %, N = 6.33 %

Found: C = 60.45 %, H = 5.06 %, N = 6.07 %

[C₂C₁Im][Tf₂N]

A solution of 1.1 molar equivalents of Li[Tf₂N] in water was added drop-wise to a solution of [C₂C₁Im]Br in water ($\approx 1 : 2 \nu : \nu$) and stirred at 40 °C for 12 hours. The lower ionic liquid phase was separated and washed with water (washing continued until bromide and lithium content was below 100 ppm as measured by IC, typically 3 washes were required) before being dried *in vacuo*.

$^1\text{H NMR}$ (400.13 MHz, $\text{DMSO-}d_6$) δ = 9.15 - 9.02 (m, 1 H), 7.78 - 7.75 (m, 1 H), 7.69 - 7.66 (m, 1 H), 4.19 (q, J = 7.3 Hz, 2 H), 3.84 (s, 3 H), 1.41 (t, J = 7.3 Hz, 3 H)

$^{13}\text{C NMR}$ (100.61 MHz, $\text{DMSO-}d_6$) δ = 136.2, 123.6, 122.0, 119.5 (q, J = 322 Hz, 1C), 44.1, 35.7, 15.0

$^{19}\text{F NMR}$ (376.5 MHz, $\text{DMSO-}d_6$) δ = -78.79 (s, 1 F)

m/z [(C₆H₁₁N₂)₂(NS₂O₄C₂F₆)⁺]: 502 (100 %), 503 (17 %), 504 (10 %)

[C₄C₁Im][Tf₂N]

A solution of 1.1 molar equivalents of Li[Tf₂N] in water was added drop-wise to a solution of [C₄C₁Im][Cl] in water ($\approx 1 : 2 v : v$) and stirred at 40 °C for 12 hours. The lower ionic liquid phase was separated and washed with water (washing continued until chloride and lithium content was below 100 ppm as measured by IC, typically 3 washes were required) before being dried *in vacuo*.

¹H NMR (400.13 MHz, DMSO-*d*₆) δ = 9.15 - 9.02 (m, 1 H), 7.76 - 7.73 (m, 1 H), 7.70 - 7.67 (m, 1 H), 4.16 (t, J = 7.2 Hz, 2 H), 3.85 (s, 3 H), 1.82 - 1.72 (m, 2 H), 1.32 - 1.20 (m, 2 H), 0.90 (t, J = 7.4 Hz, 3 H)

¹³C NMR (100.61 MHz, DMSO-*d*₆) δ = 136.5, 123.6, 122.3, 119.5 (q, J = 322 Hz, 1C), 48.5, 35.7, 31.4, 18.8, 13.2

¹⁹F NMR (376.5 MHz, DMSO-*d*₆) δ = -78.82 (s, 1 F)

m/z [(C₈H₁₅N₂)₂(NS₂O₄C₂F₆)⁺]: 558 (100 %), 559 (20 %), 560 (10 %)

[C₈C₁Im][Tf₂N]

A solution of 1.1 molar equivalents of Li[Tf₂N] in water was added drop-wise to a solution of [C₈C₁Im][Cl] in water ($\approx 1 : 2 v : v$) and stirred at 40 °C for 12 hours. The lower ionic liquid phase was separated and washed with water (washing continued until chloride and lithium content was below 100 ppm as measured by IC, typically 3 washes were required) before being dried *in vacuo*.

¹H NMR (400MHz, DMSO-*d*₆) δ = 9.12 - 9.06 (m, 1 H), 7.77 - 7.73 (m, 1 H), 7.70 - 7.67 (m, 1 H), 4.14 (t, J = 7.2 Hz, 2 H), 3.84 (s, 3 H), 1.84 - 1.71 (m, 2 H), 1.35 - 1.16 (m, 10 H), 0.86 (t, J = 6.8 Hz, 3 H)

¹³C NMR (101MHz, DMSO-*d*₆) δ = 136.5, 123.6, 122.2, 119.5 (q, J = 322 Hz, 1C), 48.8, 35.7, 31.1, 29.4, 28.4, 28.3, 25.5, 22.0, 13.9

¹⁹F NMR (376.5 MHz, DMSO-*d*₆) δ = -78.77 (s, 1 F)

m/z [C₁₂H₂₃N₂]⁺: 195 (100 %), 196 (22 %)

