Electronic Supplementary Material (ESI) for Polymer Chemistry.

Expanding the monomer scope of linear and branched vinyl polymerisations via copper-catalysed reversible-deactivation radical polymerisation of hydrophobic methacrylates using anhydrous alcohol solvents.

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Electronic Supplementary Information

Materials & Characterisation

Materials

Methyl methacrylate (MMA, 99 %) ethyl methacrylate (EMA, 99%), *n*-butyl methacrylate (*n*BMA 99 %), *t*-butyl methacrylate (*t*BMA 99 %), n-hexyl methacrylate (*n*HMA, 99 %), cyclohexyl methacrylate (CHMA, 99 %), benzyl methacrylate (BzMA, 96 %), 2-ethyl hexyl methacrylate (EHMA, 99 %), lauryl methacrylate (LMA, 99 %), steryl methacrylate (SMA, 99 %), copper (I) chloride (Cu(I)Cl, 99 %), deuterated chloroform ($CDCl_3$, 98.8 atom % D), pyrene (99 %), α-bromo isobutyryl bromide (99 %), benzyl alcohol (99 %), anhydrous tetrahydrofuran (a. THF, 99.8 %) anhydrous triethyl amine (TEA, 99 %), dimethyl amino pyridine (DMAP, 99 %), 2,2' – bipyridine (bpy, 99%), anhydrous methanol (a. MeOH, 99.8 %) and anhydrous propan-2-ol (a. IPA, 99.8 %) were purchased from Sigma Aldrich. Tetrahydrofuran (THF, reagent grade), chloroform ($CHCl_3$, reagent grade), methanol (MeOH, reagent grade), acetone (reagent grade), ethyl acetate (reagent grade), ethanol (reagent grade), Toluene (reagent grade) and petroleum ether (40-60 ° C, reagent grade) were purchased from Fisher. All materials were used as received.

Characterisation

^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ using a Bruker Avance spectrometer operating at 400 and 100 MHz respectively. Triple detection size exclusion chromatography (SEC) was conducted using a Malvern Viscotek instrument equipped with a GPCmax VE2001 auto-sampler, two viscotek T6000 columns (and a guard column), a refractive index (RI) detector VE3580 and a dual 270 detector (light scattering and viscometer). SEC was performed at a flow rate of 1 mL min^{-1} using THF containing 2 v/v % of TEA as the mobile phase. Fluorescence spectra were obtained using a Shimadzu RF-5301PC spectrofluorophotometer. Emission spectra for pyrene were recorded between 350 and 500 nm. An excitation wavelength of λex = 335 nm was used for all studies as well as an excitation slit width of 2.5 nm and an emission slit width of 2.5 nm with a scan rate of 60 nm min^{-1}.

Experimental Details

Preliminary Feasibility Studies

Monomer-solvent miscibility studies were conducted at a monomer concentration of 50 weight percent (50 wt %) with respect to the total mass of the monomer-solvent mixture. Solvent miscibility was assessed visually at both ambient (20 ℃) and elevated (60 ℃) temperatures. In a typical experiment, MMA (1.00 g, 9.99 mmol) and anhydrous methanol (1.00 g, 1.26 mL) were added to a

glass vial and sealed. The vial was agitated gently in order to give ample opportunity for mixing, after which monomer-solvent miscibility at ambient temperature was assessed visually. A magnetic stirrer bar was then added, the vial was re-sealed with a rubber septum and placed in an oil bath at 60 °C under magnetic stirring. After 10 minutes, the vial was withdrawn from the oil bath and monomer-alcohol miscibility at an elevated temperature was assessed visually.

