Exploring the homogeneous controlled radical polymerisation of hydrophobic monomers in anti-solvents for their polymers: RAFT and ATRP of various alkyl methacrylates in anhydrous methanol to high conversion and low dispersity.

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Supplementary Information

Experimental details

Materials

Poly(ethylene glycol) mono methyl ether (nominal M_n = 750, 2000, and 5000 g/mol), *n*-butyl methacrylate (*n*BuMA, 99%), toluene (anhydrous 99.8 %), triethylamine (> 99 %), α-bromoisobutyryl bromide (98 %), copper(I) chloride (Cu(I)Cl, 99 %), D_2O (99.9 atom % D), $CDCl_3$ (99.8 atom % D), methanol (MeOH, anhydrous 99.8 %), 2,2'-bipyridine (bpy, 99 %), aluminium oxide (activated, neutral, Brockmann I), ethylene glycol dimethacrylate (EGDMA, 98 %), methyl methacrylate (MMA, 99 %), ethyl-α-bromoisobutyrate (EBiB, 98%), *t*-butyl methacrylate (*t*BuMA, 98 %), DOWEX marathon ion-exchange resin (hydrogen form), 4,4'-azobis(4-cyanopentanoic acid) (ACVA, 98 %) and 2-cyano-2-propyl benzodithioate (CPBD, 97 %) were purchased from Sigma Aldrich. Tetrahydrofuran (THF, HPLC-grade), methanol (anhydrous MeOH), acetone (analytical grade), petroleum ether (analytical grade, bp 40-60 °C), N,N-dimethylformamide (DMF, HPLC-grade) were purchased from Fisher. Poly(ethylene glycol) (nominal M_n = 4000 g/mol) was purchased from Alfa Aesar. All materials were used as received.

Characterisation

^1H nuclear magnetic resonance (NMR) spectra were recorded either in D_2O or $CDCl_3$ using a Bruker Avance spectrometer operating at 400 MHz. Triple detection size exclusion chromatography (SEC) was performed using Malvern Viscotek instruments. One instrument was equipped with a GPCmax VE2001 auto-sampler, two Viscotek D6000 columns (and a guard column) and a triple detector array TDA305 (refractive index, light scattering and viscometer) with a mobile phase of DMF containing 0.01 M lithium bromide at 60 °C and a flow-rate of 1 mL min^{-1}. The second instrument was equipped with a GPCmax VE2001 auto-sampler, two Viscotek T6000 columns (and a guard column), a refractive index (RI) detector VE3580 and a 270 Dual Detector (light scattering and viscometer) with a mobile phase of THF containing 2 v/v % of triethylamine and a flow-rate of 1 mL min^{-1}.

RAFT polymerisations

The DP_n of homopolymers synthesised by RAFT were assessed by ^1H NMR spectroscopy in $CDCl_3$ of purified samples by comparison of the aromatic signal attributed to the CTA Z-group with clear resonances assigned to *n*BuMA monomer (e.g. $\text{-COO-C}\underline{\mathbf{H}}_{\mathbf{2}}\text{-CH}_2\text{-}$ 3.9 ppm and $\text{-C(C}\underline{\mathbf{H}}_{\mathbf{3}}\text{)COO-(CH}_2)_3\text{-C}\underline{\mathbf{H}}_{\mathbf{3}}$ 0.5-1.25 ppm) and MMA residues (e.g. $\text{-C(CH}_3\text{)COO-C}\underline{\mathbf{H}}_{\mathbf{3}}$ 3.3-3.8 ppm), (Electronic Supplementary Information (ESI) Figure S1 -2)

Poly(*n*butyl methacrylate) *p*(*n*BuMA$_x$) homopolymer synthesis by methanolic RAFT at 60 ºC

In a typical synthesis, targeting a number average degree of polymerisation DP_n = 60 monomer units, ACVA (17.2 mg, 0.06 mmol), CPBD (67.8 mg, 0.30 mmol) and *n*BuMA (2.55 g, 18.0 mmol) were added to a 25 mL round-bottomed flask equipped with a magnetic stirrer bar. Anhydrous methanol (3.22 mL, 50 wt % wrt monomer, deoxygenated via N_2 purge) was added and the resulting solution was sparged with nitrogen for 15 minutes. The reaction flask was placed into a pre-heated oil-bath (60 ºC) and stirred for 24 hours after which the reaction medium was observed to be slightly turbid. The polymerisation was stopped by cooling the flask to room temperature causing the polymer to precipitate and sediment to the bottom of the flask. The methanol supernatant was decanted and the resultant polymer dissolved in THF. The solution was concentrated by rotary evaporation and precipitated into cold methanol to give a pink solid.

Kinetic studies of the polymerisation of *n*BuMA using RAFT at 60 ºC

Sampling of aliquots from a single reaction often led to precipitation, therefore, multiple small reactions were initiated to model individual time points.

In a typical kinetic experiment, targeting DP_n = 100 monomer units, CPBD (98.40 mg, 0.422 mmol, 1 equivalent), ACVA (23.65 mg, 0.084 mmol, 0.2 equivalents) and *n*BuMA (6.00 g, 42.19 mmol, 100 equivalents) were placed in a round bottom flask fitted with a stirrer bar and a rubber septum. The reactor and its contents were degassed (N_2 sparge for 20 mins) after which anhydrous methanol (7.58 mL, 50 wt %; degassed *via* N_2 sparge) was added to the round bottom flask under positive N_2 pressure. The reactor was flushed with argon for an additional 10 mins and the homogeneous reaction mixture transferred into several 1.5 mL vials fitted with stirrer bars under an argon blanket. The vials were sealed and placed in an oil bath at 60 ºC. The samples were removed successively over a period of 34 hours and analysed by ^{1}H NMR and triple detection SEC (THF). NB Kinetic experiments targeting a $DP_n = 1000$ monomer units utilised *n*BuMA (18.00 g) and the reaction was split across four 10 mL round bottom flasks fitted with stirrer bars and samples were removed over 50 hours.

ATRP polymerisations

All ATRP polymerisations were conducted at a constant ratio to initiator bromine atoms of [Br]:[Cu(I)Cl]:[Bpy] = 1:1:2.

Synthesis of poly(ethylene glycol) mono methyl ether-derived ATRP macro-initiators (PEG_{17}-Br, PEG_{45}-Br and PEG_{113}-Br).

In a typical synthesis, PEG_{113}-OH (30 g, 6 mmol) was dissolved in 100 mL of anhydrous toluene in the presence of triethylamine (0.91 g, 9 mmol) in a two-neck round-bottomed flask fitted with an addition funnel, a nitrogen inlet/outlet and a stirrer bar. α-Bromoisobutytyl bromide (2.07 g, 9 mmol), diluted with 20 mL of anhydrous toluene, was placed in the addition funnel. Whilst stirring the contents of the flask, the α-bromoisobutyryl bromide solution was added slowly over a period of 20-30 min. After the addition was completed, the reaction was left to stir for 24 hours at room temperature. The formation of a white precipitate (triethylammonium bromide salt) indicated the progress of the reaction. Once the reaction was complete, the reaction medium was warmed in a water bath at about 50 ºC, filtered and concentrated on the rotary evaporator. The resulting product was diluted in acetone and purified by precipitation in petroleum ether (40-60). The last step was repeated and the product was finally dried under vacuum at 40 ºC for 24 hours. The resulting macro-initiator was recovered with 70 % yield and its structure was confirmed by ^{1}H NMR (D_2O) and triple detection SEC with a mobile phase of DMF.

Synthesis of poly(ethylene glycol)-*b*-poly(*n*butyl methacrylate) (*p*(PEG_x-*block*-*n*$BuMA_y$)) A-B block copolymers by methanolic ATRP.

In a typical synthesis, targeting DP_n = 60 monomer units and using PEG_{113}–Br as the macro-initiator, PEG_{113}-Br (0.50 g, 0.1 mmol), *n*BuMA (0.85 g, 6 mmol) and bpy (31.20 mg, 0.2 mmol) were added to a 15 mL round-bottomed flask equipped with a magnetic stirrer bar. Anhydrous methanol (1.07 mL, 50 wt % wrt. monomer; deoxygenated via N_2 purge) was added and the resulting solution was sparged with N_2 for 15 minutes. Cu(I)Cl (9.90 mg, 0.1 mmol) was rapidly added to the flask whilst maintaining a positive N_2 flow, instantly forming a brown coloured mixture. The reactor was heated in an oil bath and left to stir. The polymerisation was stopped by cooling the flask to room temperature, exposing its contents to air and diluting the reaction medium with THF. The polymer solution was passed through a neutral alumina column to remove the catalyst using THF as the mobile phase and the resulting solution was concentrated by rotary evaporation and precipitated into cold petroleum-ether (40-60) to give a white solid. The sample was dried under vacuum at 40 °C for 24 hours and analysed by ^{1}H NMR in $CDCl_3$ (50 °C) and SEC with a mobile phase of DMF.

Synthesis of hyperbranched poly(ethylene glycol)-*b*-poly(*n*butyl methacrylate-*co*-ethylene glycol dimethacrylate) (*p*(PEG_{113}-block-(*n*BuMA-*co*-EGDMA)) copolymers by methanolic ATRP at 60 °C.

In a typical synthesis, targeting DP_n = 60 monomer units of *n*BuMA in the primary polymer chains, PEG_{113}-Br (0.50 g, 0.1 mmol), *n*BuMA (0.85 g, 6 mmol), EGDMA (16.80 mg, 0.085 mmol; 0.85 equiv. relative to initiator) and bpy (31.20 mg, 0.2 mmol) were added to a 15 mL round-bottomed flask equipped with a magnetic stirrer bar. Anhydrous methanol (1.07 mL, 50 wt % wrt. monomer; deoxygenated via N_2 purge) was added and the resulting solution was sparged with N_2 for 15 minutes. Cu(I)Cl (9.9 mg, 0.1 mmol) was rapidly added to the flask whilst maintaining a positive N_2 flow, instantly forming a brown coloured mixture. The reactor was submerged placed into an oil bath pre-heated at 60 °C, and left to stir. The polymerisation was stopped by cooling the flask to room temperature, exposing its contents to air, and diluting the reaction medium with THF. The polymer solution was passed through a neutral alumina column to remove the catalyst using THF as the mobile phase. The solution was concentrated by rotary evaporation and precipitated into cold petroleum-ether (40-60) to give a white solid. The sample was dried under vacuum at 40 °C for 24 hours and analysed by ^1H NMR in $CDCl_3$ and GPC with a mobile phase of DMF.

Synthesis of poly(ethylene glycol) bi-functional ATRP macro-initiator (Br-PEG_{91}-Br)

PEG_{91}-diOH (20 g, 5 mmol) was dissolved in 100 mL of anhydrous toluene in the presence of triethylamine (1.52 g, 15 mmol) in a two-neck round-bottomed flask fitted with an addition funnel, a nitrogen inlet/outlet and a stirrer bar. α-Bromoisobutytyl bromide (3.45 g, 15 mmol i.e. 1.5 eq. per hydroxyl group = 3 eq. per PEG chain) diluted with 20 mL of anhydrous toluene was placed in the addition funnel. Whilst stirring, the reactor was cooled to 0 °C in an ice bath and the α-bromoisobutyryl bromide solution was added slowly over a period of 20-30 min. After the addition was completed, the reactor was allowed to reach room temperature and left to stir for 24 hours. After purification by filtration and precipitation in petroleum ether (40-60), the structure of the resulting bi-functional macro-initiator was confirmed by ^1H NMR in D_2O and triple detection GPC with a mobile phase of DMF.

Synthesis of poly(ethylene glycol)-b-poly(*n*-butyl methacrylate) A-B-A block copolymers by methanolic ATRP at 25 °C or 60 °C

For all the polymerisations, the amount of catalytic system with respect to the bromine atoms from the initiator was kept constant, [Br]:[Cu(I)Cl]:[Bpy] = 1:1:2.

Synthesis of pBMA-PEG-pBMA A-B-A triblock copolymers. In a typical synthesis, targeting a number average degree of polymerisation DP_n = 80 monomer units on each side of the PEG bi-functional macro-initiator (in this specific case, $DP_{n\ total}$ = 160 monomer units), Br-PEG_{91}-Br initiator (0.473 g, 0.11 mmol), *n*BuMA (2.5 g, 17.6 mmol), bpy (69 mg, 0.44 mmol) were placed into a 25 mL round-bottomed flask and deoxygenated via nitrogen sparge for 10 minutes under stirring. Anhydrous methanol (3.75 mL, 50 wt %) (deoxygenated via nitrogen purge prior to use) was added and the resulting solution was purged with nitrogen for 5 more minutes. Finally, Cu(I)Cl (22 mg, 0.22 mmol) was added rapidly to the solution whilst maintaining a positive nitrogen flow and the reactor was placed in a preheated oil bath at 60 °C. After 27 hours, the reaction was stopped by exposure to air and addition of THF (approximately 10 mL) until appearance of a green colour which is evidence of the catalytic system being oxidised. The reaction medium was transferred into a larger container at room temperature, another addition of THF (approximately 50 mL) was performed and the catalytic system was removed by addition of ion-exchange resin beads followed by filtration. Finally, the resulting solution was concentrated on the rotary evaporator, diluted in THF and precipitated in cold petroleum ether (40-60). After collection, the sample was dried under vacuum at 40 °C for 24 hours and analysed by ^1H NMR in $CDCl_3$ and GPC with a mobile phase of DMF.

For all the *p*(PEG-*block*-*n*BuMA) copolymers after purification, the DP_n of the *n*BuMA block could be assessed by ^1H NMR spectroscopy in $CDCl_3$ at 50 °C. The proton signal due to the PEG block is apparent at 3.6 ppm. The intensity of this signal is proportional to the known DP_n of the PEG block. Comparison of this integrated signal with those due to the *p*(*n*BuMA) repeat units (e.g. $-COO-C\underline{\mathbf{H_2}}-CH_2-$ at 3.9 ppm or $-C(C\underline{\mathbf{H_3}})COO-(CH_2)_3-C\underline{\mathbf{H_3}}$ between 0.5 ppm and 1.25 ppm) allowed the DP_n of the *p*(*n*BuMA) block to be calculated.

Kinetic studies. Kinetic studies (i.e. plots $\ln([M]_0/[M]) = f(t)$ and Mn = f(conversion)) were performed by taking samples from the reaction medium under positive pressure of nitrogen and analysing them by ^{1}H NMR in $CDCl_3$ and triple detection GPC.

