Electronic Supplementary Material (ESI) for Polymer Chemistry.

Is methanol really a bad solvent for poly(*n*-butyl methacrylate)? Low dispersity and high molecular weight polymers of *n*-butyl methacrylate synthesised via ATRP in anhydrous methanol.

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Supplementary Information

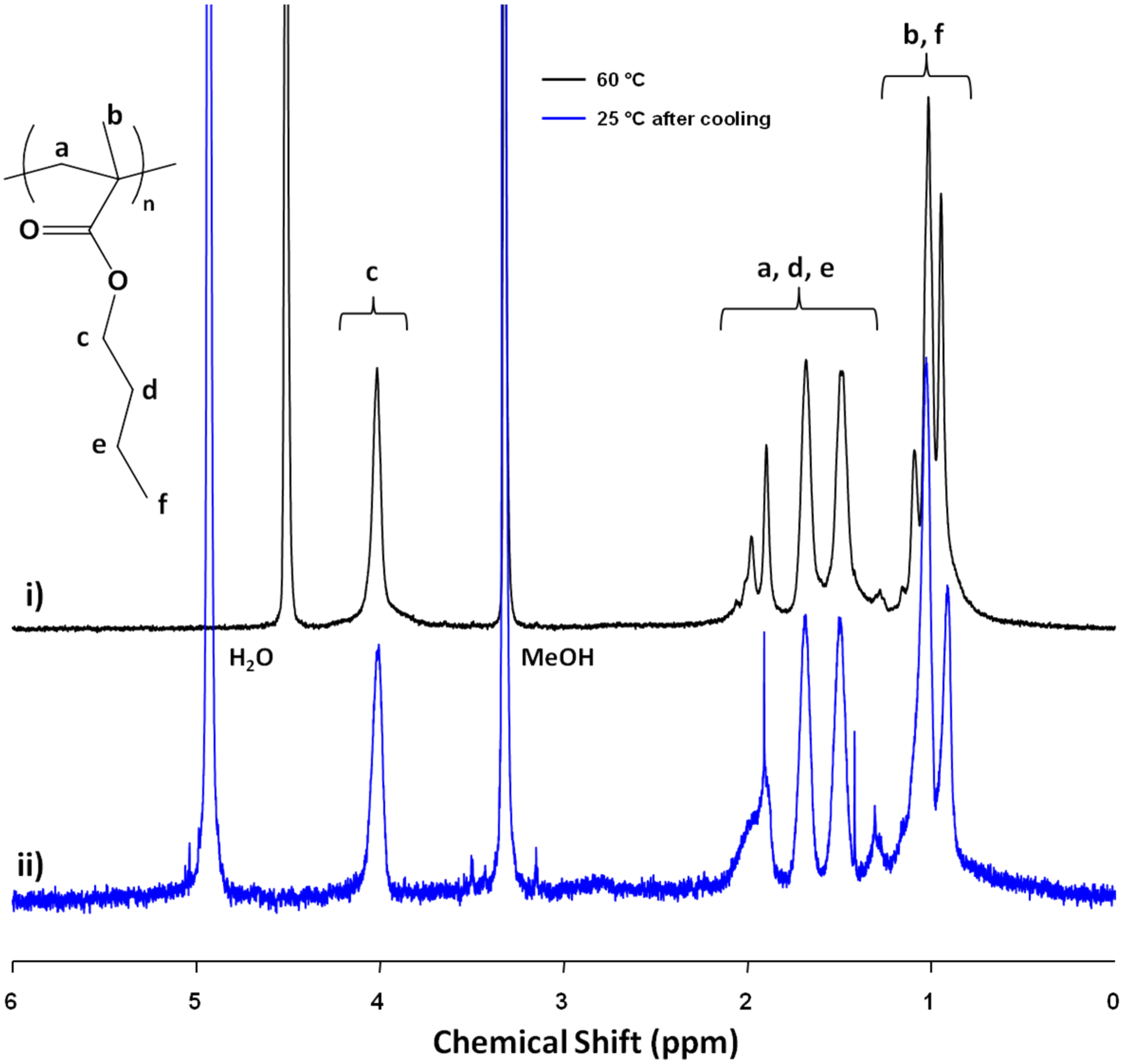

Figure S1: Studies of *p*(*n*BuMA) solubility in MeOH-d_4. ^{1}H NMR spectra of i) *p*(*n*BuMA) heated to 60 °C, ii) *p*(*n*BuMA) after heating and cooling to 25 °C. In ii) the intensity of the peaks owing to residual polymer in solution has been considerably increased in order to allow comparison with i).