Table S1. Monomer-alcohol miscibility studies conducted for all methacrylate monomers

	MMA	EMA	*n*BMA	*t*BMA	*n*HMA	CHMA	BzMA	EHMA	LMA	SMA
a) Anhydrous MeOH										
Ambient (20 °C)	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**N[a]**
Elevated (60 °C)	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**N[b]**
b) Anhydrous IPA										
Ambient (20 °C)	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**
Elevated (60 °C)	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**

Y = Miscible monomer-alcohol mixture obtained. N = Immiscible monomer-alcohol mixture obtained. [a] Mixture consisting of a white SMA powder dispersed in MeOH. [b] Biphasic mixture obtained consisting of two clear immiscible liquids.

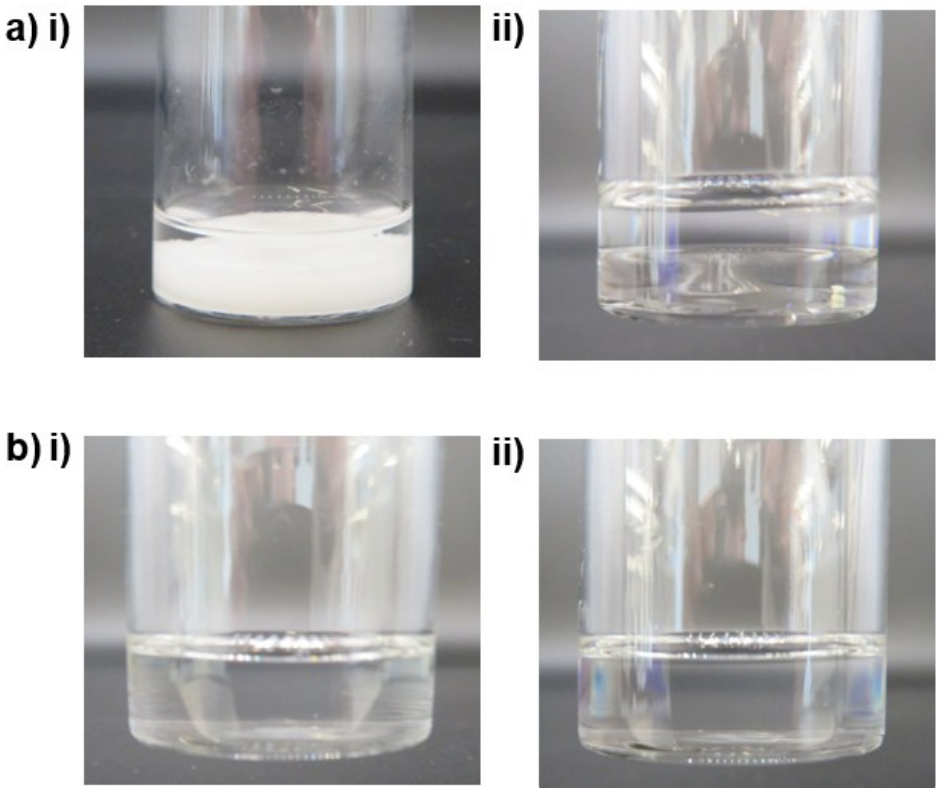


Figure S1 SMA–alcohol miscibility studies at ambient and elevated temperatures. a) SMA-MeOH (50 wt %) at (i) 20 °C and (ii) 60 °C. b) SMA-IPA mixtures (50 wt %) at (i) 20 °C and (ii) 60 °C.

Fluorescence Emission Spectroscopy

Pyrene emission fluoresence spectroscopy was conducted at a pyrene concentration of 10 nM. Solutions were prepared containing pyrene dissolved in: neat methacryllic monomers, common organic solvents, monomer-MeOH mixtures and monomer-IPA mixtures. As in the miscibility studies described above, monomer-alcohol mixtures were prepared at a monomer concentration of 50 wt %. In a typical experiment, an stock solution of pyrene in acetone was added to a glass vial (300 µL, 0.1 mg mL^{-1}). The vial was left in a low velocity fumehood overnight, allowing complete evaporation of acetone, to give a known quantity of solid pyrene (0.03 mg, 1.48 x 10^{-4} mmol). Following addition of the MMA-MeOH mixture (14.8 mL, 50 wt %), the vial was sealed and placed on an orbital mixer to ensure full dissolution of pyrene. The solution (*ca.* 1.00 mL) was added to a quartz cuvette and placed in a Shimadzu RF-5301PC spectrofluorophotometer. A fluorescence emission spectrum was recorded between 350 nm and 500 nm following excitation at 335 nm. The polarity of all pyrene solutions were determined using the I_1/I_3 ratio, by comparison of the relative intensities of the first (I_1, *ca.* 373 nm) and third (I_3, *ca.* 384 nm) vibrational bands of the pyrene fluorescence emission (Figure S2, Table S1).