The monomer conversion was determined by ^{1}H NMR spectroscopy in $CDCl_3$ for crude samples of the reaction medium. The vinyl protons ($C\underline{H_2}$=C(CH3)COO-*n*-Bu) due to the residual monomer can possibly be seen at 5.5 ppm and 6.05 ppm. Comparison of these integrated signals with those due to the CH_2 next to the ester group for both the polymer repeat units and the monomer (between 3.8 ppm and 4.3 ppm) allowed the conversion to be estimated using the following equation:

$\text{Conversion} = [1 - (2*I_6 / I_4)] \times 100$

Where I_6 and I_4 are respectively the integrals of the NMR signals at 5.5 ppm (or 6.05 ppm) and between 3.8 ppm and 4.3 ppm.

Alternatively, it is also possible to calculate the conversion by comparing the signals due to the vinyl protons with those due to the 6 protons from the two methyl groups of the polymer repeat units (both backbone and pendant group) between 0.5 ppm and 1.25 ppm.

The catalytic system was removed from the kinetic samples prior to GPC analysis by passing them through an alumina column.

Synthesis of poly(methyl methacrylate) *p*(MMA) and poly(ethylene glycol) methyl ether-b-poly(methyl methacrylate) *p*(PEG-*block*-MMA) A-B block copolymers by methanolic ATRP at 25 °C or 60 °C

Synthesis of *p*(MMA) homopolymers. In a typical synthesis, targeting a number average degree of polymerisation $DP_n = 60$ monomer units and using ethyl-α-bromoisobutyrate (EBiB) as initiator, MMA (2.52g, 25.2 mmol) and bpy (130 mg, 0.8 mmol) were added to a 25 mL round-bottom flask equipped with a magnetic stirrer bar. Anhydrous methanol (3.16 mL, 50 wt % wrt. monomer) (deoxygenated via nitrogen purge prior to use) was added and the resulting solution was sparged with nitrogen for 15 minutes. Cu(I)Cl (41.2 mg, 0.4 mmol) was rapidly added to the flask whilst maintaining a positive nitrogen flow, instantly forming a brown coloured mixture. EBiB (61.1 µL, 0.4 mmol) was added to the reaction flask which was then submerged into an oil bath pre-heated at 60 °C and left to stir for 26 hours. The polymerisation was stopped by cooling the flask to room temperature, exposing its contents to air, and diluting the reaction medium with THF to poison the catalytic system. The polymer solution was then passed through a neutral alumina column to remove the catalytic system using THF as the mobile phase. The solution was concentrated by rotary evaporation and precipitated into cold methanol to give a white solid. The sample was dried under vacuum at 40 °C and analysed by ^{1}H NMR in $CDCl_3$ and GPC with a mobile phase of THF.

Synthesis of *p*(PEG-*block*-MMA) diblock copolymers. In a typical synthesis, targeting a number average degree of polymerisation $DP_n = 60$ monomer units and using PEG_{113}-Br as macro-initiator, PEG_{113}-Br (0.5 g, 0.1 mmol), MMA (0.6 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. Anhydrous methanol (1.44 mL, 50 wt %) (deoxygenated via nitrogen purge prior to use) was added and the resulting solution was sparged with nitrogen for 15 minutes. Cu(I)Cl (9.9 mg, 0.1 mmol) was rapidly added to the flask whilst maintaining a positive nitrogen flow, instantly forming a brown coloured mixture, and the reactor was submerged into an oil bath pre-heated at either 25 °C or 60 °C and left to stir. The polymerisation was stopped by cooling the flask to room temperature, exposing its contents to air, and diluting the reaction medium with THF to poison the catalytic system. The polymer solution was then passed through a neutral alumina column to remove the catalytic system using THF as the mobile phase. The solution was concentrated by rotary evaporation and precipitated into cold petroleum ether (40-60) to give a white solid. The sample was dried under vacuum at 40 °C and analysed by ^{1}H NMR in $CDCl_3$ and GPC with a mobile phase of DMF.

For all the purified *p*(PEG-*block*-MMA) copolymers, the DP_n of the MMA block could be assessed by ^{1}H NMR spectroscopy in $CDCl_3$ at 50°C. The proton signal due to the PEG block is apparent at 3.6 ppm. The intensity of this signal is proportional to the known DP_n of the PEG block. Comparison of this integrated signal with those due to the *p*(MMA) repeat units (e.g. $-C(C\underline{\mathbf{H_3}})COO-CH_3$ between 0.5 ppm and 1.25 ppm) allowed the DP_n of the *p*(MMA) block to be calculated.

Synthesis of poly(*n*-butyl methacrylate–*stat*–methyl methacrylate) *p*(*n*BuMA-*stat*-MMA) statistical copolymers by methanolic ATRP at 60 °C

In a typical synthesis, targeting a number average degree of polymerisation DP_n = 60 monomer units for each monomer, and using ethyl-α-bromoisobutyrate (EBiB) as initiator, *n*BuMA (1.34 g, 9.45 mmol), MMA (0.95 g, 9.45 mmol) and bpy (49.2 mg, 0.315 mmol) were added to a 25 mL round-bottomed flask equipped with a magnetic stirrer bar. Anhydrous methanol (2.89 mL, 50 wt % wrt. monomer) (deoxygenated via nitrogen purge prior to use) was added and the resulting solution was sparged with nitrogen for 15 minutes. Cu(I)Cl (15.5 mg, 0.157 mmol) was rapidly added to the flask whilst maintaining a positive nitrogen flow, instantly forming a brown coloured mixture. EBiB (23.0 μL, 0.157 mmol) was added to the reaction flask and the reaction flask was submerged into an oil bath pre-heated at 60 °C and left to stir for 43 hours. The polymerisation was stopped by cooling the flask to room temperature, exposing its contents to air, and diluting the reaction medium with THF to poison the catalytic system. The polymer solution was then passed through a neutral alumina column to remove the catalytic system using THF as the mobile phase. The solution was concentrated by rotary evaporation and precipitated into cold methanol to give a white solid. The sample was dried under vacuum at 40 °C and analysed by ^{1}H NMR in $CDCl_3$ and GPC with a mobile phase of THF.

Synthesis of poly(*tert*-butyl methacrylate) *p*(*t*BuMA) homopolymers by methanolic ATRP at 25 °C or 60 °C

In a typical synthesis, targeting a number average degree of polymerisation DP_n = 80 monomer units and using ethyl-α-bromoisobutyrate (EBiB) as initiator, *t*BuMA (1g, 7.03 mmol) and bpy (27.5 mg, 0.18 mmol) were added to a 25 mL round-bottom flask equipped with a magnetic stirrer bar. Anhydrous methanol (1.33 mL, 50 wt %) (deoxygenated via nitrogen purge prior to use) was added and the resulting solution was sparged with nitrogen for 15 minutes. Cu(I)Cl (8.7 mg, 0.09 mmol) was rapidly added to the flask whilst maintaining a positive nitrogen flow, instantly forming a brown coloured mixture. EBiB (12.9 μL, 0.09 mmol) was added to the reaction flask which was then submerged into an oil bath pre-heated at 60 °C and left to stir for 25 hours. The polymerisation was stopped by cooling the flask to room temperature, exposing its contents to air, and diluting the reaction medium with THF to poison the catalytic system. The polymer solution was then passed through a neutral alumina column to remove the catalytic system using THF as the mobile phase. The solution was concentrated by rotary evaporation, precipitated into cold methanol/water (80/20), and washed with methanol to give a white solid. The sample was dried under vacuum at 40 °C and analysed by ^{1}H NMR in $CDCl_3$ and GPC with a mobile phase of THF.

Synthesis of poly(methyl methacrylate) *p*(MMA) homopolymers by methanolic RAFT at 60 °C

In a typical experiment, targeting a number average degree of polymerisation DP_n = 100 monomer units per chain, 31.13 mg of chain transfer agent CPBD (0.1406 mmol; 1 equivalent), 7.9 mg of ACVA (0.02812 mmol; 0.2 equivalents) and 1.4077 g of MMA (14.06 mmol; 100 equivalents) were placed in a round bottom flask fitted with a stirrer bar and a rubber septum. The reactor and its content were degassed by nitrogen sparge for 15 minutes then 1.82 mL of anhydrous methanol (50 wt %; thoroughly degassed *via* nitrogen sparge prior to use) were added to the round bottom flask under positive pressure of nitrogen using a syringe. The reaction mixture was flushed with nitrogen for an additional 5 minutes and the reactor was placed in an oil bath at 60 °C. After 27 hours, an aliquot of the crude material was taken for NMR analysis in order to assess the monomer conversion and the reactor was cooled down to room temperature resulting in the phase separation of polymer and methanol. THF was added to the reaction mixture until obtaining a clear homogeneous solution and the material was purified by precipitation into methanol (THF:MeOH = 1:10 v/v). The sample was collected by filtration and dried under vacuum at 40 °C overnight.

Monomer conversion was assessed using ^{1}H NMR spectroscopy in $CDCl_3$ for the crude samples by comparing the integrated signals of the residual MMA at 5.5 ppm and 6 ppm with those due to the methacrylic backbone between 0.5 ppm and 2.5 ppm and/or –for comparison purposes- with the integrated signals from the pendant group ($\text{-O-C}\underline{H_3}$, MMA + *p*(MMA)) between 3.5 ppm and 3.8 ppm.

^{1}H NMR in $CDCl_3$ at 50 °C was also used to estimate the number average degree of polymerisation, DP_n, of the precipitated *p*(MMA) samples. Comparison of the integrated signals of the CTA chain-end “Z” group between 7.25 ppm and 7.9 ppm with those due to the methacrylic backbone between 0.5 ppm and 2.2 ppm and/or –for comparison purposes- with the integrated signals from the pendant group ($\text{-O-C}\underline{H_3}$) between 3.3 ppm and 3.8 ppm allowed the assessment of the $DP_{n\,NMR}$. Therefore, $M_{n\,NMR}$ could be calculated using the following equation $M_{n\,NMR} = (DP_{n\,NMR} * M_{MMA}) + M_{CTA}$ and making the assumption that all the polymer chains are initiated with the “R” group and terminated with the “Z” group of the CTA (which is evidently not the case due to the nature of the RAFT process but allowed a reasonable assessment of the molecular weight).

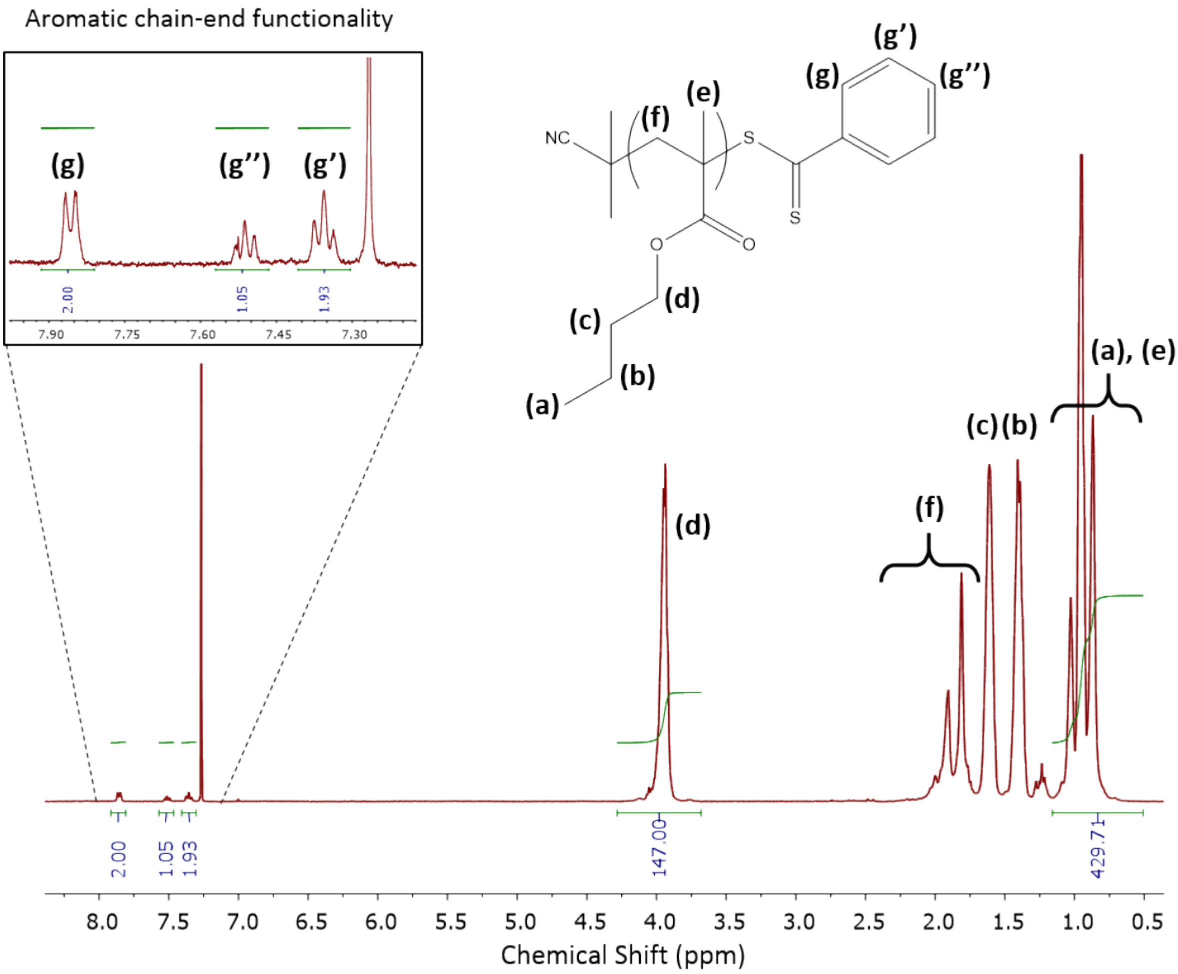

Figure S1 ^{1}H-NMR ($CDCl_3$) analysis of purified *p*(*n*BuMA)$_{60}$ obtained *via* RAFT to determine the DPn. Inset: magnification of the aromatic region of the spectrum showing resonances attributed to the CTA Z-group chain-end functionality.