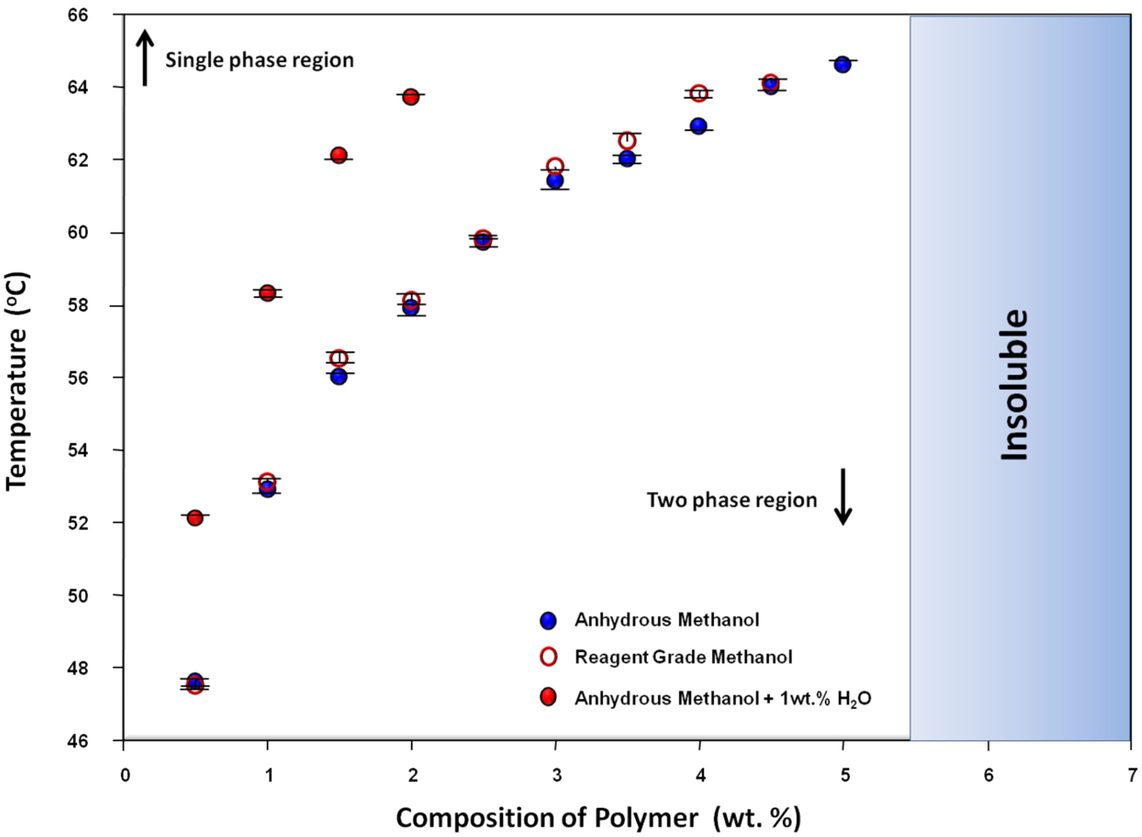

Figure S2: Cloud Point behaviour for *p*(*n*BuMA) in MeOH with varying water content within the organic solvent. The reagent grade methanol was reported by the supplier to contain < 0.05 % H_2O content. Asymmetric error bars shown.

Table S1: Cloud point temperatures for *p*(*n*BuMA) in MeOH with varying water content within the organic solvent. Measurements recorded in triplicate for each composition.

	Anhydrous MeOH			**Analytical Grade MeOH (<0.05% H_2O)**			**Anhydrous MeOH+$H_2$0 (1wt %)**		
	Cloud Point Temperature (°C)			**Cloud Point Temperature (°C)**			**Cloud Point Temperature (°C)**		
Composition (wt %)	**#1**	**#2**	**#3**	**#1**	**#2**	**#3**	**#1**	**#2**	**#3**
0.5	47.6	47.5	47.5	47.7	47.5	47.4	52.1	52.2	52.1
1	52.8	52.9	52.9	53.1	53.1	53.2	58.3	58.2	58.4
1.5	56.1	56.0	56.0	56.7	56.4	56.5	62.1	62.1	62.0
2	57.9	57.7	58.0	58.1	58.3	58.1	63.8	63.7	63.7
2.5	59.6	59.7	59.8	59.9	59.6	59.8	---	---	---
3	61.2	61.4	61.4	61.8	61.8	61.7	---	---	---
3.5	62.1	62.0	61.9	62.7	62.5	62.5	---	---	---
4	62.9	62.9	62.8	63.9	63.8	63.7	---	---	---
4.5	64.0	64.0	63.9	64.1	64.2	64.1	---	---	---