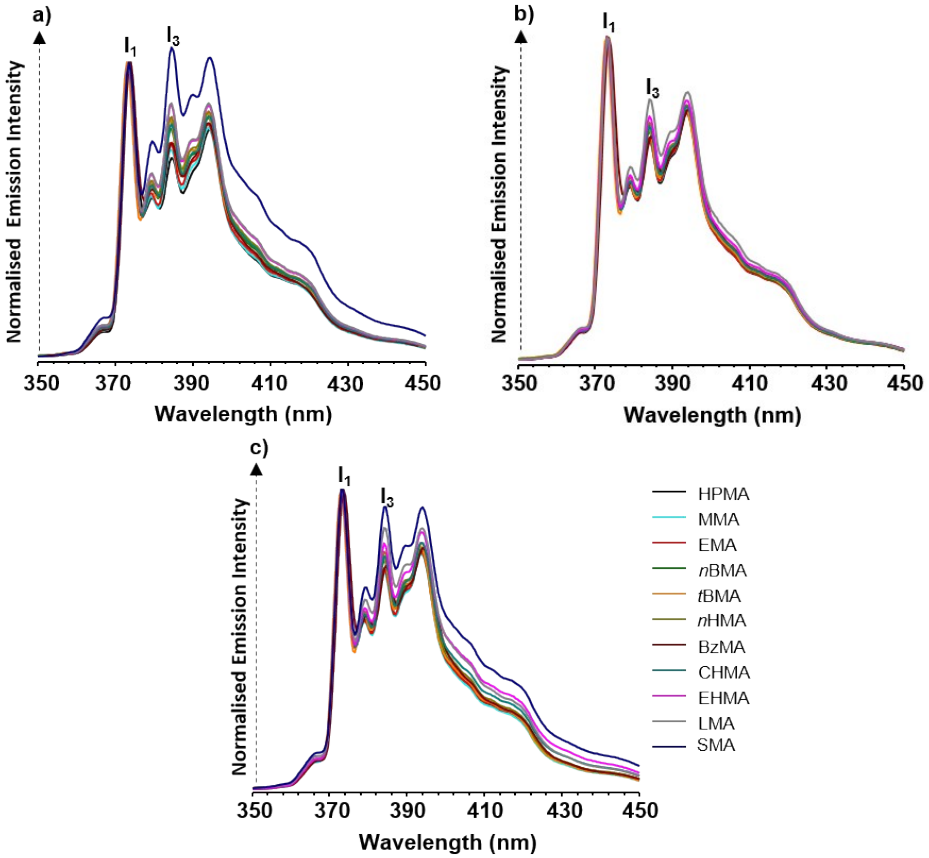


Figure S2 Determination of monomer and monomer-alcohol mixture polarity using fluorescence emission spectroscopy. Overlaid fluorescence emission spectra, normalised with respect to the emission at 373 nm (I_1), obtained from pyrene dissolved within a) neat monomer, b) monomer-MeOH mixtures and c) monomer-IPA mixtures consisting of: HPMA (black), MMA (cyan), EMA (red), *n*BMA (green), tBMA (orange), nHMA (gold), BzMA (maroon), CHMA (teal), EHMA (pink), LMA (grey) and SMA (blue).