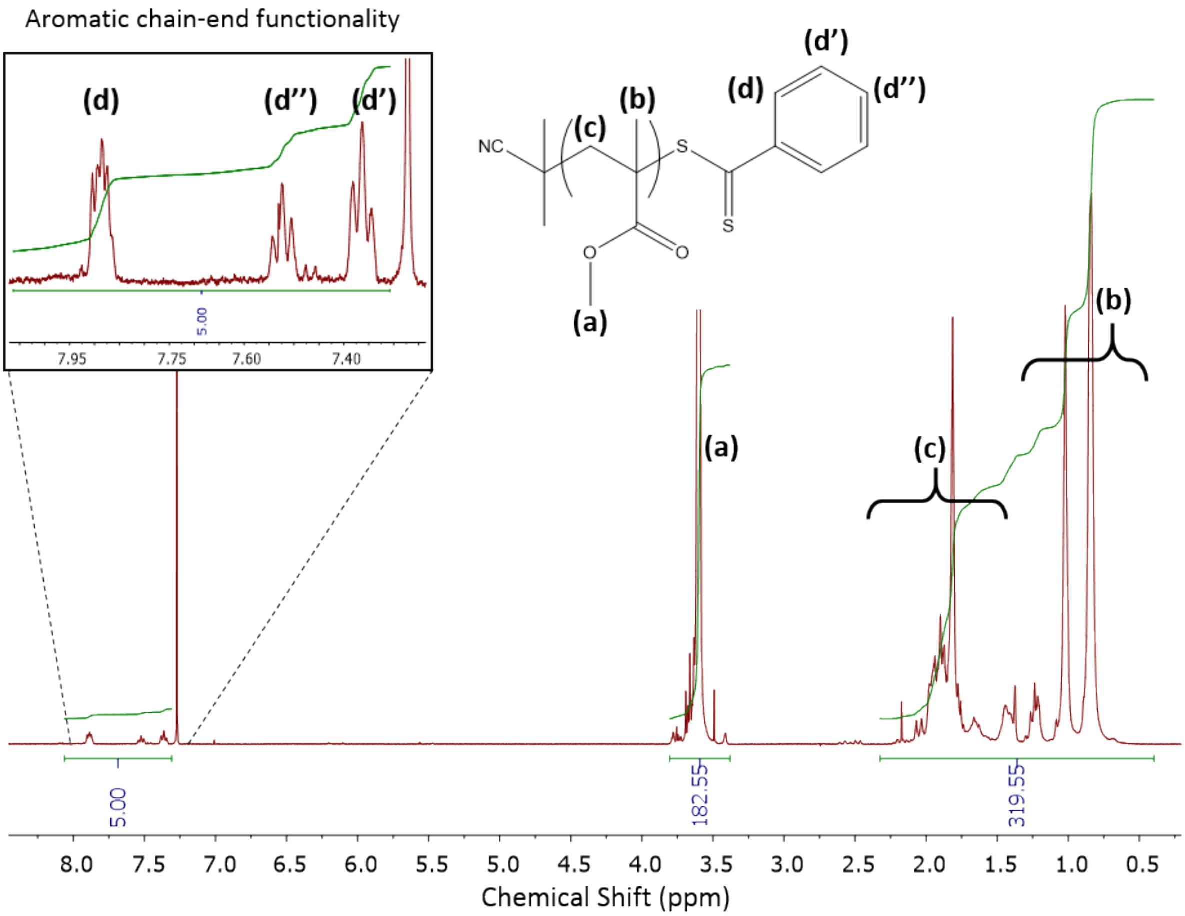

Figure S2 ^{1}H-NMR ($CDCl_3$) analysis of purified *p*(MMA)$_{60}$ obtained *via* RAFT to determine the DPn. Inset: magnification of the aromatic region of the spectrum showing resonances attributed to the CTA Z-group chain-end functionality.

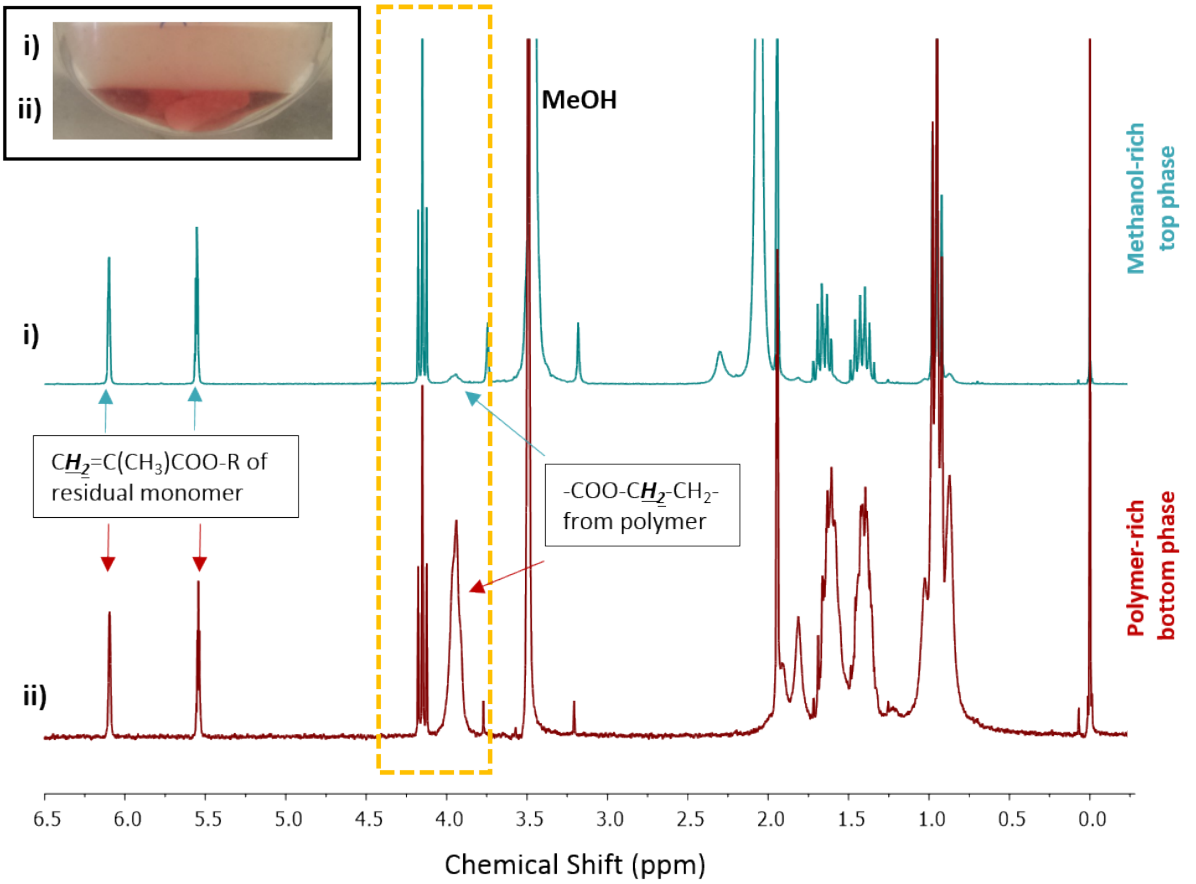

Figure S3 ^{1}H-NMR ($CDCl_3$) spectra of the biphasic system observed during the RAFT polymerisation of *n*BuMA in anhydrous methanol at 60 °C: i) methanol-rich phase (top) showing resonances attributed to residual *n*BuMA monomer and weak signals attributed to *p*(*n*BuMA) (yellow dotted box); ii) polymer-rich phase (bottom) showing resonances attributed to residual *n*BuMA monomer, and strong signals attributed to *p*(*n*BuMA) (yellow dotted box). Inset: photograph of the biphasic system (when stirring had ceased) from which samples were taken for analysis.

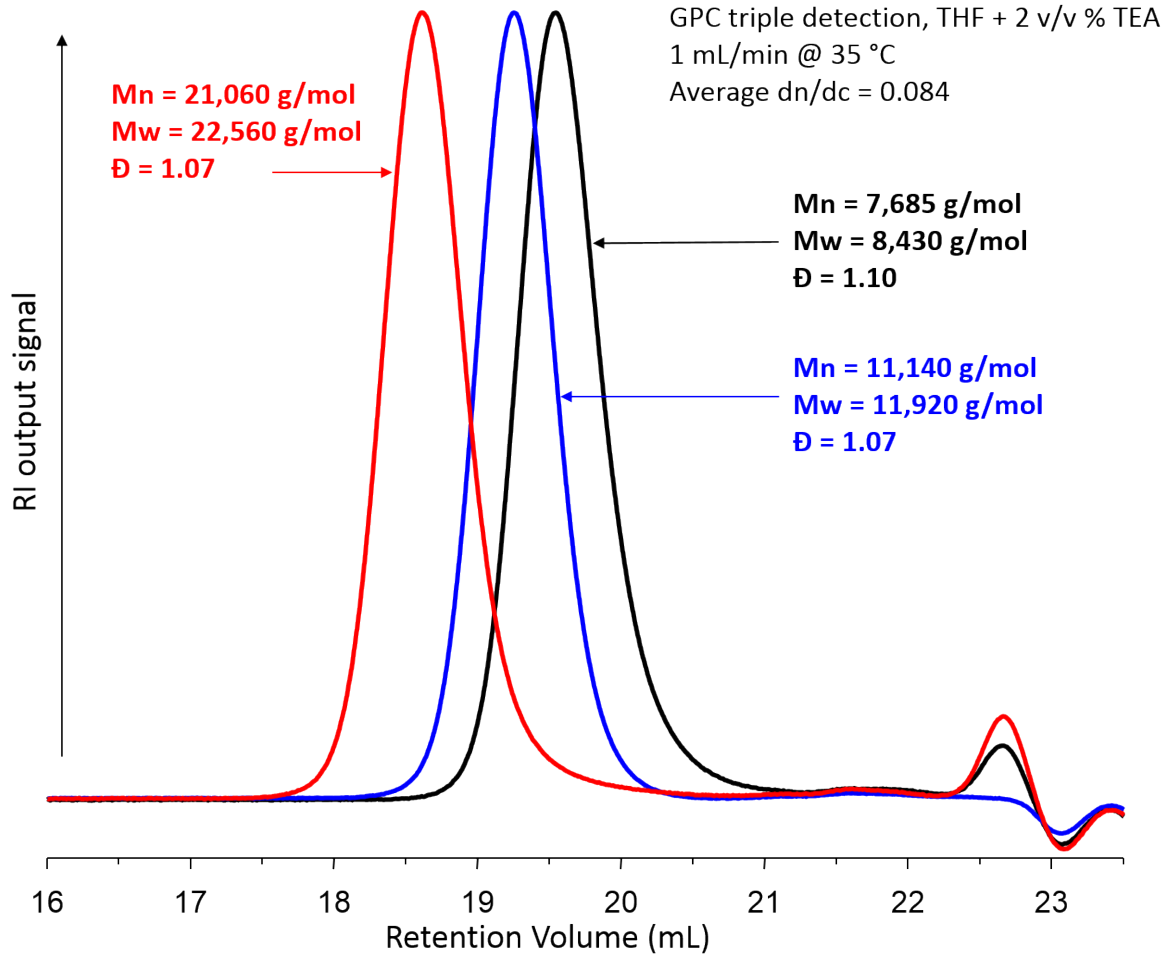

Figure S4 Overlaid SEC chromatograms (RI) of linear homopolymers produced using methanolic RAFT of MMA at 60 °C across the targeted DP_n = 60-200 monomer units. Analysis performed by triple detection SEC with a mobile phase of THF (+ 2 v/v % TEA) at 1 mL/min, 35 °C.

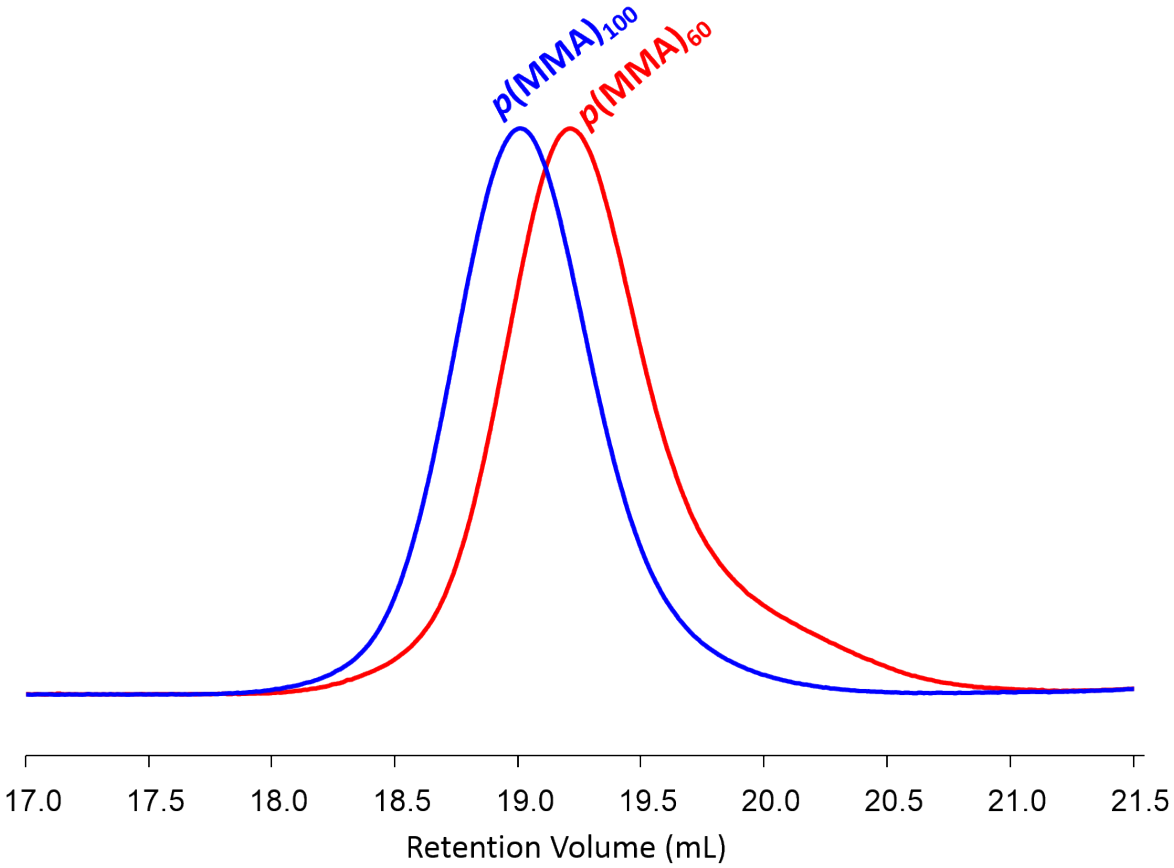

Figure S5 Overlaid SEC chromatograms (RI) of linear homopolymers produced using methanolic Cu-catalysed ATRP of MMA at 60 °C, targeting DP_n = 60 and 100 monomer units. Analysis performed by triple detection SEC with a mobile phase of THF (+ 2 v/v % TEA) at 1 mL/min, 35 °C.