5	64.6	64.6	64.7	---	---	---	---	---	---

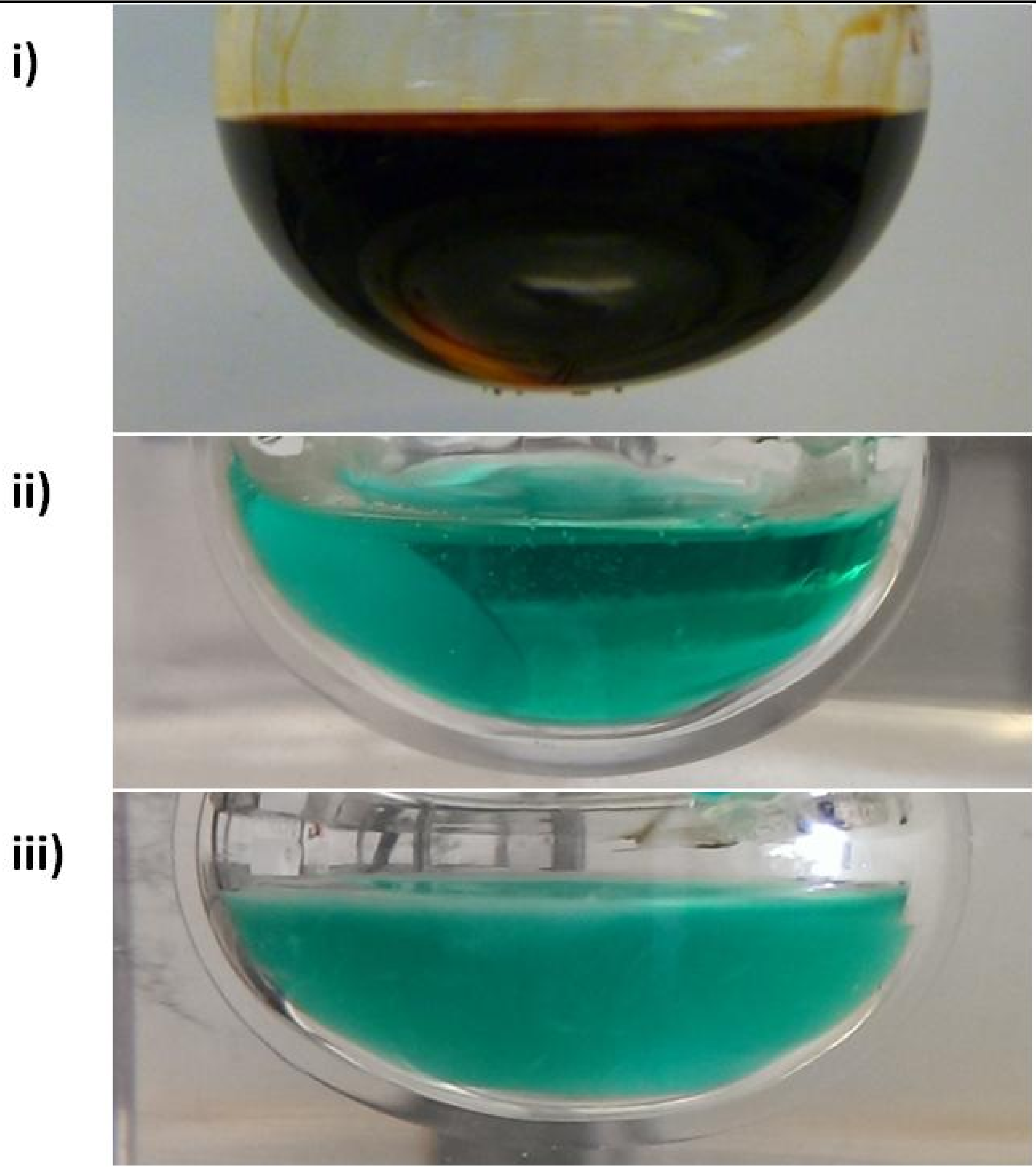

Figure S3: Expanded photographs of the polymerisation showing i) the strong dark brown catalyst complex during polymerisation, ii) the homogeneous polymerisation at 60 °C after oxygen was allowed into the reaction, and iii) precipitation of *p*(*n*BuMA) during cooling (57 °C).

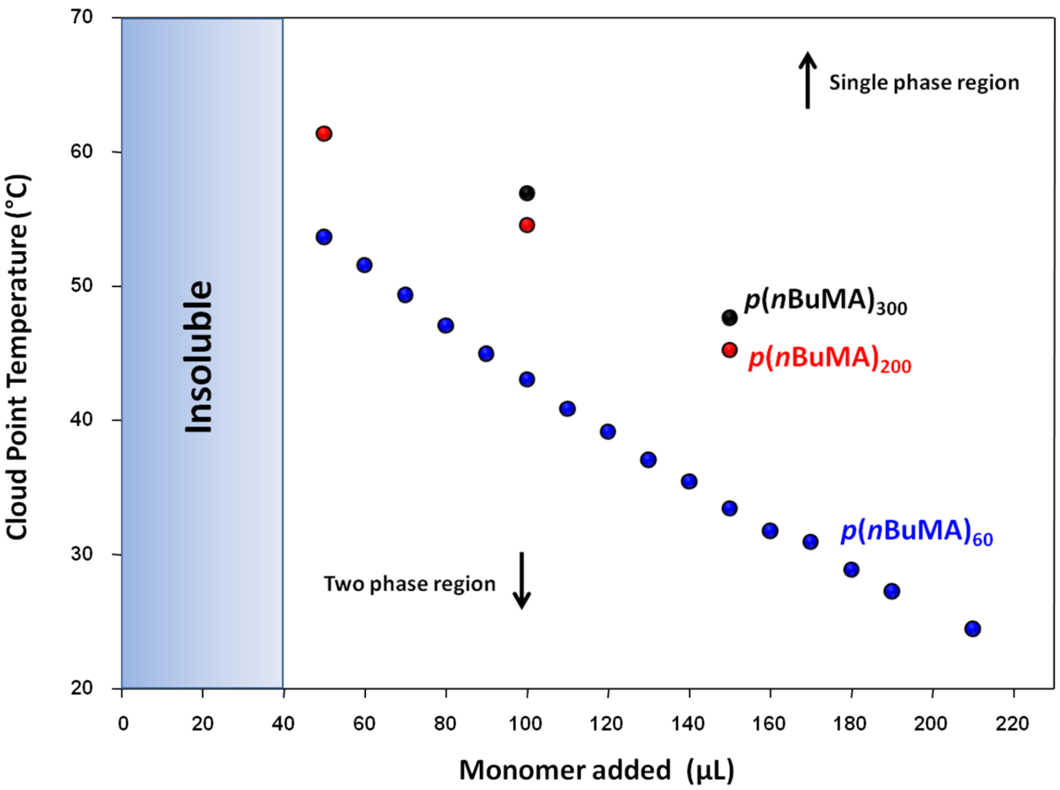

Figure S4: Cloud point measurement of $p(n\text{BuMA})_x$ in anhydrous MeOH with increasing concentrations of *n*(BuMA) monomer.

Table S2: Cloud point temperatures for $p(n\text{BuMA})_x$ in anhydrous MeOH (50 wt% composition) with increasing concentrations of *n*(BuMA) monomer.

Monomer Addition (µL)	**Cloud Point Temperature (°C)**		
	$p(n\text{BuMA})_{60}$	**$p(n\text{BuMA})_{200}$**	**$p(n\text{BuMA})_{300}$**
50	**53.6**	**61.3**	**insoluble**
60	**51.5**	**---**	**---**
70	**49.3**	**---**	**---**
80	**47.0**	**---**	**---**
90	**44.9**	**---**	**---**
100	**43.0**	**54.5**	**56.9**
110	**40.8**	**---**	**---**
120	**39.1**	**---**	**---**
130	**37.0**	**---**	**---**
140	**35.4**	**---**	**---**
150	**33.4**	**45.2**	**47.6**
160	**31.7**	**---**	**---**
170	**30.9**	**---**	**---**
180	**28.8**	**---**	**---**
190	**27.2**	**---**	**---**
210	**24.4**	**---**	**---**

Table S3: Calculation of an average *dn/dc* value obtained over 18 samples of *p*(*n*BuMA) analysed via THF GPC.