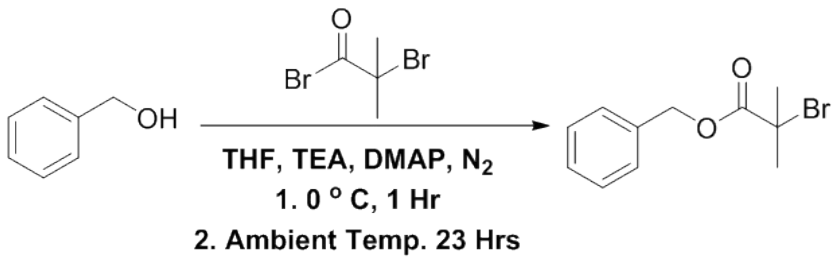
Table S2 I_1/I_3 ratios obtained by fluorescence emission spectroscopy of pyrene dissolved within: neat methacryllic monomers, monomer-MeOH mixtures, monomer-IPA mixtures and common organic solvents.

	Neat Monomer	Monomer-MeOH	Monomer-IPA	Solvent
HPMA	1.48	1.49	1.37	
MMA	1.44	1.49	1.39	
EMA	1.39	1.48	1.37	
*n*BMA	1.30	1.42	1.32	
*t*BMA	1.25	1.41	1.29	
*n*HMA	1.23	1.37	1.27	
BzMA	1.39	1.46	1.35	
CHMA	1.27	1.39	1.29	
EHMA	1.17	1.33	1.22	
LMA	1.16	1.24	1.15	
SMA	0.95	-[a]	1.06	
MeOH				1.53
THF				1.46
Ethanol				1.36
IPA				1.21
Toluene				1.16
Diethyl Ether				1.09

[a] An I_1/I_3 ratio could not be obtained for the SMA-MeOH mixture due to monomer-alcohol immiscibility.

Organic Synthesis

Synthesis of benzyl 2-bromo-2-methylpropanoate



Scheme S1 Synthesis of 2-bromo-2-methylpropanote *via* esterification of benzyl alcohol with α-bromoisobutyryl bromide.

Benzyl alcohol (5.00g, 46.2 mmol), anhydrous TEA (7.02g, 69.4 mmol) and DMAP (0.565g, 4.62mmol) were added to an oven dried round bottomed flask containing a magnetic stirrer bar and was equipped with a pressure equalising dropping funnel. The round bottom flask was purged with nitrogen followed by addition of anhydrous THF (100 mL) and the solution was cooled to 0 °C in an ice bath. α-bromo isobutyryl bromide (13.8 g, 7.43 mL, 60.1 mmol) and anhydrous THF (25.0 mL) were added dropwise over 30 minutes *via* the pressure equalising dropping funnel and the reaction could be observed immediately by the formation of the of a white precipitate. After one hour the ice bath was removed and the reaction was allowed to proceed for a further 23 hours. The precipitate was removed by filtration and the THF was removed *in vacuo*. The product was then extracted using diethyl

ether and dried *in vacuo* to give a colourless oil. The pure product was isolated by silica gel column chromatography using a hexane/ethyl acetate mobile phase (95/5 volume %), Rf = 0.44, giving a colourless oil (71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.40 – 7.30 (m, 5H), 5.21 (s, 2H), 1.95 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.5, 135.4, 128.6, 128.4, 127.9, 67.6, 55.7, 30.8. *m/z* (ES MS) 274.0 $[M+NH_4]^+$ m/z required 256.01 $[M]^+$ $C_{11}H_{13}BrO_2$ requires C, 51.38; H, 5.98; Br, 18.96; O, 15.19 %. Found C, 51.62; H, 5.75 %.