Table S1: Calculation of an average *dn/dc* value obtained over 6 samples of *p*(MMA) analysed *via* triple-detection SEC (THF).

		SEC (THF) [a]	
Sample	**Technique**	***dn/dc*** (mL/g)	**Average *dn/dc*** (mL/g)
***p*(MMA)$_{105}$ Standard**	**-**	**0.0865**	**0.084**
***p*(MMA)$_{60}$**	**RAFT**	**0.0825**	
***p*(MMA)$_{100}$**		**0.0941**	
***p*(MMA)$_{200}$**		**0.0731**	
***p*(MMA)$_{60}$**	**ATRP**	**0.0810**	
***p*(MMA)$_{100}$**		**0.0853**	

[a] Determined by SEC triple detection (THF (+ 2 v/v % TEA), 1mL/min, 35 °C).

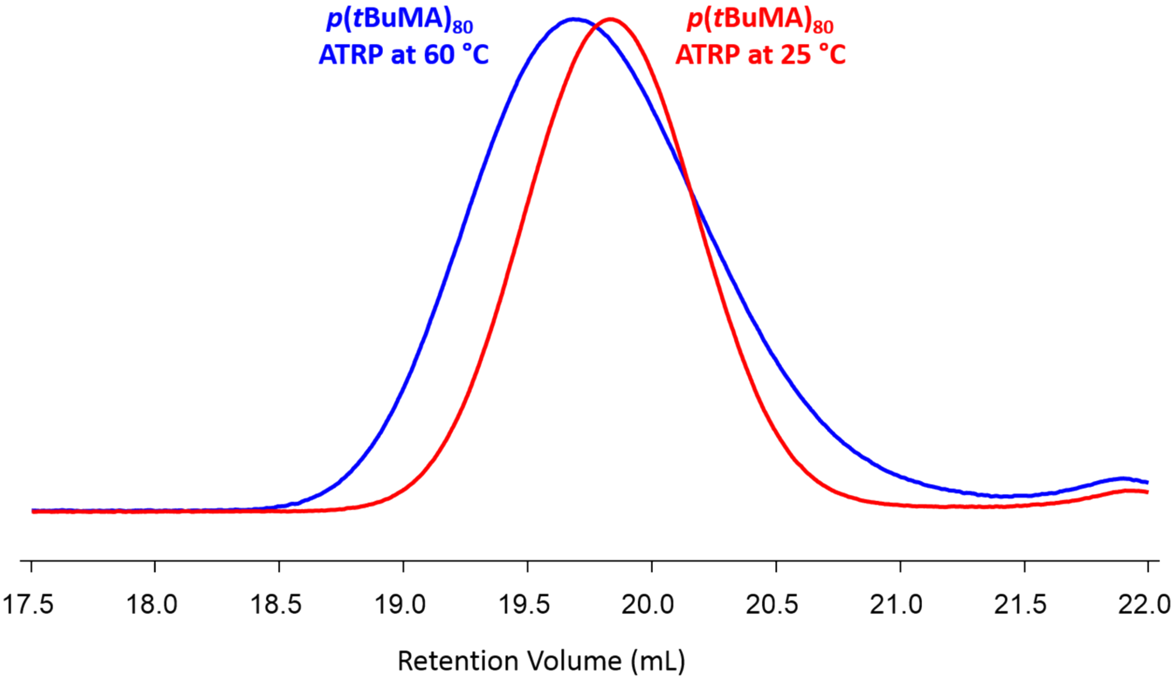

Figure S6 Overlaid SEC chromatograms (RI) of linear homopolymers produced using methanolic Cu-catalysed ATRP of *t*BuMA at 25 °C (red) and 60 °C (blue), targeting DP_n = 80 monomer units. Analysis performed by triple detection SEC with a mobile phase of THF (+ 2 v/v % TEA) at 1 mL/min, 35 °C.

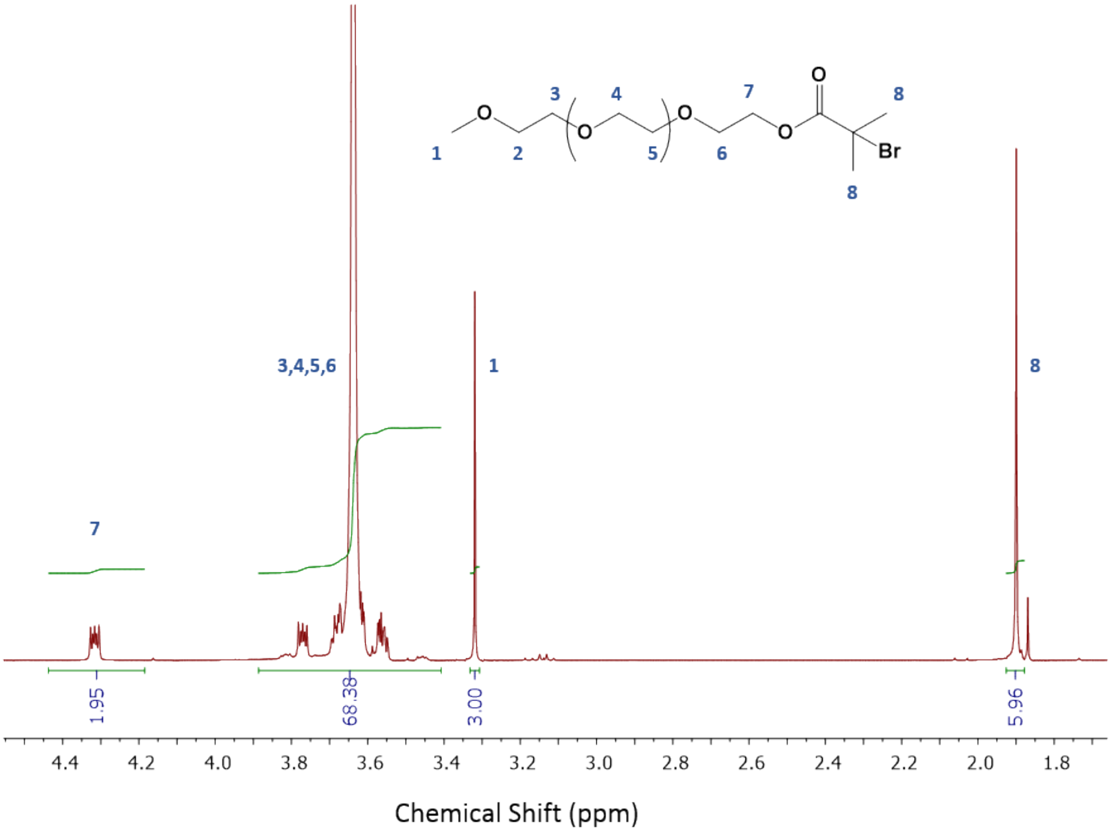

Figure S7 ^{1}H-NMR (D_2O) spectrum of $PEG_{17}Br$ macroinitiator.

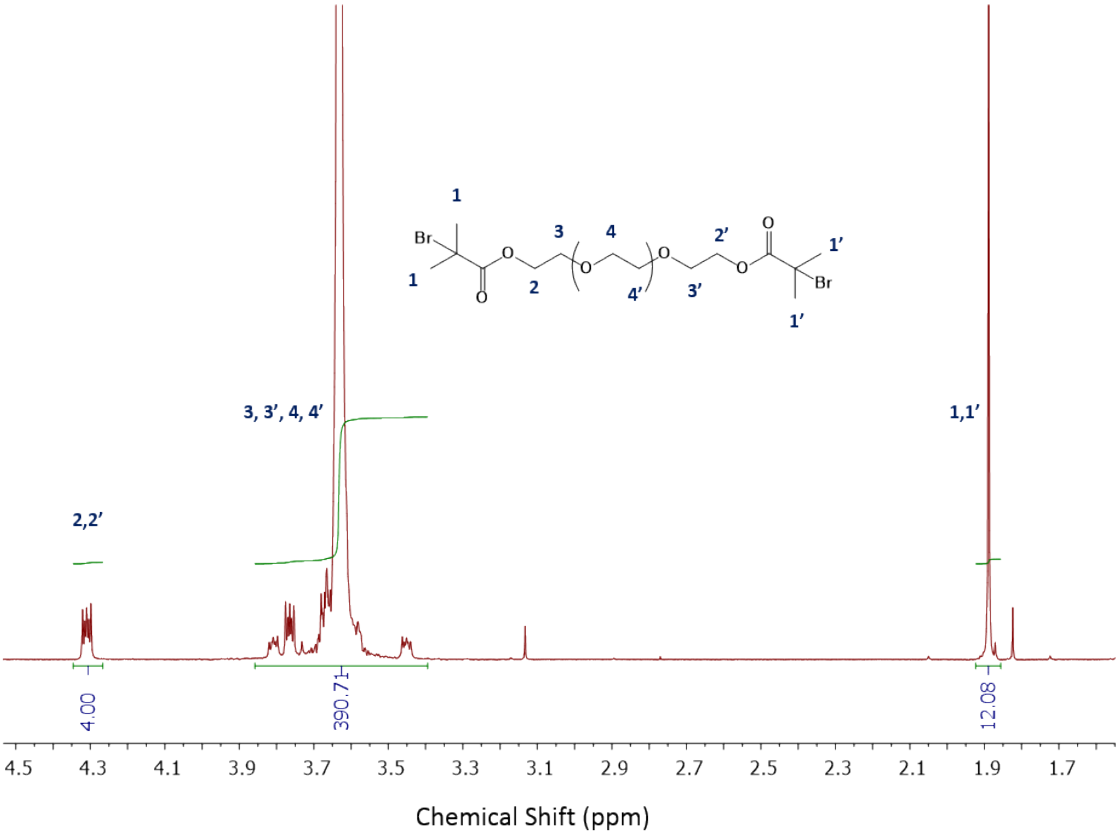

Figure S8 ^{1}H-NMR (D_2O) spectrum of the α,ω-bifunctional Br-PEG_{91}-Br macroinitiator.

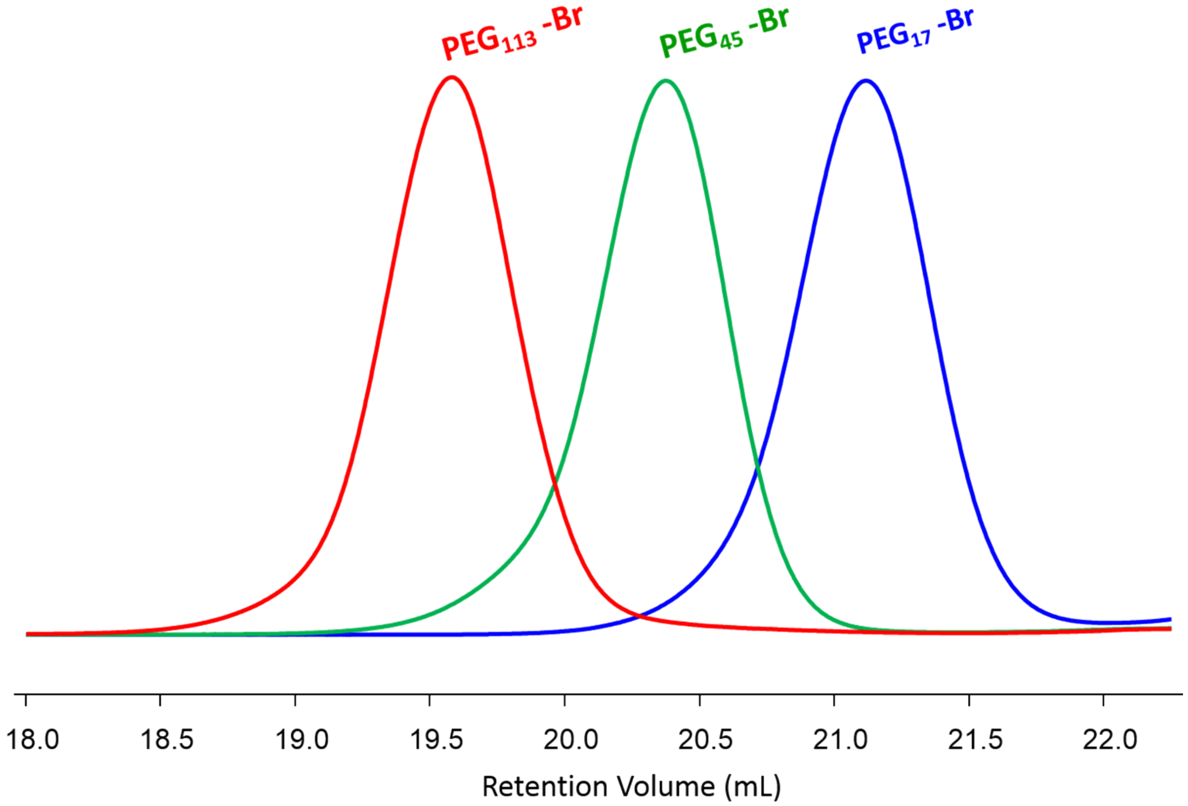

Figure S9 Overlaid SEC (RI) chromatograms of the monofunctional PEG$_{17}$-Br, PEG$_{45}$-Br, and PEG$_{113}$-Br macroinitiators. Analysis performed by triple detection SEC with a mobile phase of DMF (+ 0.01M LiBr) at 1mL/min, 60 °C.

Table S2: Calculation of the average *dn/dc* values for PEG and *p*(*n*BuMA) homopolymers used in equation [1] in order to generate (*dn/dc*)$_{\text{copolymer}}$ values for the *p*(PEG-*b*-*n*BuMA) A-B block copolymers.

	SEC (DMF) [a]	
Sample	***dn/dc*** (mL/g)	**Average *dn/dc*** (mL/g)
PEG 19 kg/mol	**0.0571**	
PEG 32.6 kg/mol	**0.0553**	**0.0566**
PEG 32.6 kg/mol	**0.0573**	
***p*(*n*BuMA)$_{80}$**	**0.0616**	
***p*(*n*BuMA)$_{80}$**	**0.0627**	**0.0624**
***p*(*n*BuMA)$_{80}$**	**0.0630**	

[a] Determined by SEC triple detection (DMF (+ 0.01M LiBr), 1 mL/min, 60 °C).