Target DP$_n$	***dn/dc***
60	0.0809
80	0.0786
100	0.0848
100	0.0712
150	0.0787
200	0.0763
300	0.076
400	0.0772
500	0.0865
1000	0.0901
60	0.0755
100	0.0747
200	0.0683
60	0.0709
100	0.0688
200	0.0697
60	0.0734
200	0.0708
Average	**0.0762**

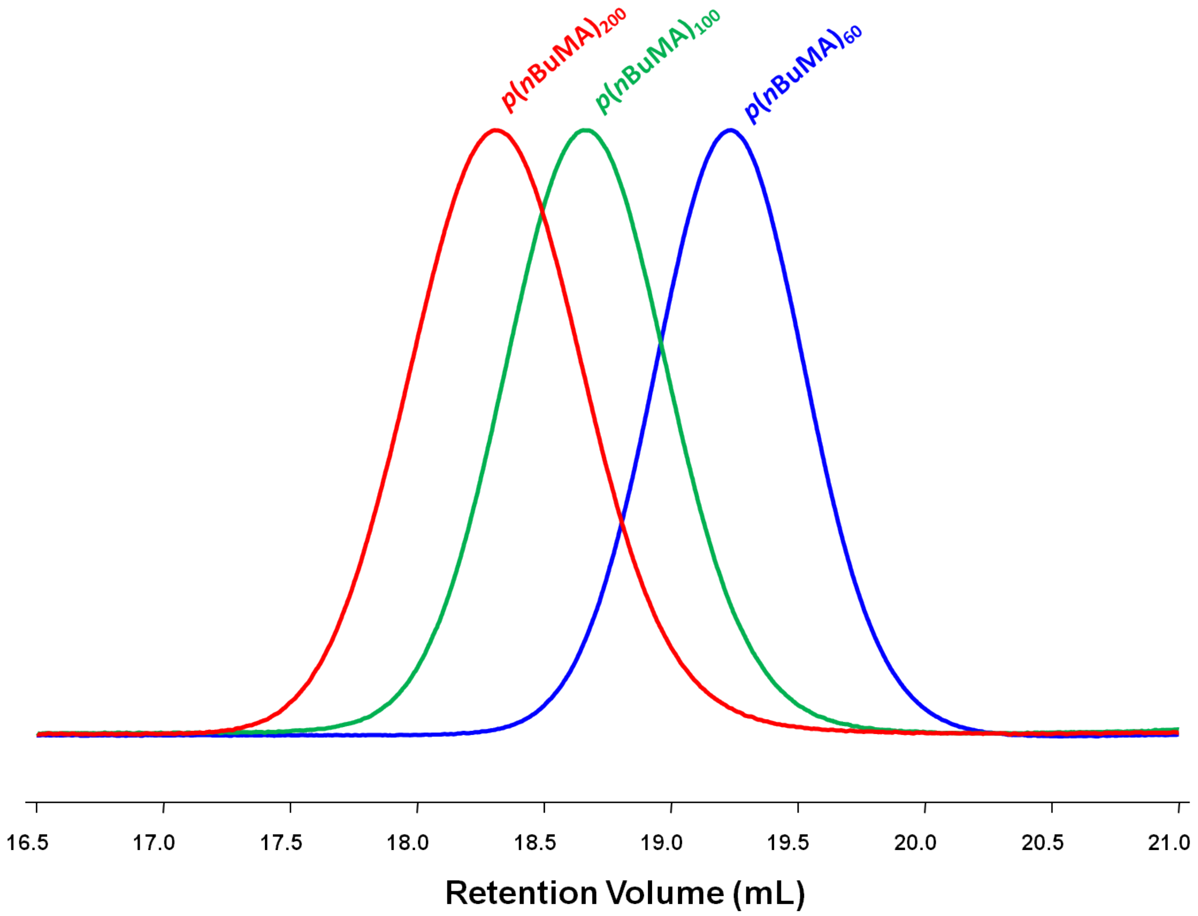

Figure S5: GPC chromatograms (RI) showing *p*(*n*BuMA) molecular weight distributions across targeted $DP_n = 60 – 200$ monomer units; polymerised in anhydrous MeOH at 25 °C.

Synthesis of *p*(*n*BuMA)$_x$ homopolymers in IPA

In a typical synthesis, targeting a DP$_n$ = 60 monomer units, *p*(*n*BuMA)$_{60}$, *n*BuMA (0.85 g, 6 mmol) and bpy (31.2 mg, 0.2 mmol) were added to a 15 mL round-bottomed flask equipped with a magnetic stirrer bar. IPA (1.08 mL; 50 wt%) (deoxygenated via N_2 purge prior to use) was added and the resulting solution was sparged with N_2 for 10 minutes. Cu(I)Cl (9.9 mg, 0.1 mmol) was rapidly added to the flask, instantly forming a brown coloured mixture and purged with N_2 for a further 5 minutes. The flask was submerged into an oil bath pre-heated at 60 °C and ethyl α-bromoisobutyrate (14.7 μL, 0.1 mmol) was added under N_2 flow using a micro-syringe. The mixture was stirred at 60 °C for 24 hours before termination by dilution with THF until appearance of a blue/green colour. The solution was passed though a neutral alumina column to remove residual catalyst and concentrated by rotary evaporation. The polymer was precipitated into cold MeOH to give a white solid.