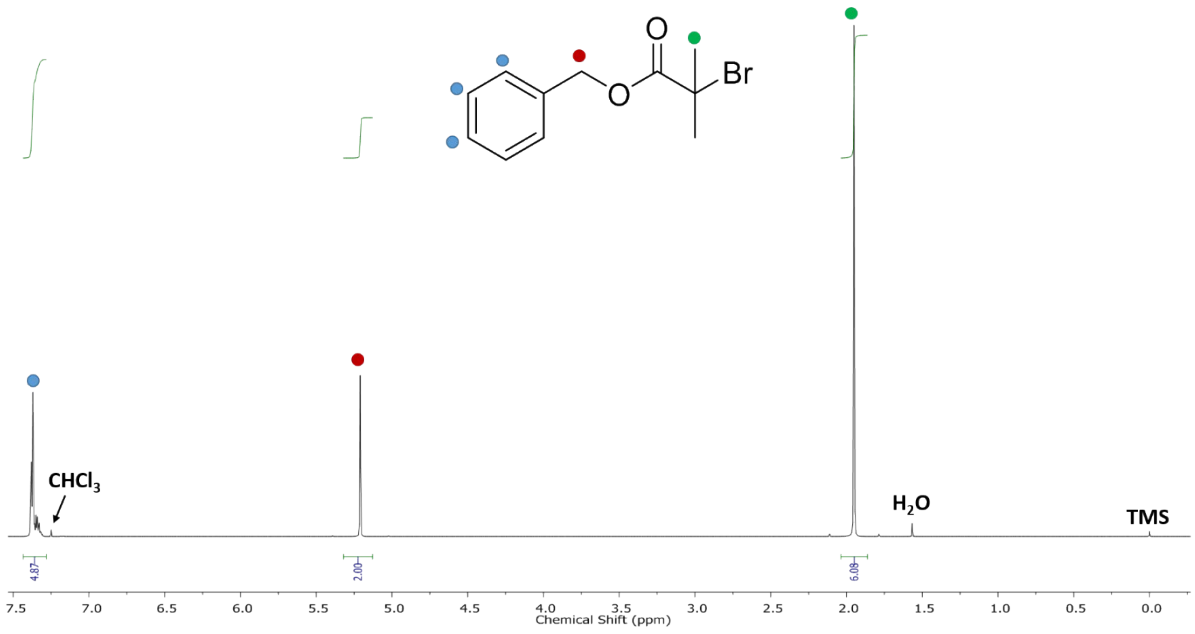


Figure S3 – ^{1}H NMR characterisation of 2-bromo 2-methylpropanoate

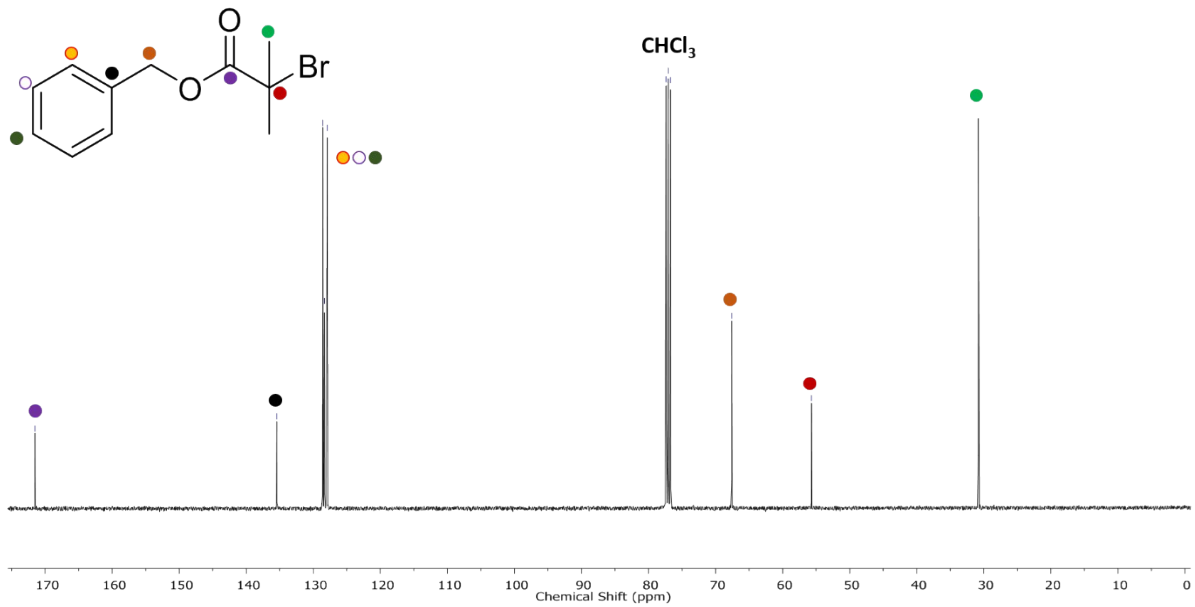


Figure S4 – ^{13}C NMR spectra (100 MHz, $CDCl_3$) obtained for 2-bromo 2-methylpropanoate.

Polymer Synthesis

General procedure for the synthesis of linear homopolymers by Cu-Catalysed RDRP (MMA, EMA, *n*BMA, *t*BMA, nHMA, CHMA, BzMA, EHMA, LMA and SMA)

Prior to use, all monomers and initiators were deoxygenated *via* gentle bubbling with N_2 for 60 minutes. In a typical synthesis of a methacryllic linear homopolymer targeting DP_n = 60 monomer units, *n*HMA (5.00 g, 29.4 mmol), bpy (153 mg, 0.979 mmol) and