[(C₁₂H₂₃N₂)₂(NS₂O₄C₂F₆)⁺]: 670 (23 %), 671 (7 %), 672 (3 %)

[C₄C₁Im][PF₆]

A 40 % aqueous solution of HPF₆ (equivalent to 1.1 moles HPF₆) was added slowly drop-wise to a solution of [C₄C₁Im][Cl] in water ($\approx 1 : 2 v : v$) using a plastic syringe whilst stirring at 0 °C under a dry argon atmosphere. Following addition, the resulting mixture was stirred at 40 °C for 12 hours. The lower ionic liquid phase was separated and washed with water until pH = 7 (tested by Litmus paper) before being dried *in vacuo*. The ionic liquid was further washed until the chloride content was > 100 ppm as measured by IC.

¹H NMR (400.13 MHz, DMSO-*d*₆) δ = 9.12 - 9.04 (m, 1 H), 7.76 - 7.73 (m, 1 H), 7.70 - 7.66 (m, 1 H), 4.15 (t, J = 7.2 Hz, 2 H), 3.84 (s, 3 H), 1.81 - 1.71 (m, 2 H), 1.32 - 1.20 (m, 2 H), 0.90 (t, J = 7.4 Hz, 3 H)

δ_C (100.61 MHz, *d*₆-DMSO) x

¹⁹F NMR (376.5 MHz, DMSO-*d*₆) δ = -70.19 (d, J = 711 Hz, 6 F)

³¹P NMR (161.98 MHz, DMSO-*d*₆) δ = -144.93 (spt, J = 711 Hz, 1 P)

m/z [(C₈H₁₅N₂)₂(PF₆)⁺]: 423 (100 %), 424 (16 %), 425 (1 %)

[C₄C₁Im][BF₄]

A solution of 1.1 molar equivalents of NaBF₄ in water was added drop-wise to a solution of [C₄C₁Im][Cl] in water ($\approx 1 : 2 v : v$) and stirred at 40 °C for 12 hours. The ionic liquid was extracted with dichloromethane and washed with water (washing continued until chloride and sodium content was below 100 ppm as measured by IC, typically 3 washes were required). The dichloromethane was evaporated and the ionic liquid dried *in vacuo*.

¹H NMR (400.13 MHz, DMSO-*d*₆) δ = 9.10 - 8.99 (m, 1 H), 7.75 - 7.72 (m, 1 H), 7.68 - 7.65 (m, 1 H), 4.16 (t, J = 7.2 Hz, 2 H), 3.84 (s, 3 H), 1.83 - 1.67 (m, 2 H), 1.35 - 1.14 (m, 2 H), 0.90 (t, J = 7.4 Hz, 3 H)

¹³C NMR (100.61 MHz, DMSO-*d*₆) δ = 136.5, 123.6, 122.3, 48.5, 35.7, 31.4, 18.8, 13.2

¹⁹F NMR (376.5 MHz, DMSO-*d*₆) δ = -148.299 (m, 4F (Coupled to ¹⁰B, 22 %)), -148.35 (q, J = 1.2 Hz, 4 F (Coupled to ¹¹B, 100 %))

¹¹B NMR (128.38 MHz, *d*₆-DMSO-*d*₆) δ = -1.23 (s, 1B)

m/z [(C₈H₁₅N₂)₂(BF₄)⁺: 364 (22 %), 365 (100 %), 366 (16 %), 367 (1 %)

Monitoring of RAFT controlled polymerisations

All RAFT controlled polymerisations were monitored by ¹H NMR to follow conversion with increasing time. Conversion was calculated as the ratio of the integral of the MeO resonance of MMA and the MeO resonance of PMMA as shown in **Figure 1**.