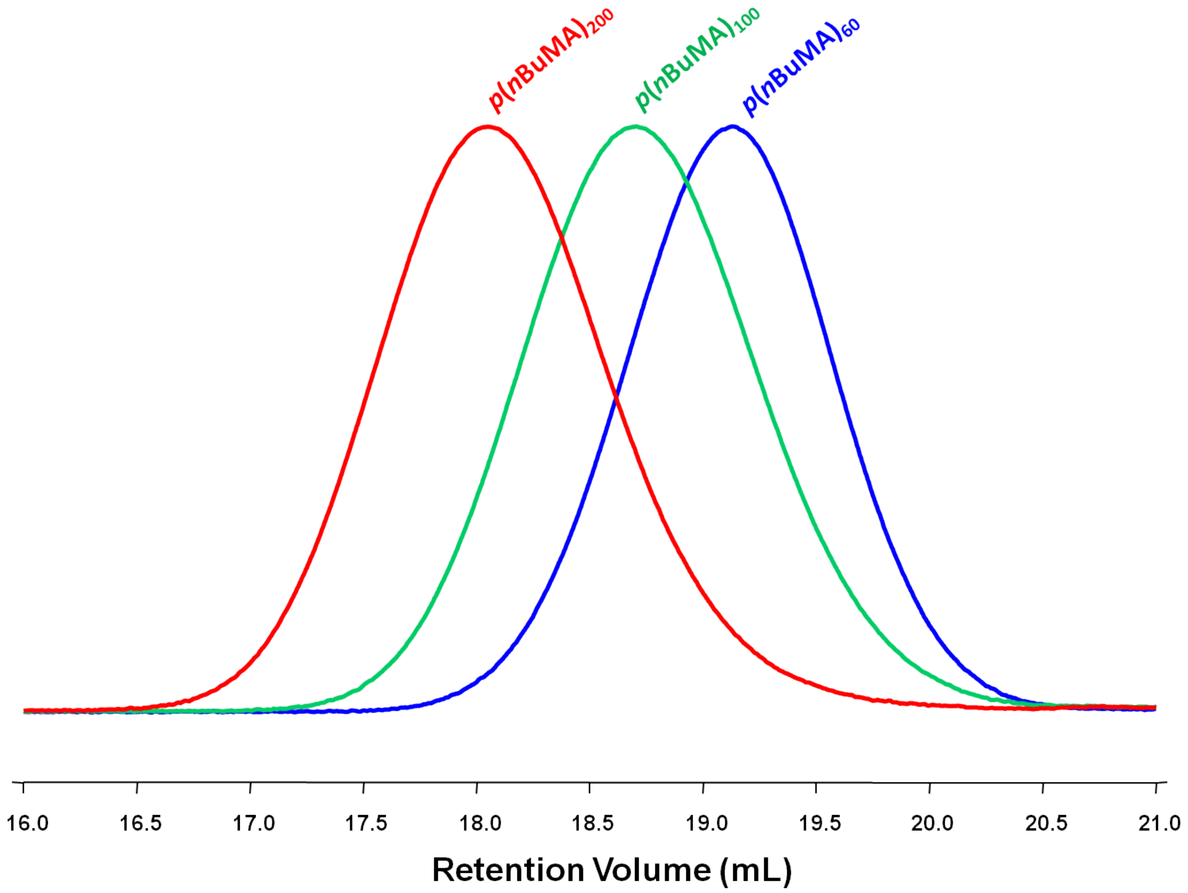

Figure S6: GPC chromatograms (RI) showing *p*(*n*BuMA) molecular weight distributions across targeted $DP_n = 60 – 200$ monomer units; polymerised in IPA at 60 °C.