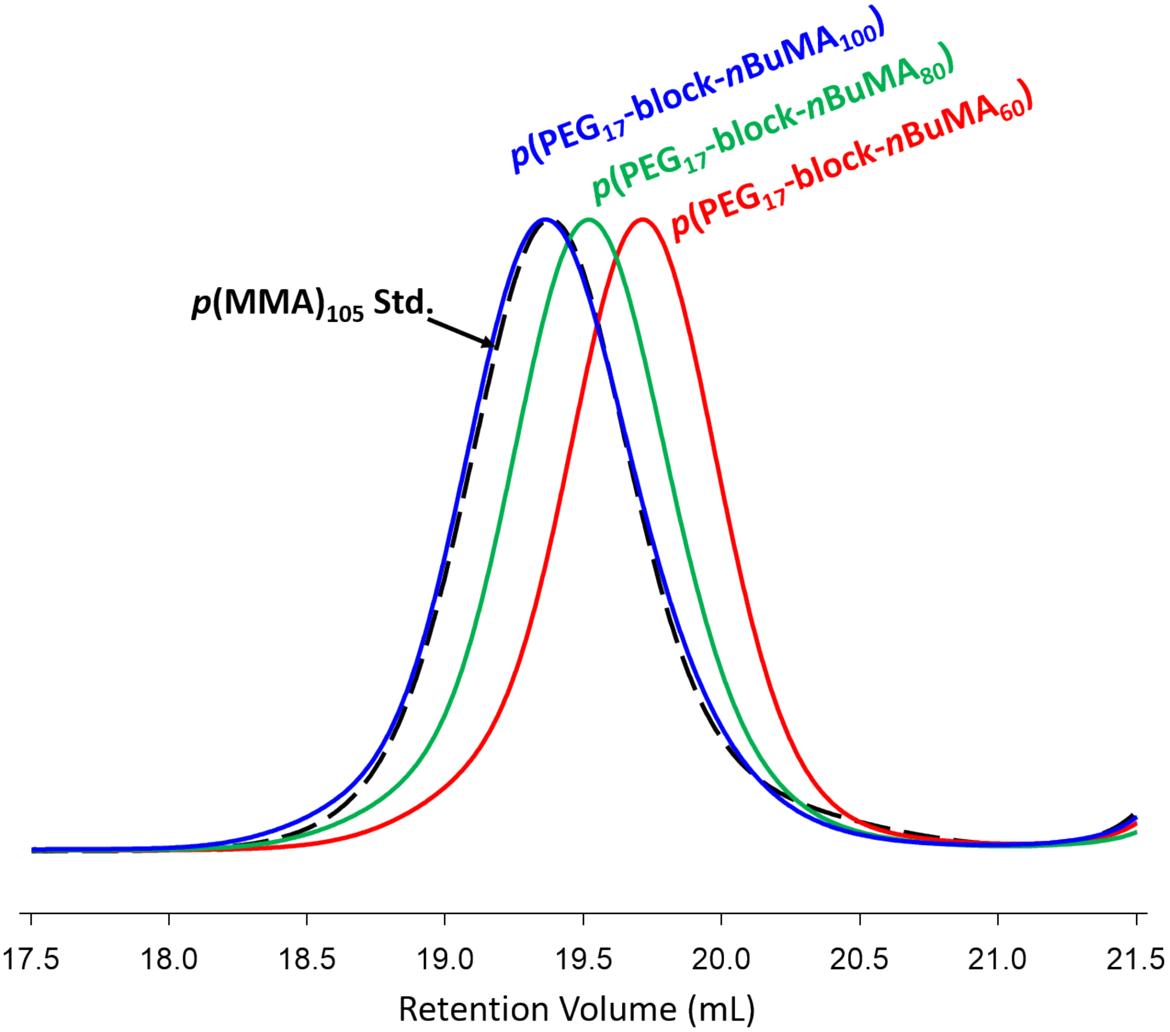

Figure S10 Overlaid SEC chromatograms (RI) of *p*(PEG_{17}-*b*-*n*BuMA$_x$) A-B block copolymers produced *via* methanolic Cu-catalysed ATRP of *n*BuMA at 60 °C using PEG_{17}-Br macroinitiator across the targeted DP_n = 60-100 monomer units - *p*(MMA)$_{105}$ standard (black dotted trace) shown for comparison. Analysis performed by triple detection SEC with a mobile phase of DMF (+ 0.01M LiBr) at 1 mL/min, 60 °C.

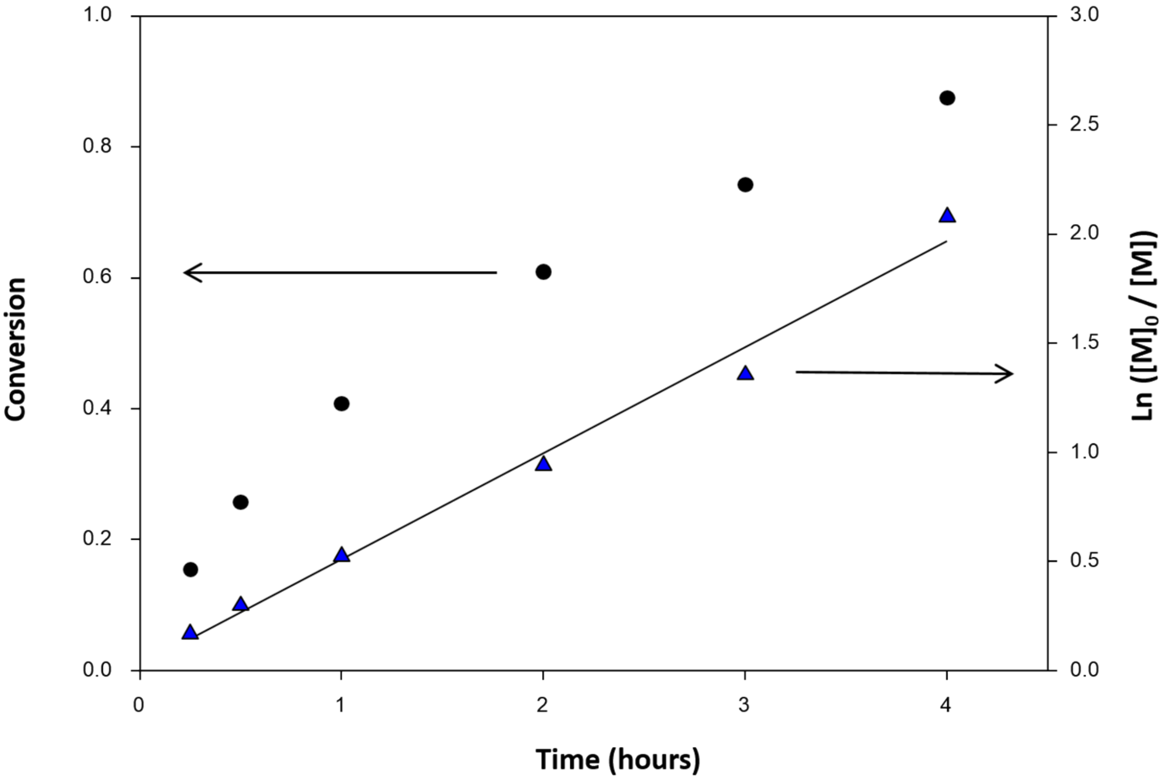

Figure S11 Kinetic studies of p(PEG$_{17}$-b-nBuMA$_{80}$) synthesis *via* Cu-Catalysed ATRP in anhydrous methanol at 60 °C showing conversion and semilogarithmic plots *vs.* time.

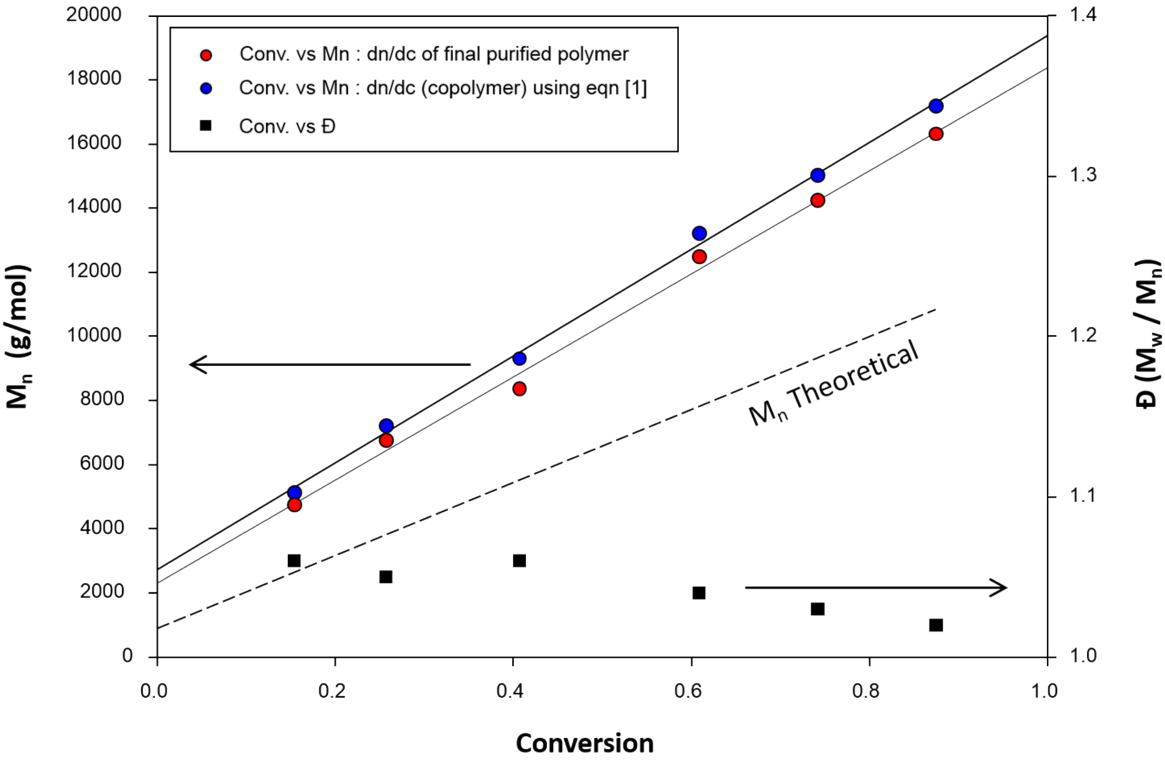

Figure S12 Kinetic studies of p(PEG$_{17}$-b-nBuMA$_{80}$) synthesis *via* Cu-Catalysed ATRP in anhydrous methanol at 60 °C showing the evolution of M$_n$ and dispersity with conversion.

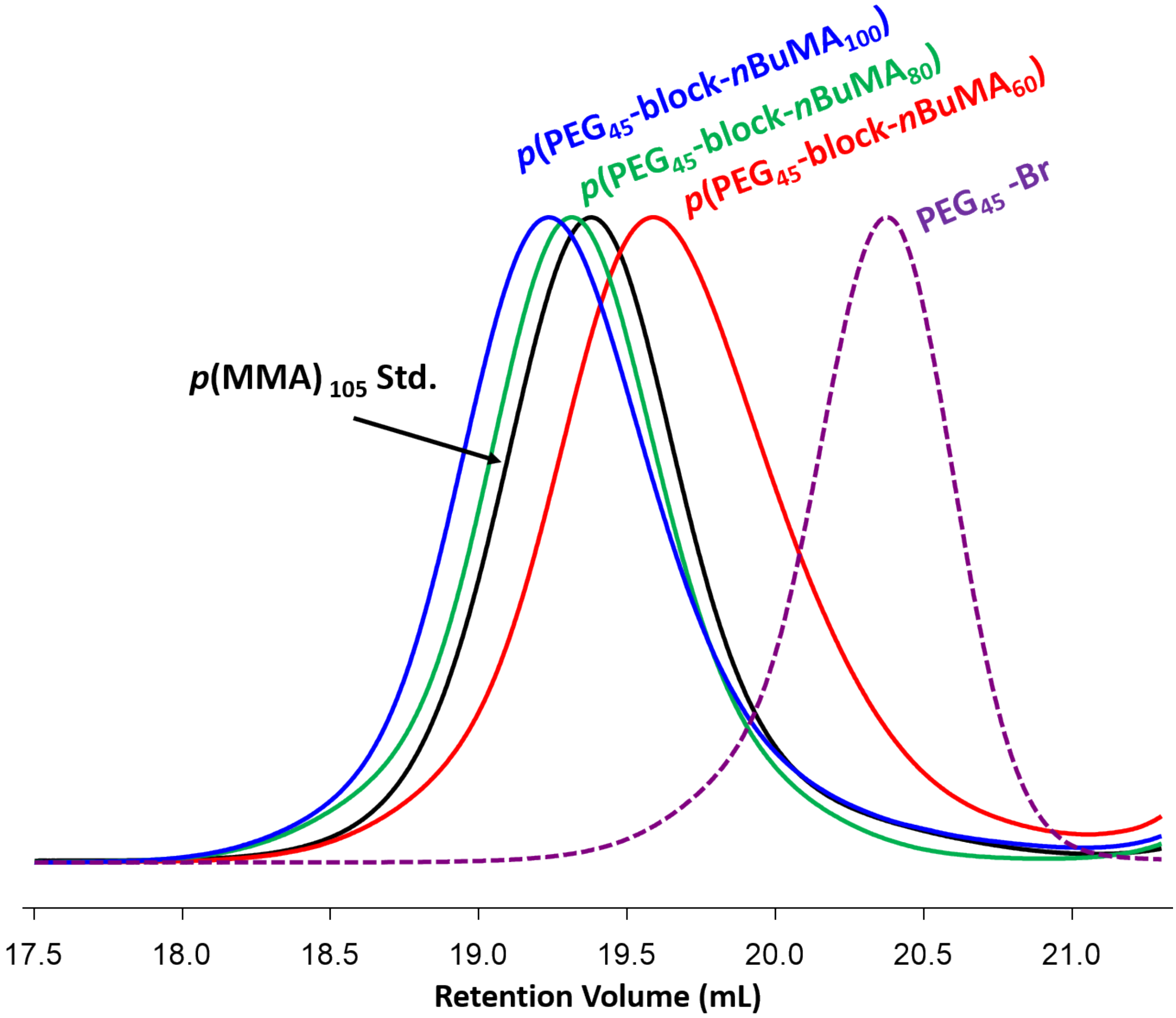

Figure S13 Overlaid SEC chromatograms (RI) of *p*(PEG_{45}-*b*-*n*$BuMA_x$) A-B block copolymers produced *via* methanolic Cu-catalysed ATRP of *n*BuMA at 60 °C using PEG_{45}-Br macroinitiator across the targeted DP_n = 60-100 monomer units - PEG_{45}-Br macroinitiator (purple dotted trace) and *p*$(MMA)_{105}$ standard (black trace) shown for comparison. Analysis performed by triple detection SEC with a mobile phase of DMF (+ 0.01M LiBr) at 1 mL/min, 60 °C.