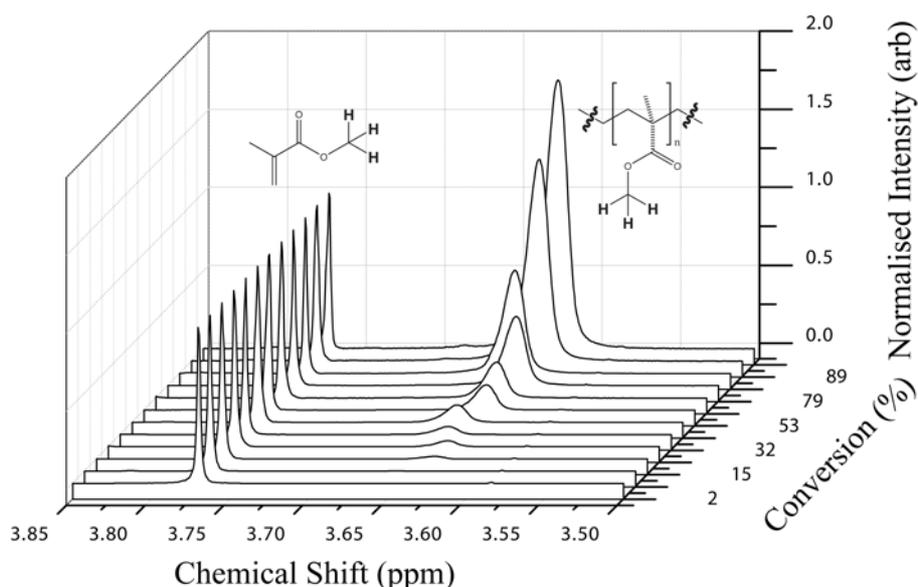


Figure 1: Example ¹H NMR spectra taken from a RAFT controlled polymerisation of MMA at increasing conversion. Spectra are referenced to the chemical shift of the MeO resonance of MMA at 3.77 ppm and normalised to the intensity of the data point at 3.77 ppm for clarity.

Aliquots of the reactions mixture were taken at increasing conversion for analysis by GPC to follow the increase of molecular weight with conversion. The polymer product was extracted from the ionic liquid with chloroform (1 mL) and dried *in vacuo* before being dissolved in HPLC grade THF and filtered through a 3 μ m filter. GPC traces were recorded on a PL120 GPC system fitted with 2 x C-packed columns in series (Polymer Laboratories). The polymer was eluted with HPLC grade THF at a flow rate of 1 mL min⁻¹ and detected using a refractive index detector. Molecular weights are reported relative to polystyrene standards. **Figure 2** shows sequential GPC traces for the polymer extracted at increasing conversion during the reactions in all ionic liquids studied.