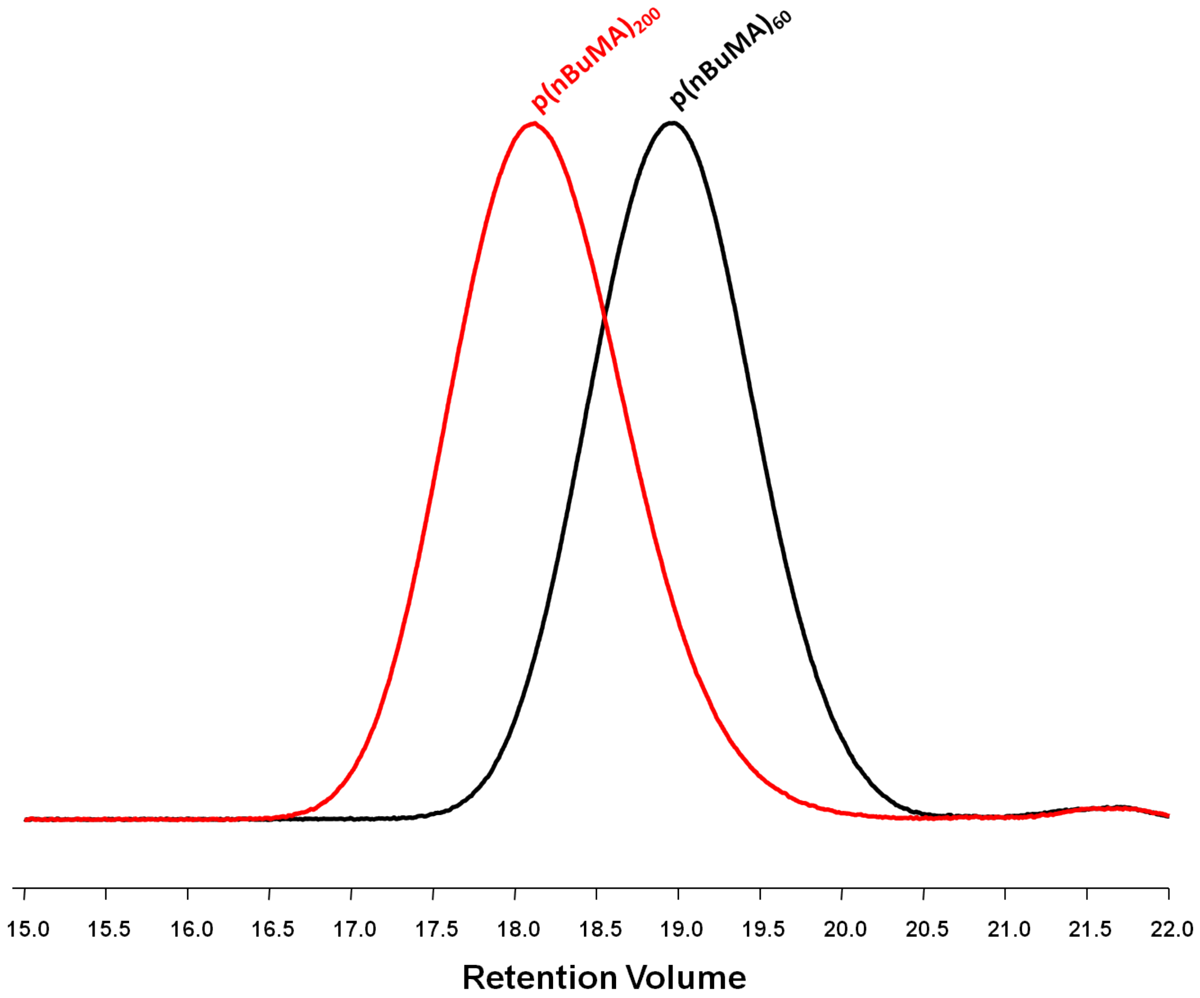

Figure S7: GPC chromatograms (RI) showing *p*(*n*BuMA) molecular weight distributions across targeted $DP_n = 60 - 200$ monomer units; polymerised in IPA at 25 °C.

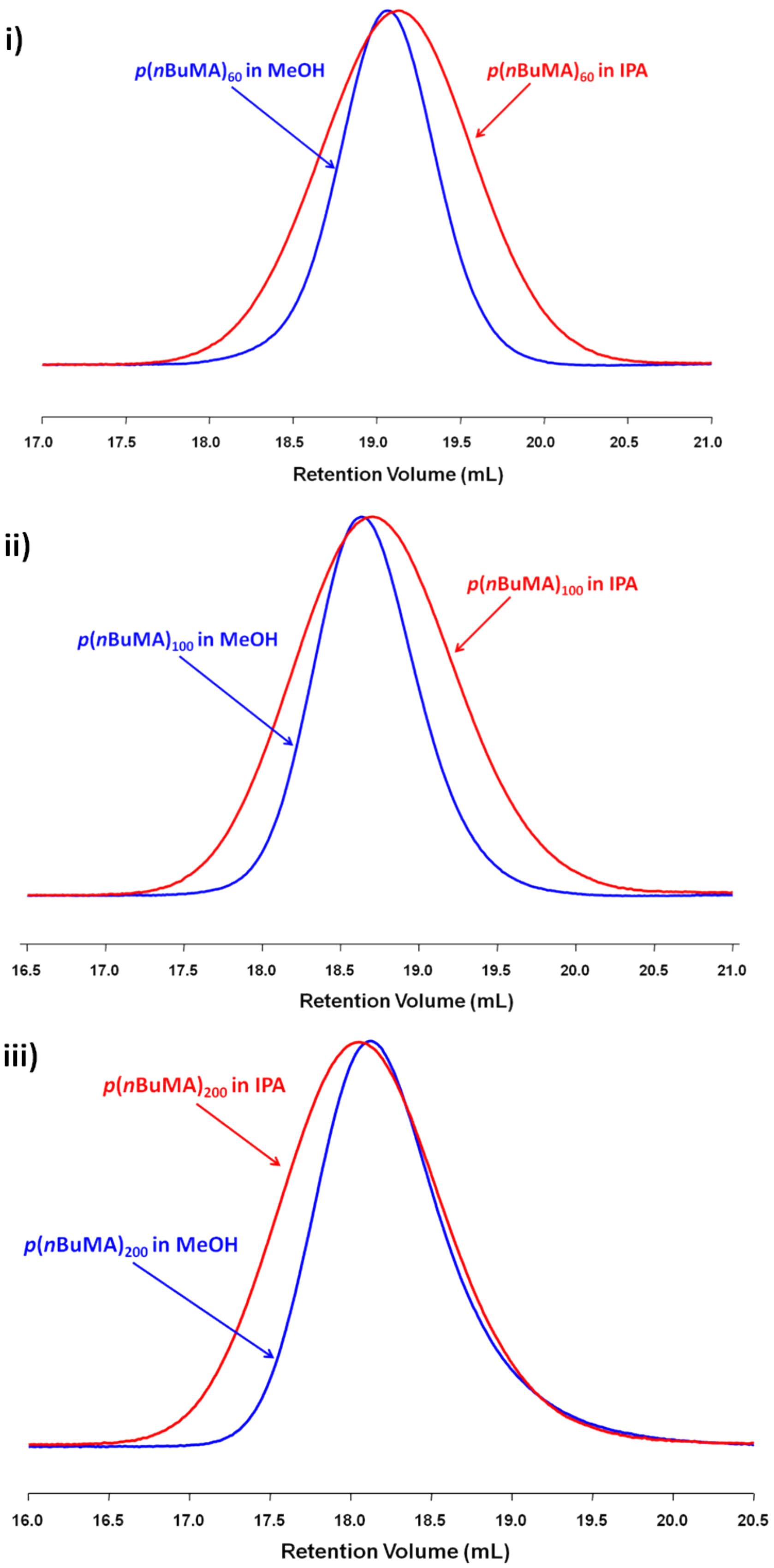

Figure S8: Chromatographic (RI) molecular weight distributions of *p*(*n*BuMA)$_x$ polymerised in anhydrous MeOH (blue traces) and IPA (red traces) at 60 °C; i) *p*(*n*BuMA) targeting DP$_n$ = 60 monomer units, ii) *p*(*n*BuMA) targeting DP$_n$ = 100 monomer units, and iii) *p*(*n*BuMA) targeting DP$_n$ = 200 monomer units.