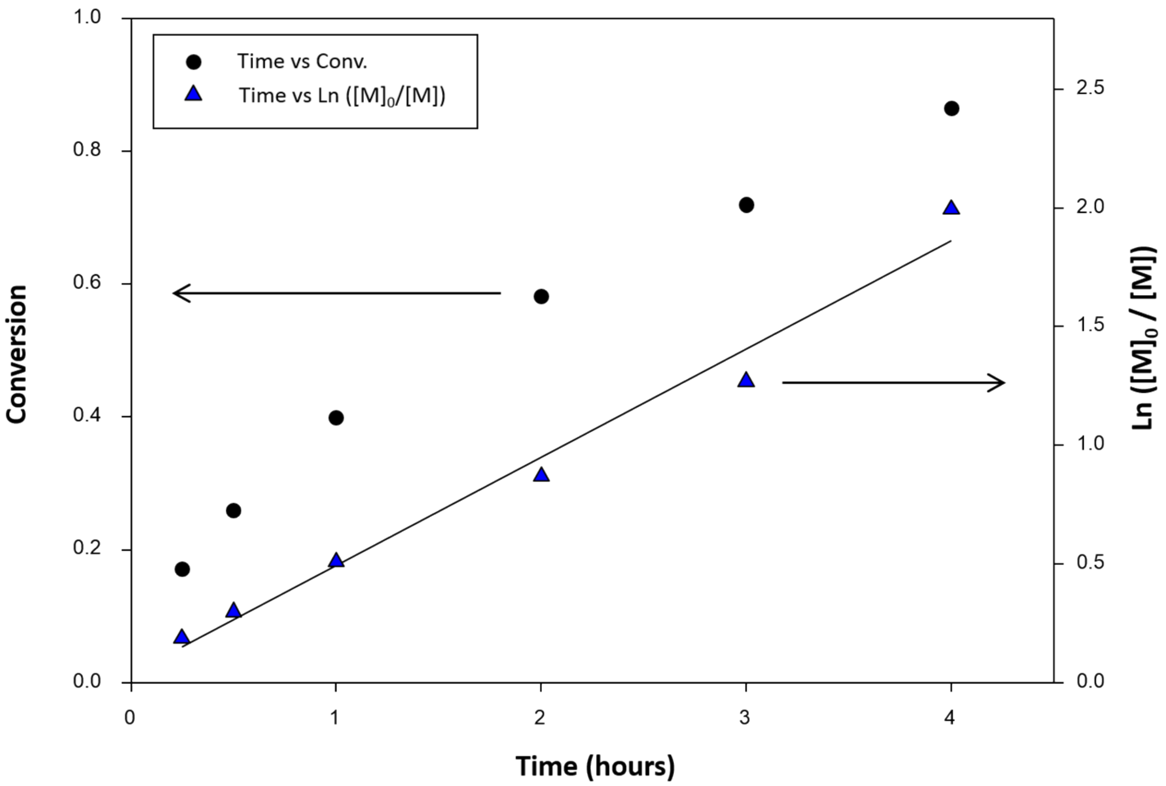

Figure S14; Kinetic studies of *p*(PEG_{45}-*b*-*n*$BuMA_{80}$) synthesis *via* Cu-Catalysed ATRP in anhydrous methanol at 60 °C showing conversion and semilogarithmic plots *vs.* time.

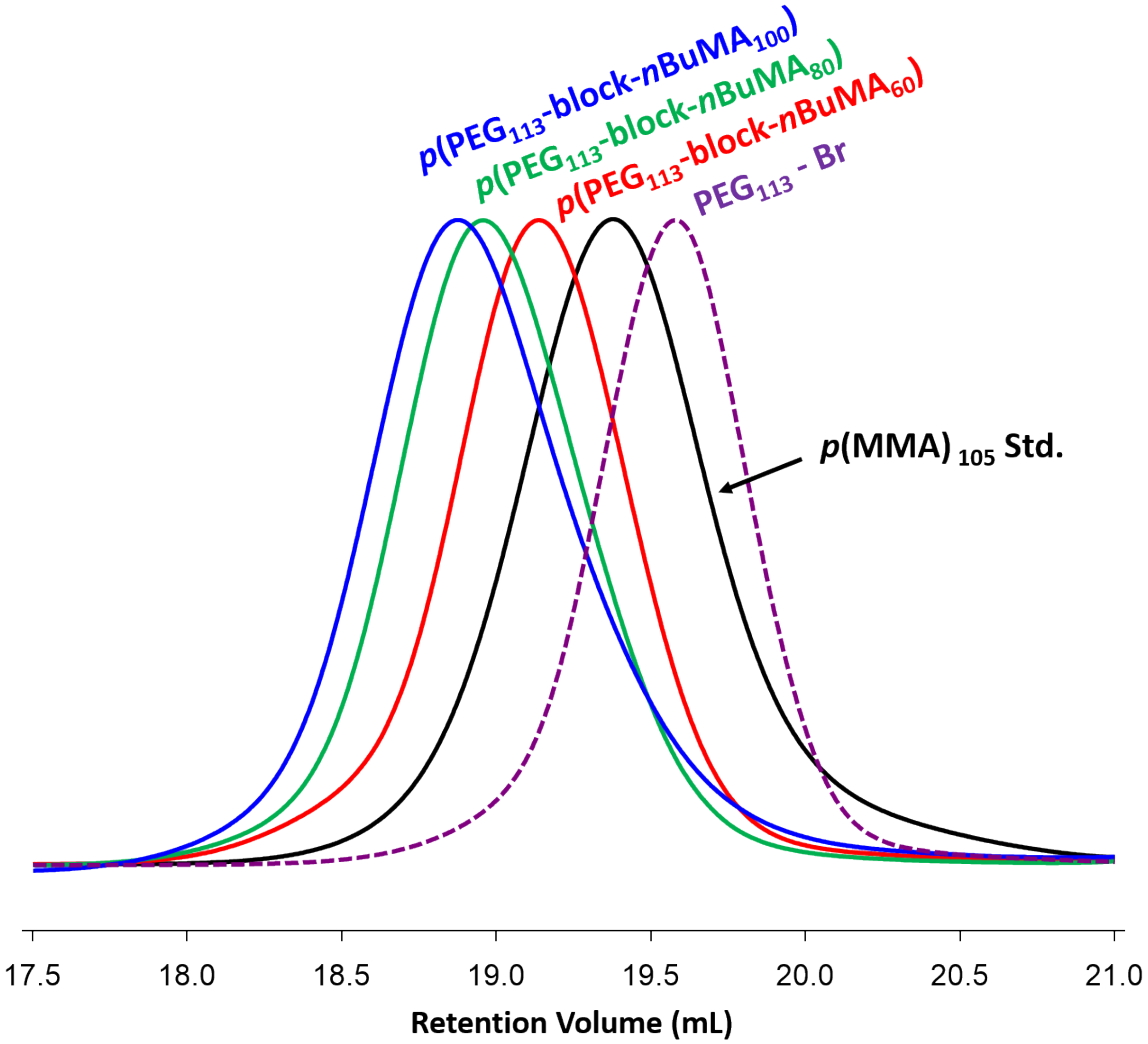

Figure S15 Overlaid SEC chromatograms (RI) of *p*(PEG_{113}-*b*-*n*$BuMA_x$) A-B block copolymers produced *via* methanolic Cu-catalysed ATRP of *n*BuMA at 60 °C using PEG_{113}-Br macroinitiator across the targeted DP_n = 60-100 monomer units – PEG_{113}-Br macroinitiator (purple dotted trace) and *p*$(MMA)_{105}$ standard (black trace) shown for comparison. Analysis performed by triple detection SEC with a mobile phase of DMF (+ 0.01M LiBr) at 1 mL/min, 60 °C.

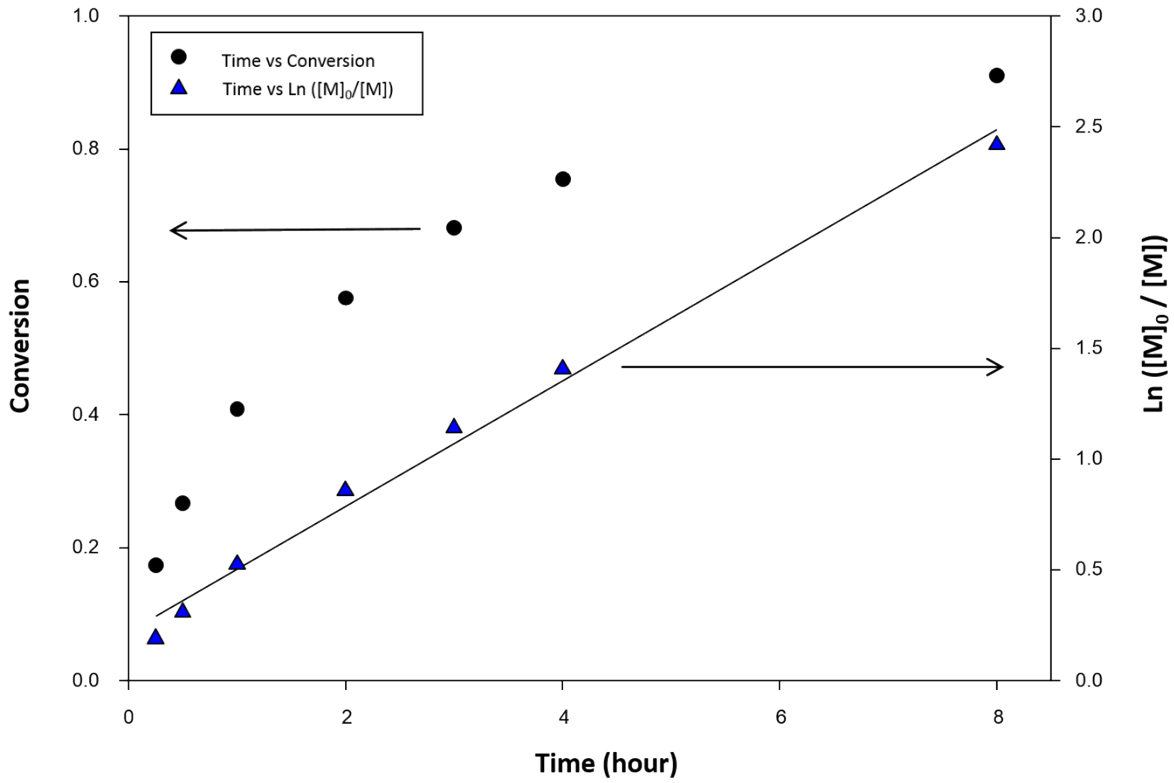

Figure S16; Kinetic studies of *p*(PEG$_{113}$-*b*-*n*BuMA$_{80}$) synthesis *via* Cu-Catalysed ATRP in anhydrous methanol at 60 °C showing conversion and semilogarithmic plots *vs.* time.

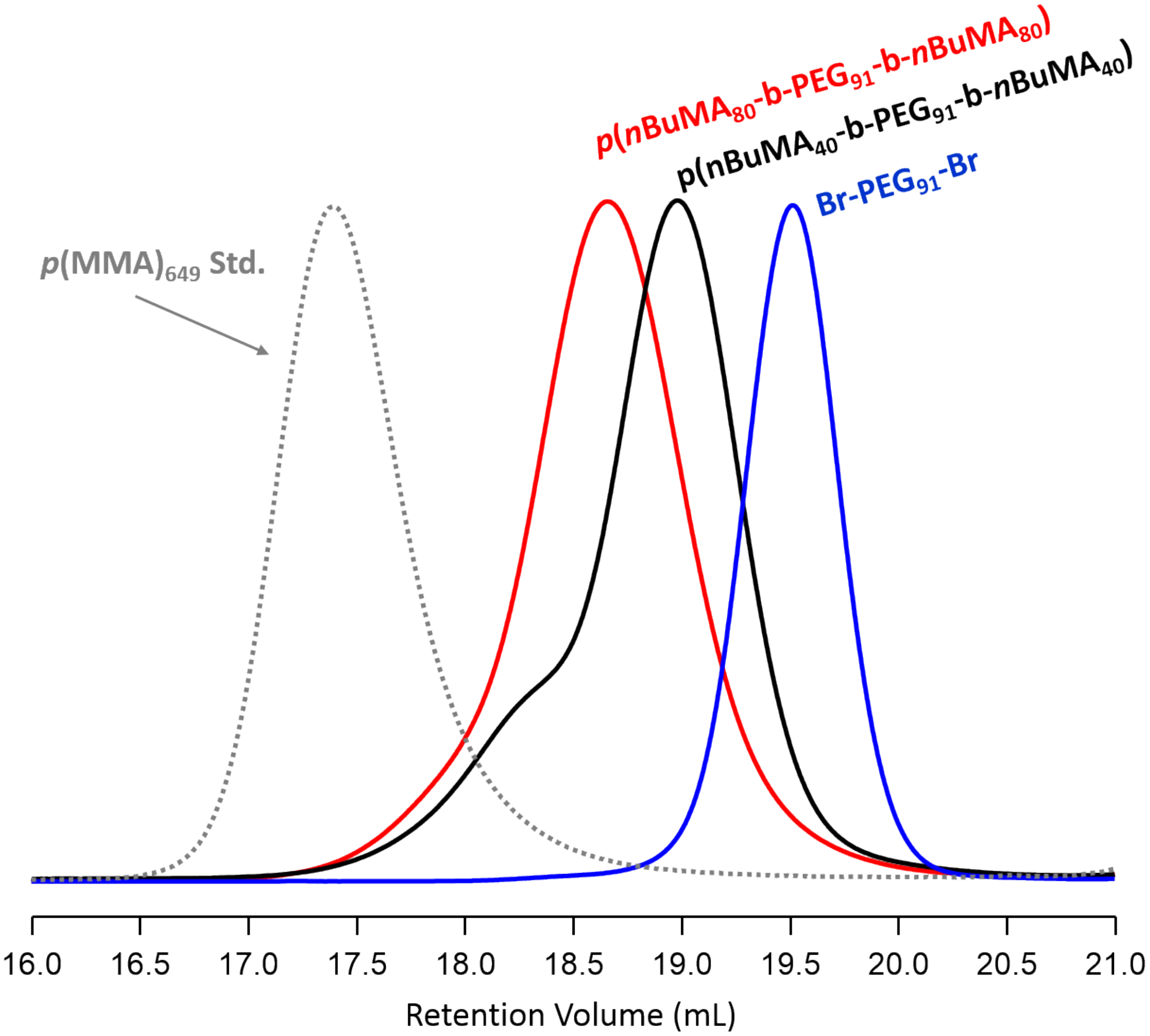

Figure S17 Overlaid SEC chromatograms (RI) of *p*(*n*BuMA$_x$-*b*-PEG$_{91}$-*b*-*n*BuMA$_x$) A-B-A block copolymers produced *via* methanolic Cu-catalysed ATRP of *n*BuMA at 60 °C using Br-PEG$_{91}$-Br α,ω-bifunctional macroinitiator, targeting DP$_n$ = 40 and 80 monomer units per bromide (i.e. DP$_n$ = 80 and 160 monomer units per chain) – Br-PEG$_{91}$-Br bifunctional macroinitiator (blue trace) and *p*(MMA)$_{649}$ standard (grey dotted trace) shown for comparison. Analysis performed by triple detection SEC with a mobile phase of DMF (+ 0.01M LiBr) at 1 mL/min, 60 °C.