BzBiB (126 mg, 0.489 mmol) were added to an oven dried round bottom flask (25 mL) equipped with a magnetic stirrer bar. The reaction solvent, either anhydrous MeOH (6.73 mL, 50 wt %) or anhydrous IPA (6.74 mL, 50 wt %), was added and the resulting solution was purged with N_2 for a further 15 minutes. At this point a sample was withdrawn (*ca*. 100 µL) and diluted in $CDCl_3$ allowing quantification of $[M]_0/[I]_0$ by ^1H NMR (Figure S5).

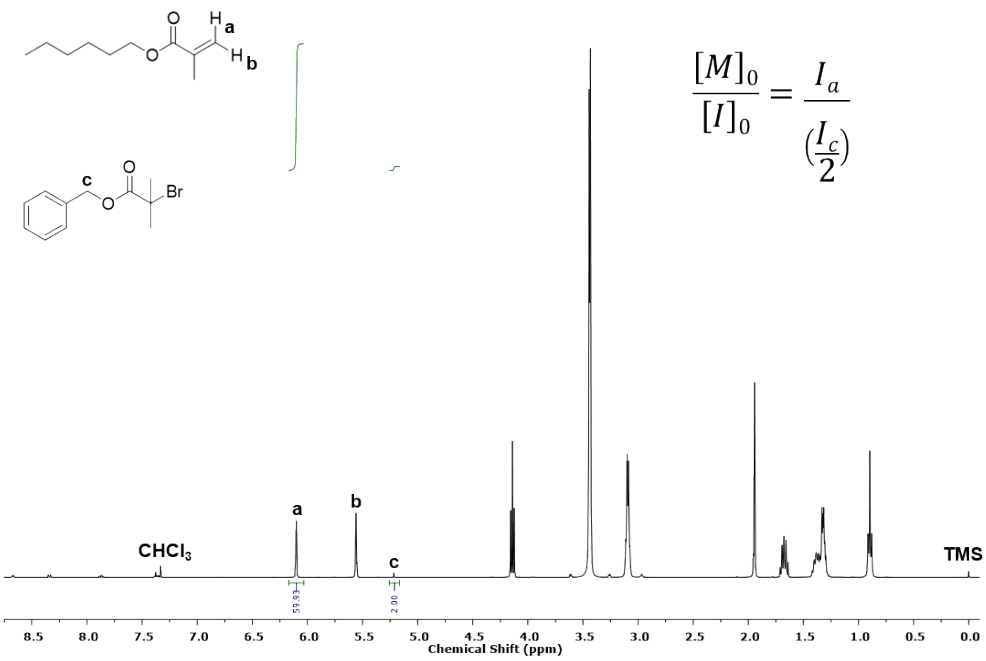


Figure S5 Quantification of $[M]_0/[I]_0$ for the polymerisation of *n*HMA by analysis of the reaction mixture, prior to initiation, using ^1H NMR spectroscopy ($CDCl_3$, 400 MHz).