Synthesis of *p*(*n*BuMA)$_x$ homopolymers using PMDETA as catalyst ligand

In a typical synthesis, targeting a DP$_n$ = 60 monomer units, *p*(*n*BuMA)$_{60}$, *n*BuMA (1.7 g, 12 mmol) and PMDETA (41.6 µL, 0.2 mmol) were added to a 25 mL round-bottomed flask equipped with a magnetic stirrer bar. MeOH (2.15 mL; 50 wt%) (deoxygenated via N_2 purge prior to use) was added and the resulting solution was sparged with N_2 for 10 minutes. Cu(I)Cl (19.8 mg, 0.2 mmol) was rapidly added to the flask, instantly forming a brown coloured mixture and purged with N_2 for a further 5 minutes. The flask was submerged into an oil bath pre-heated at 60 °C and ethyl α-bromoisobutyrate (29.4 µL, 0.2 mmol) was added under N_2 flow using a micro-syringe. The mixture was stirred at 60 °C for 48 hours before termination by dilution with MeOH until appearance of a blue/green colour. Upon cooling, the polymer precipitated and the supernatant containing the catalytic system was discarded. The polymer was dissolved in THF, passed though a neutral alumina column to remove residual catalyst and concentrated by rotary evaporation. The polymer was precipitated into cold MeOH to give a white solid.

Synthesis of *p*(*n*BuMA)$_x$ homopolymers using Me$_6$TREN as catalyst ligand

In a typical synthesis, targeting a DP$_n$ = 60 monomer units, *p*(*n*BuMA)$_{60}$, *n*BuMA (1.7 g, 12 mmol) and Me$_6$TREN (53.5 µL, 0.2 mmol) were added to a 25 mL round-bottomed flask equipped with a magnetic stirrer bar. MeOH (2.15 mL; 50 wt%) (deoxygenated via N_2 purge prior to use) was added and the resulting solution was sparged with N_2 for 10 minutes. Cu(I)Cl (19.8 mg, 0.2 mmol) was rapidly added to the flask, instantly forming a brown coloured mixture and purged with N_2 for a further 5 minutes. The flask was submerged into an oil bath pre-heated at 60 °C and ethyl α-bromoisobutyrate (29.4 µL, 0.2 mmol) was added under N_2 flow using a micro-syringe. The mixture was stirred at 60 °C for 48 hours before termination by dilution with MeOH until appearance of a blue/green colour. Upon cooling, the polymer precipitated and the supernatant containing the catalytic system was discarded. The polymer was dissolved in THF, passed though a neutral alumina column to remove residual catalyst and concentrated by rotary evaporation. The polymer was precipitated into cold MeOH to give a white solid.

Table S4: Methanolic ATRP of *n*BuMA at 60 °C using various ligands

				GPC (THF)[c]		
Target[a] DP_n	Ligand	Conversion (%)	M_n Theory[b]	M_n (g/mol)	M_w (g/mol)	Đ
60	Bpy	99	8640	13570	13950	1.03
60	PMDETA	99	8640	20350	29800	1.46
60	Me_6TREN	87	7620	38550	44550	1.16

[a] Target DP_n calculated as [*n*BuMA]/[initiator]; [b] Theoretical M_n calculated as (Target DP_n x 142.2 $gmol^{-1}$)*actual fractional conversion achieved and includes initiator residue; [c] GPC utilising THF eluent and *dn/dc* = 0.0762 (averaged across 18 samples).