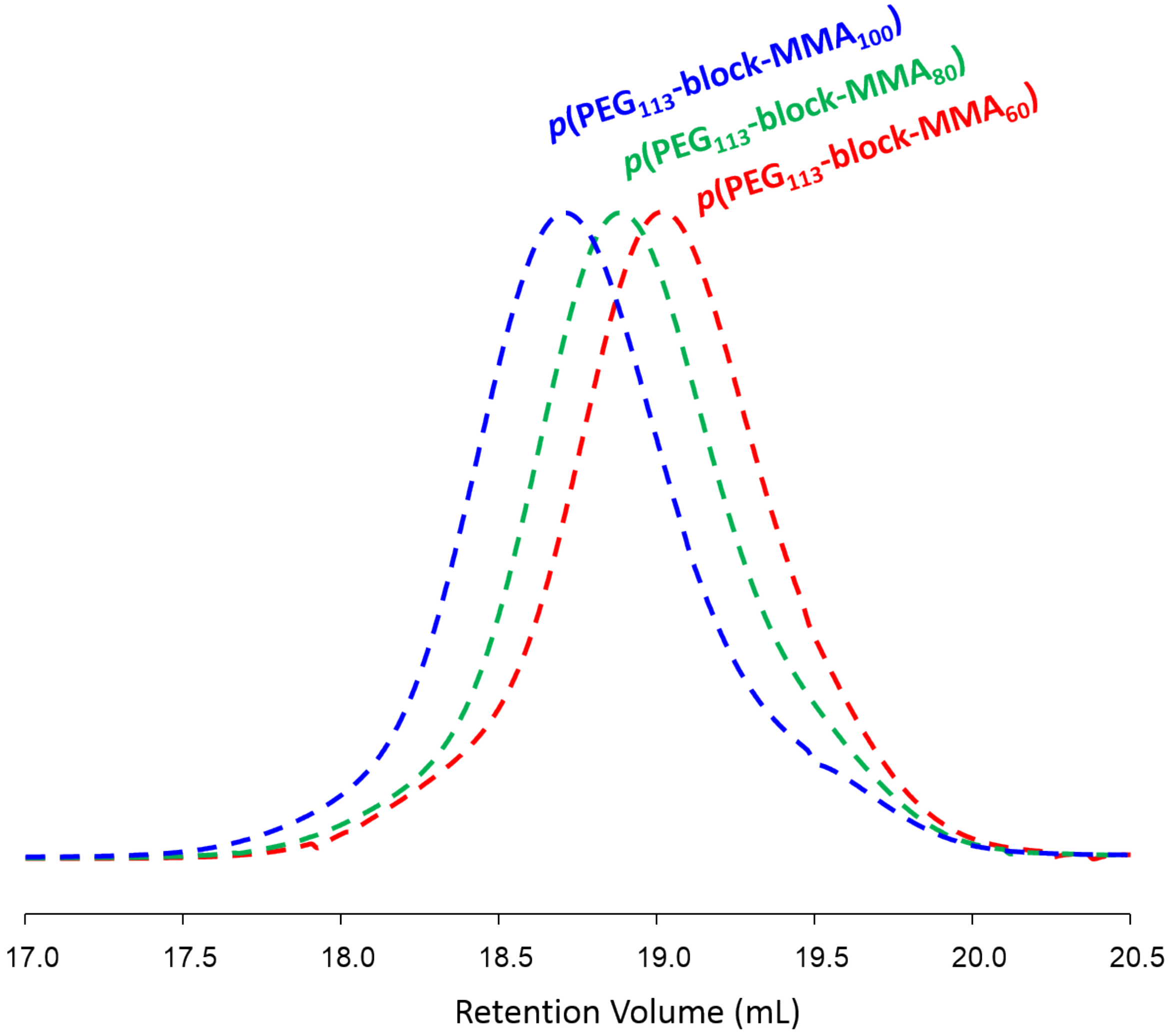

Figure S18 Overlaid SEC chromatograms (RI) of *p*(PEG_{113}-*b*-MMA_x) A-B block copolymers produced *via* methanolic Cu-catalysed ATRP of MMA at 60 °C using PEG_{113}-Br macroinitiator across the targeted DP_n = 60-100 monomer units. Analysis performed by triple detection SEC with a mobile phase of DMF (+ 0.01M LiBr) at 1 mL/min, 60 °C.

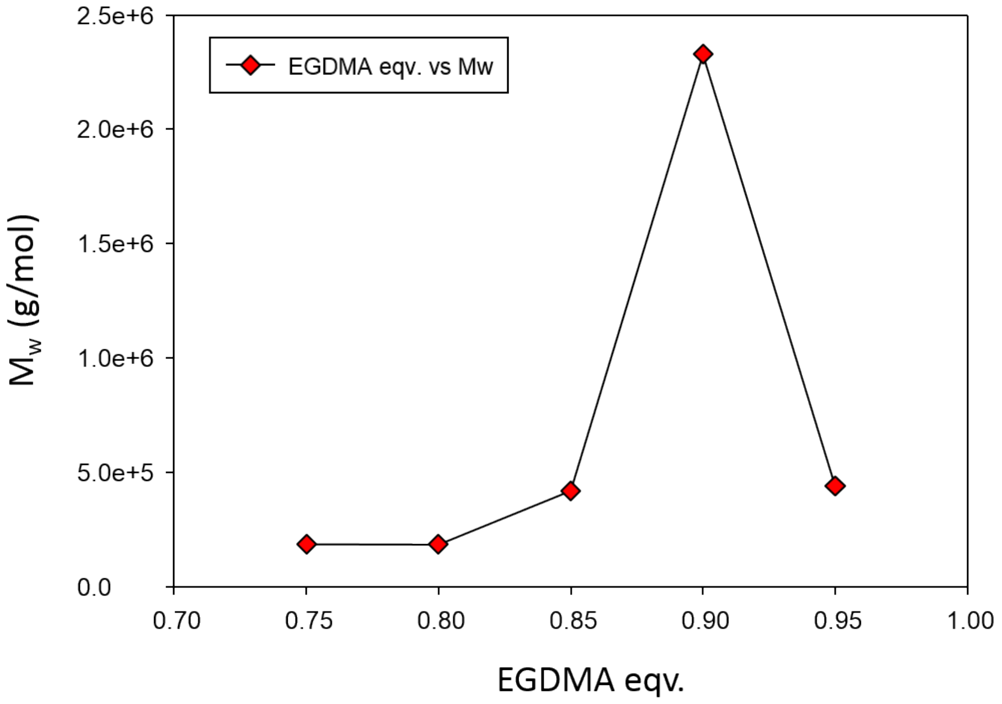

Figure S19 Evolution of the weight average molecular weight (M_w) with increasing levels of divinyl monomer, EGDMA (0.75 to 0.95 molar equivalent wrt. macroinitiator), for the Cu-catalysed branched methanolic ATRP of *n*BuMA (targeted DPn = 60 monomer units per primary chain) at 60 °C using PEG_{113}-Br macroinitiator. The observed decrease in M_w at 0.95 equivalent EGDMA indicates onset of microgel formation.

Table S3 Obtained triple detection SEC (DMF +0.01M LiBr at 1 mL/min and 60 °C) *dn/dc* values for each polymer branched Cu-catalysed methanolic ATRP copolymerisation of *n*BuMA and EGDMA at 60 °C using the PEG_{113}-Br macroinitiator.

Target[a] DP_n	**EGDMA: PEG_{113}-Br**	**SEC (DMF)**
		dn/dc (mL/g)
PEG_{113}-Br		
60	**0.95:1**	**0.0639**
60	**0.9:1**	**0.0558**
60	**0.85:1**	**0.0693**
60	**0.8:1**	**0.0676**
60	**0.75:1**	**0.0640**

[a] Target DP_n calculated as [*n*BuMA]/[initiator]

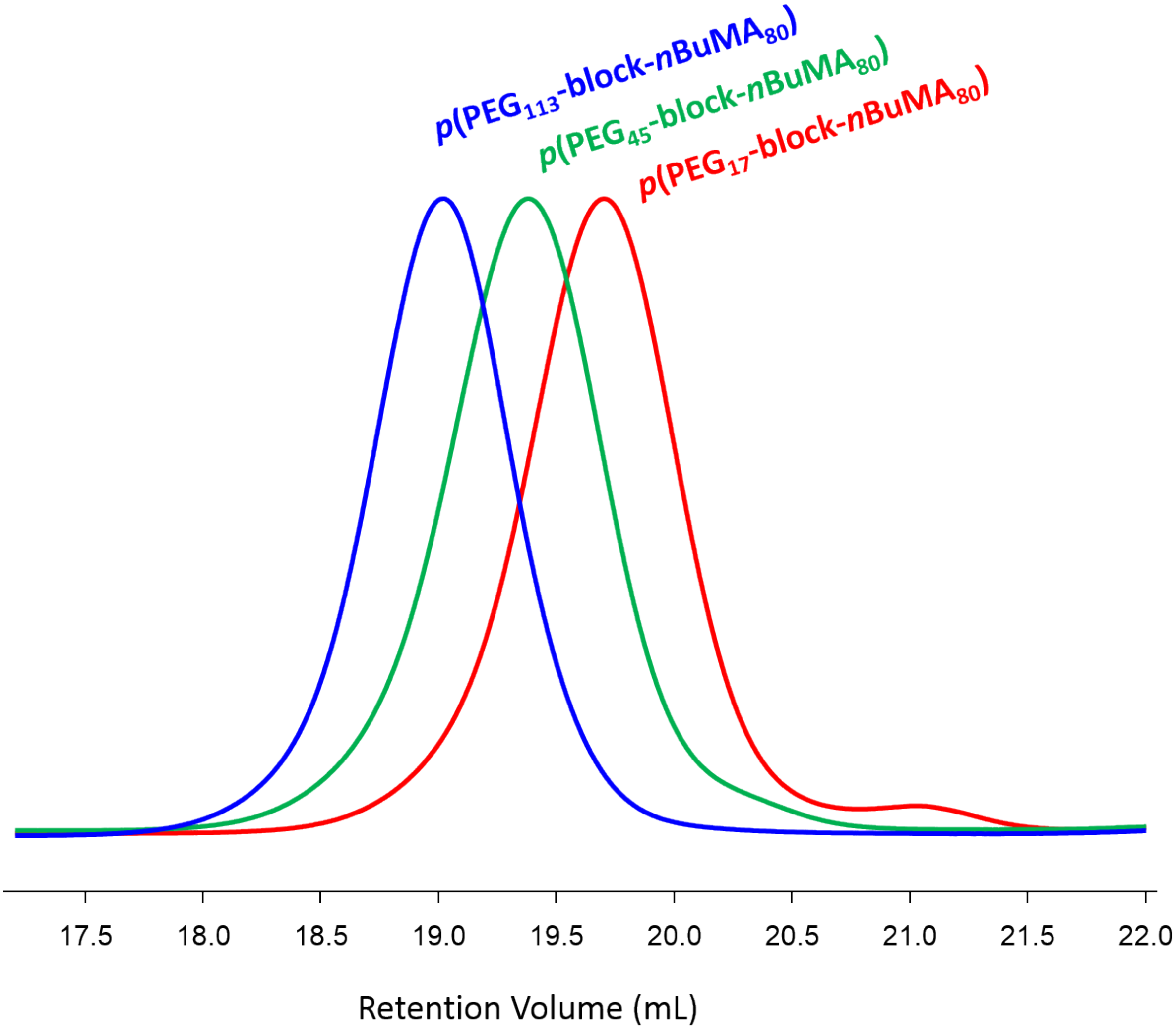

Figure S20 Overlaid SEC chromatograms (RI) of *p*(PEG$_x$-*b*-MMA$_{80}$) A-B block copolymers produced *via* methanolic Cu-catalysed ATRP of MMA at 25 °C, targeting DP$_n$ = 80 monomer units and using PEG$_{17}$-Br (red trace), PEG$_{45}$-Br (green trace) and PEG$_{113}$-Br (blue trace) macroinitiators. Analysis performed by triple detection SEC with a mobile phase of DMF (+ 0.01M LiBr) at 1 mL/min, 60 °C.