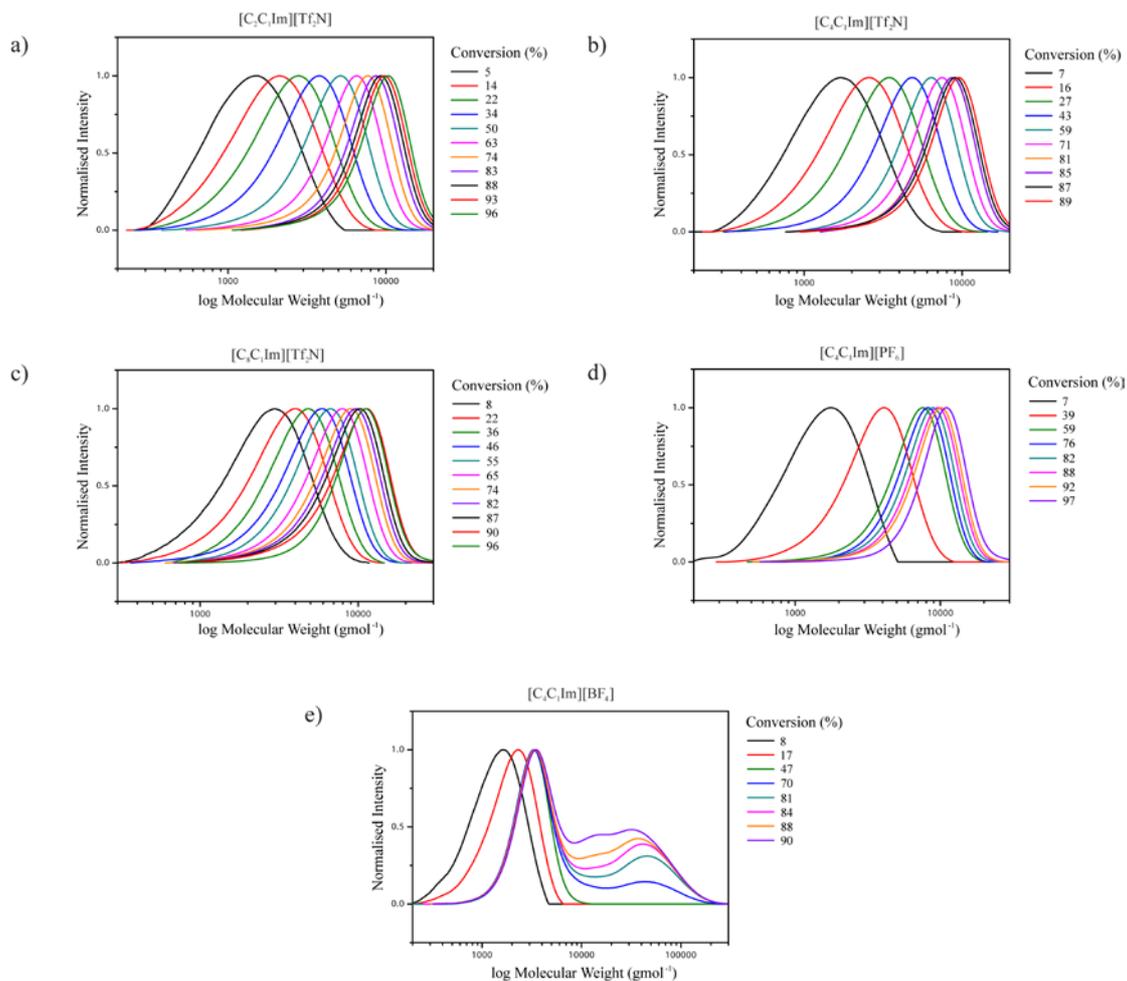


Figure 2: Sequential GPC traces for the RAFT controlled polymerisation of MMA in the ionic liquids a) $[C_2C_1Im][Tf_2N]$, b) $[C_4C_1Im][Tf_2N]$, c) $[C_8C_1Im][Tf_2N]$, d) $[C_4C_1Im][PF_6]$ and e) $[C_4C_1Im][BF_4]$

ROESY Acquisition parameters and example spectrum

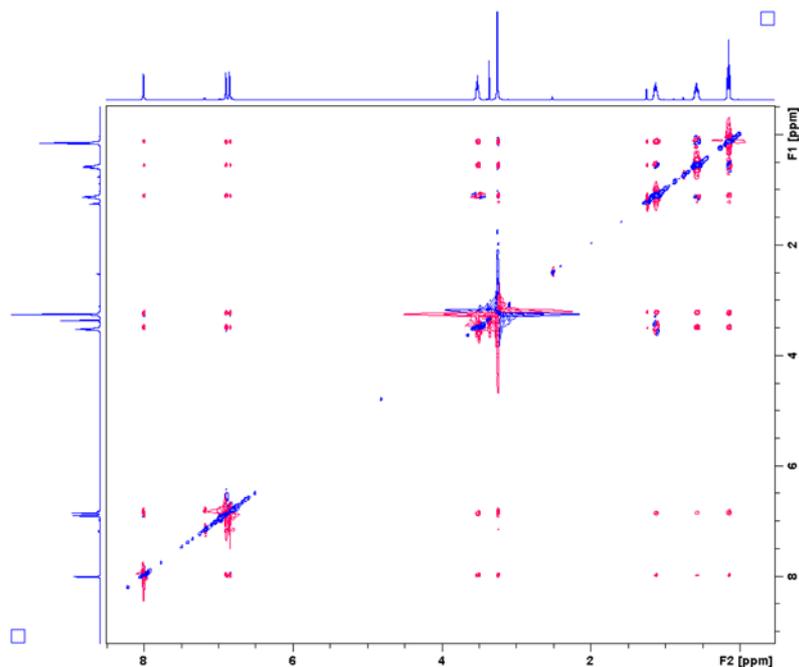


Figure 3: ROESY spectrum of the CPDB RAFT agent dissolved in $[C_4C_1Im][BF_4]$.