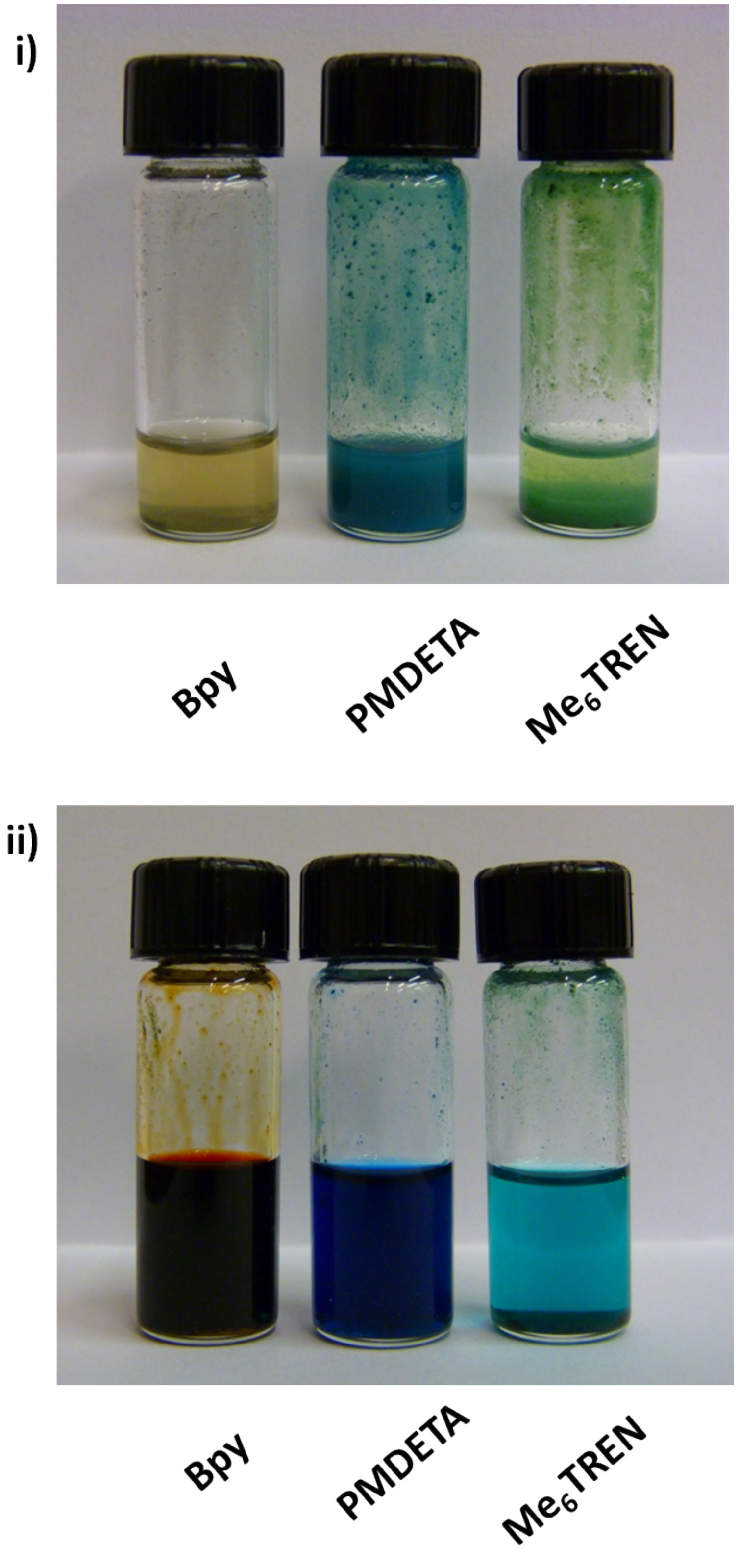

Figure S9: Photographs showing the solubility of the ligated Cu(I)Cl catalytic systems in, i) bulk, and in ii) methanolic solution.

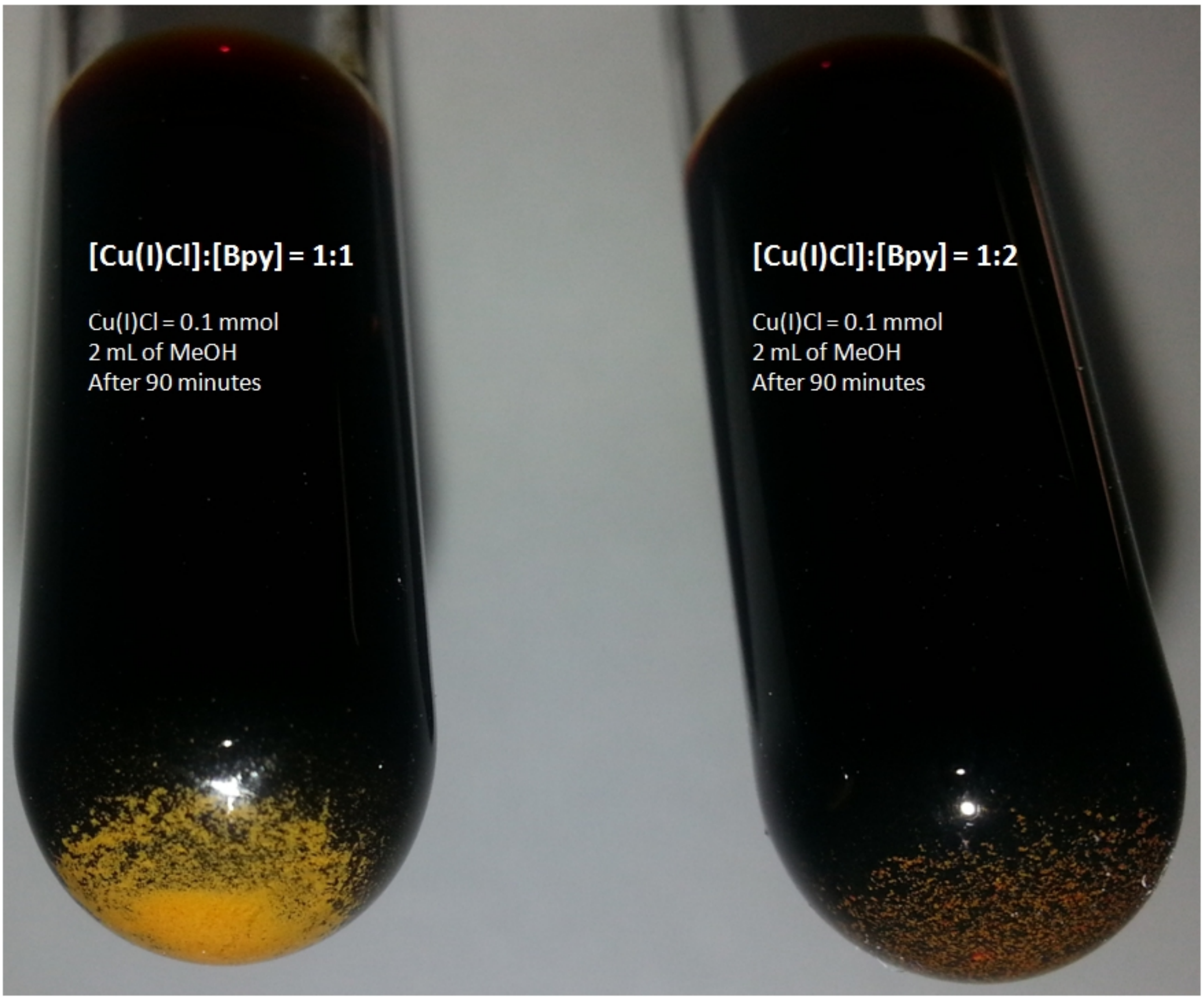

Figure S10: Photographic qualitative evaluation of Cu(I)Cl:Bpy catalytic sytems in MeOH showing variation in Cu(0) formation by disproportionation at a 1:1 ratio (left) and 1:2 ratio(right) after 90 minutes at ambient temperature.