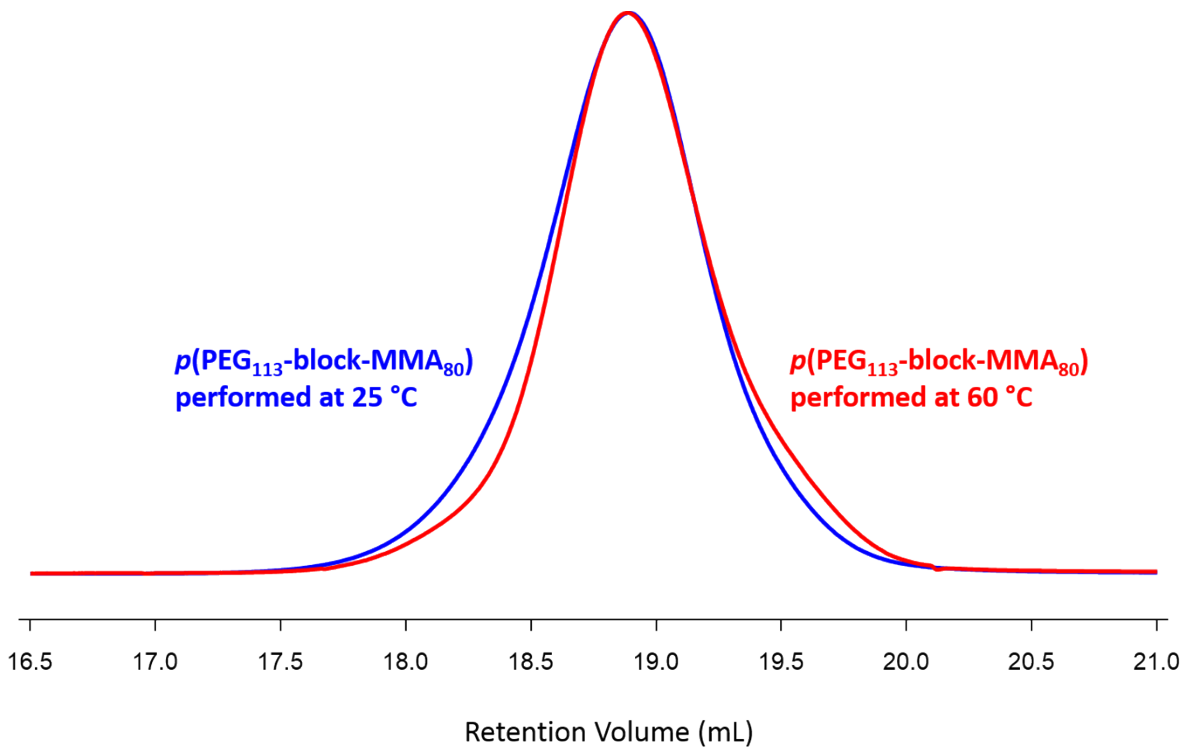

Figure S21 Overlaid SEC chromatograms (RI) of p(PEG$_{113}$-b-MMA$_{80}$) A-B block copolymers produced *via* methanolic Cu-catalysed ATRP of MMA at 25 °C (blue trace) and 60 °C (red trace), targeting DP$_n$ = 80 monomer units and using PEG$_{113}$-Br macroinitiator. Analysis performed by triple detection SEC with a mobile phase of DMF (+ 0.01M LiBr) at 1 mL/min, 60 °C.

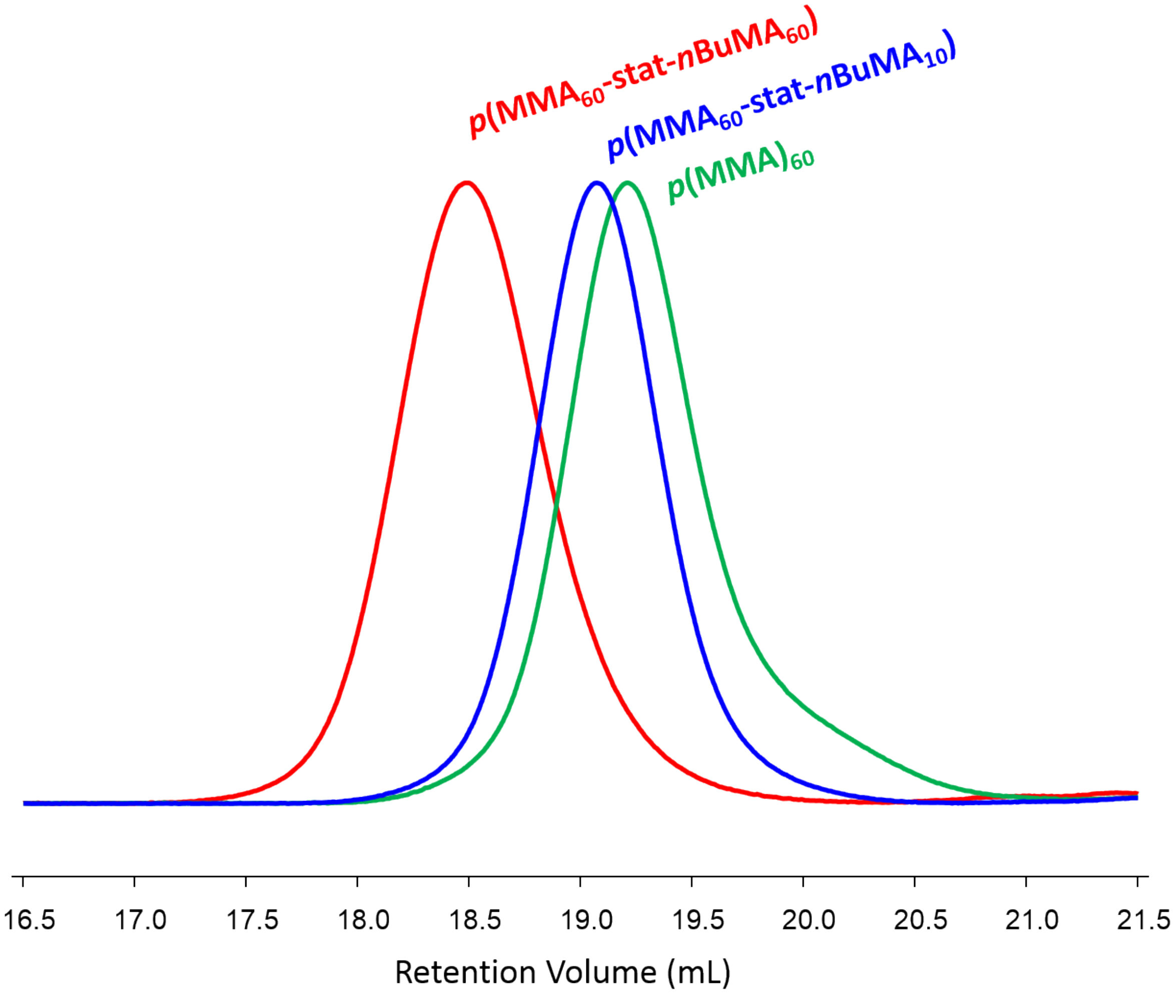

Figure S22 Overlaid SEC chromatograms (RI) of *p*(MMA$_{60}$-*stat*-*n*BuMA$_x$) statistical copolymers produced *via* methanolic Cu-catalysed ATRP of MMA and *n*BuMA at 60 °C, varying the targeted *n*BuMA DP$_n$ x = 0 (green trace), 10 (blue trace) and 60 (red trace) monomer units per chain and keeping the targeted MMA DP$_n$ = 60 monomer units per chain. Analysis performed by triple detection SEC with a mobile phase of THF (+ 2 v/v % TEA) at 1 mL/min, 35 °C.

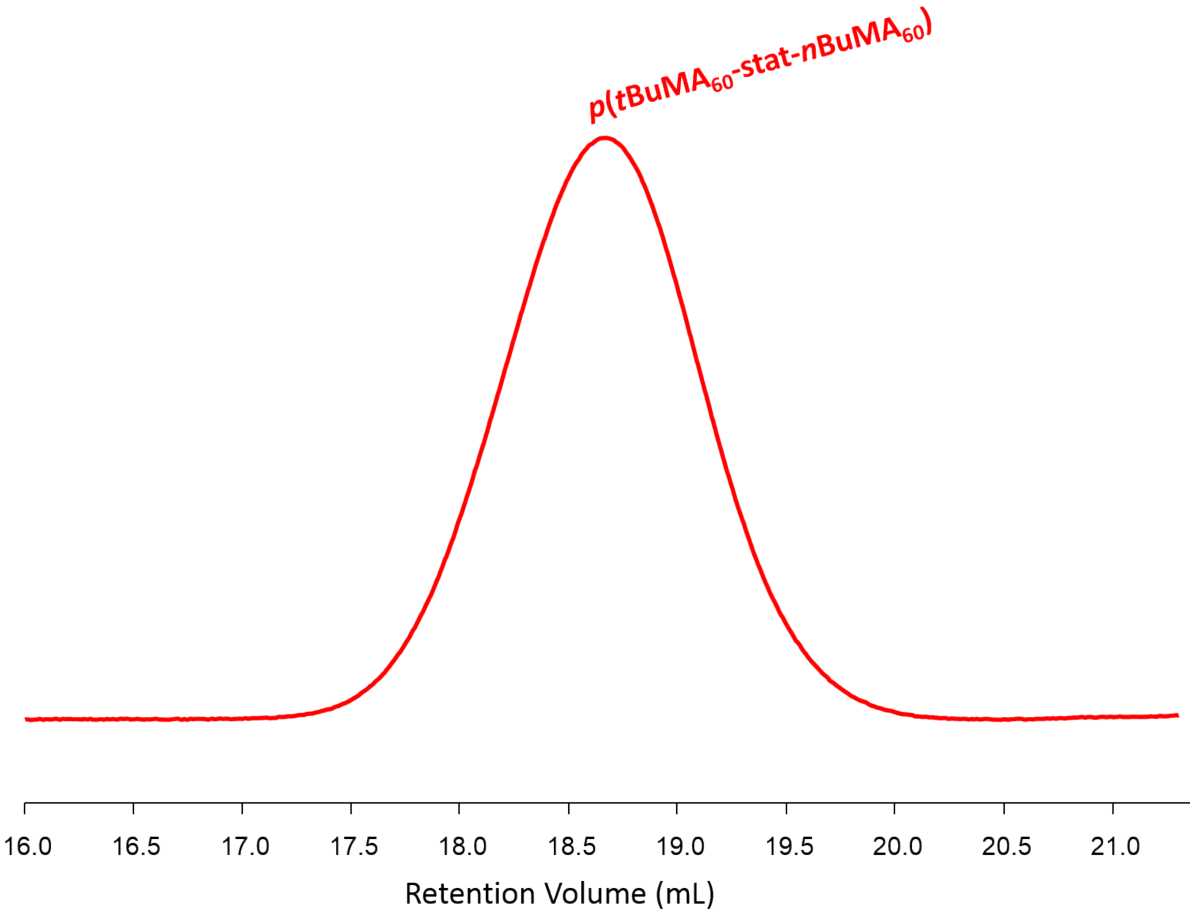

Figure S23 SEC chromatogram (RI) of the *p*(*t*BuMA$_{60}$-*stat*-*n*BuMA$_{60}$) statistical copolymer produced *via* methanolic Cu-catalysed ATRP of *t*BuMA and *n*BuMA at 60 °C, targeting DP$_n$ = 60 monomer units for each comonomer. Analysis performed by triple detection SEC with a mobile phase of THF (+ 2 v/v % TEA) at 1 mL/min, 35 °C.

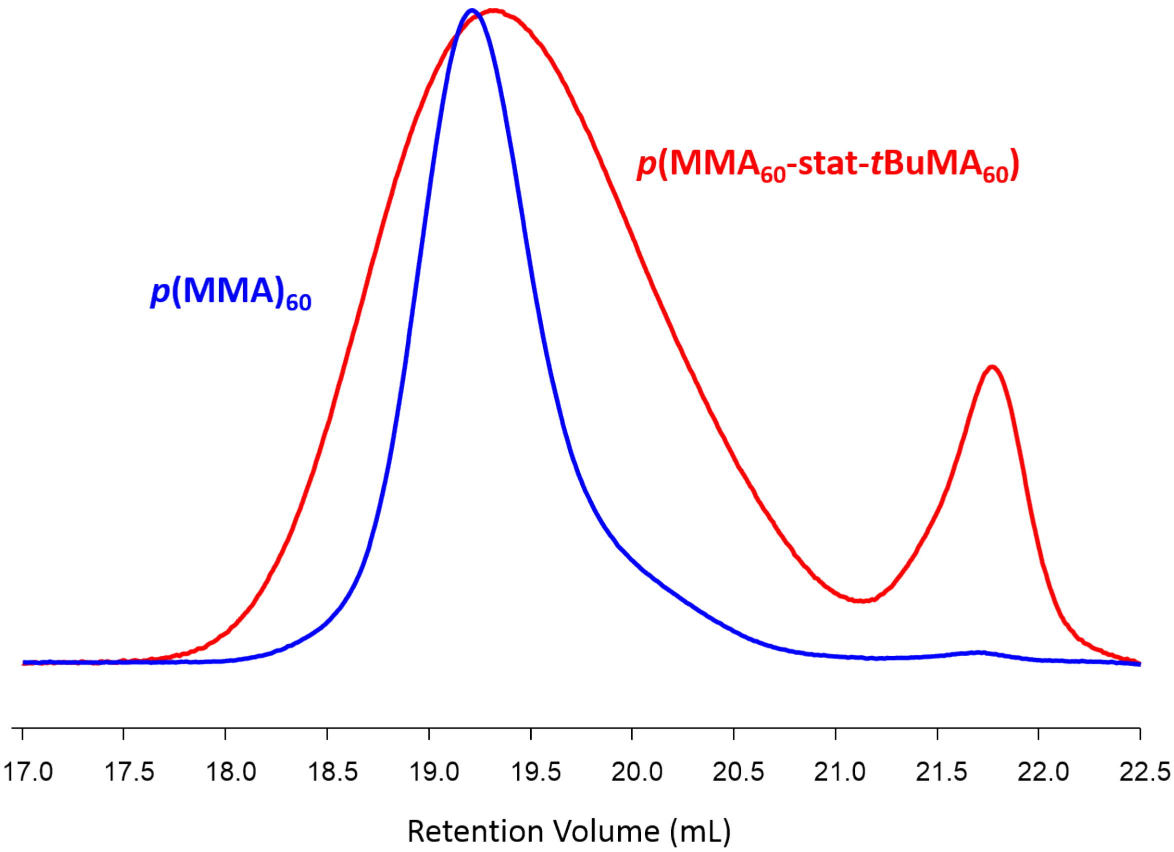

Figure S24 SEC chromatogram (RI) of the *p*(MMA$_{60}$-*stat*-*t*BuMA$_{60}$) statistical copolymer produced *via* methanolic Cu-catalysed ATRP of MMA and *t*BuMA at 60 °C, targeting DP$_n$ = 60 monomer units for each comonomer – *p*(MMA)$_{60}$ homopolymer (blue trace) overlaid for comparison. Analysis performed by triple detection SEC with a mobile phase of THF (+ 2 v/v % TEA) at 1 mL/min, 35 °C.