Table 1 Experimental parameters for the acquisition of ROESY spectra on a sample of the CPDB RAFT agent dissolved in the ionic liquids [C₂C₁Im][Tf₂N], [C₄C₁Im][Tf₂N], [C₈C₁Im][Tf₂N], [C₄C₁Im][PF₆] and [C₄C₁Im][BF₄]

Solvent	90 ° pulse (μs)	Spin lock pulse (μs)	Spin lock time (ms)	Dwell time (μs)	Sweep width (ppm)
[C ₂ C ₁ Im][Tf ₂ N]	8.7 @ 1.2 dB	166.6 @ 21.2 dB	160	77	13
[C ₄ C ₁ Im][Tf ₂ N]	8.6 @ 1.2 dB	166.6 @ 21.3 dB	180	77	13
[C ₈ C ₁ Im][Tf ₂ N]	8.6 @ 1.2 dB	166.6 @ 21.3 dB	140	77	13
[C ₄ C ₁ Im][PF ₆]	8.8 @ 1.2 dB	166.6 @ 21.1 dB	80	77	13
[C ₄ C ₁ Im][BF ₄]	8.8 @ 1.2 dB	166.6 @ 21.1 dB	100	77	13

Solvent	No. of scans	No. dummy scans	Relaxation delay (s)	Pre-scan delay (μs)	Receiver gain
[C ₂ C ₁ Im][Tf ₂ N]	32	128	3	75	57
[C ₄ C ₁ Im][Tf ₂ N]	32	128	3	75	57
[C ₈ C ₁ Im][Tf ₂ N]	32	128	3	75	57
[C ₄ C ₁ Im][PF ₆]	32	128	3	75	28.5
[C ₄ C ₁ Im][BF ₄]	32	128	3	75	28.5

ROESY spectra were recorded at 298 K using the two dimensional transverse ROESY sequence first proposed by Hwang and Shaka. **Figure 2** shows the spectra recorded for a sample of the CPDB RAFT agent dissolved in [C₄C₁Im][BF₄] as a typical spectrum. The spectra were recorded using the parameters outlined in **Table 1**.

DPIR calculation

Following acquisition, FIDs were extended to 4k data points in F2 and 1k data points in F1 by linear prediction using 32 coefficients and convoluted with a 180 ° shifted sine bell window function prior to fourier transform. Following fourier transform spectra were reduced to small regions of interest (ROIs) and re-processed to improve digital resolution. The spectra were reduced to a single frequency dimension by summing the data in the F1 direction. These pseudo 1D spectra were then deconstructed by fitting to a Voigt type function with a 30:70 Lorentzian:Gaussian weighting. The fit peaks were integrated and this value was used to calculate the DPIR. A workflow for calculation of the DPIR is shown in **Figure 3** and the values used in the calculation of the DPIR are shown in **Table 2**.

Table 2: Fitting parameters and values used in the calculation of the DPIR for the CPDB RAFT agent dissolved in the ionic liquids [C₂C₁Im][Tf₂N], [C₄C₁Im][Tf₂N], [C₈C₁Im][Tf₂N], [C₄C₁Im][PF₆] and [C₄C₁Im][BF₄]

Solvent	Probe Resonance	Cross Peak to H2-C				Cross Peak to H6-C, H8-C or H12-C			
		Position (ppm)	FWHM (ppm)	R ²	Integral	Position (ppm)	FWHM (ppm)	R ²	Integral
[C ₂ C ₁ Im][Tf ₂ N]	H3-R	7.887	0.022	0.984	292236.3	0.863	0.021	0.993	386840.7
[C ₄ C ₁ Im][Tf ₂ N]	H3-R	7.959	0.021	0.998	1996970.0	0.310	0.020	0.996	2119280.0
[C ₈ C ₁ Im][Tf ₂ N]	H3-R	8.041	0.022	0.986	781288.6	0.308	0.021	0.991	470414.1
[C ₄ C ₁ Im][PF ₆]	H3-R	7.717	0.019	0.995	219109.9	0.139	0.020	0.995	436682.4
[C ₄ C ₁ Im][BF ₄]	H3-R	7.992	0.019	0.996	371164.9	0.135	0.021	0.992	429667.0
[C ₂ C ₁ Im][Tf ₂ N]	H4-R	7.889	0.019	0.994	256915.6	0.865	0.021	0.986	1675240.0
[C ₄ C ₁ Im][Tf ₂ N]	H4-R	7.962	0.020	0.979	513902.2	0.316	0.018	0.989	3770100.0
[C ₈ C ₁ Im][Tf ₂ N]	H4-R	8.041	0.022	0.999	523682.6	0.310	0.022	0.993	3422760.0
[C ₄ C ₁ Im][PF ₆]	H4-R	7.719	0.019	0.994	190874.6	0.142	0.019	0.998	1580160.0
[C ₄ C ₁ Im][BF ₄]	H4-R	7.996	0.019	0.991	221460.6	0.139	0.018	0.998	1794180.0