Cu(I)Cl (48.5 mg, 0.489 mmol) was added rapidly to the flask, instantly forming a brown coloured solution. The reaction was then purged with N_2 for a further 60 seconds, sealed and quickly submerged into an oil bath preheated at 60 ° C. In some cases (MMA, *t*BMA and *n*BMA) the reaction mixture remained homogeneous throughout the reaction and phase separation only occurred on cooling following removal from the oil bath at 60 ° C. In all other cases (*n*HMA, CHMA, EHMA, LMA and SMA) phase separation occurred during the early stages of polymerisation and the reaction proceeded as a biphasic mixture. The reaction was stopped after 24 hours by dilution with $CDCl_3$ until a homogeneous

blue/green solution was obtained, at this point a sample (ca. 500 µL) was taken for quantification of monomer conversion by ^{1}H NMR (Figure S6).

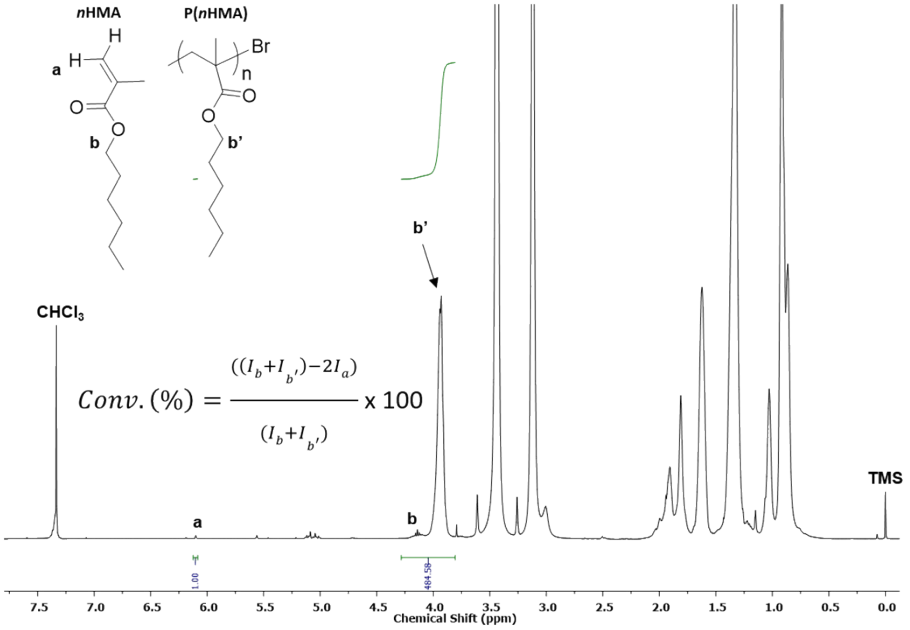


Figure S6 Quantification of the monomer conversion achieved in for the polymerisation of *n*HMA by ^{1}H NMR analysis of the reaction mixture after 18 hours ($CDCl_3$, 400 MHz).

The solution was further diluted in $CHCl_3$, passed over a neutral alumina column to remove the copper catalyst and dried *in vacuo*. The polymer was re-dissolved in a minimum amount of THF and precipitated twice from THF into cold methanol to give p(*n*HMA) as a clear viscous liquid. The polymer was then dried *in vacuo* at 40 ° C for 48 hours and characterised using ^{1}H NMR in $CDCl_3$ (Figure S7) and triple detection SEC using a THF/TEA eluent (98/2 v/v %) using a narrow poly(styrene) standard calibration. (Figure S8).

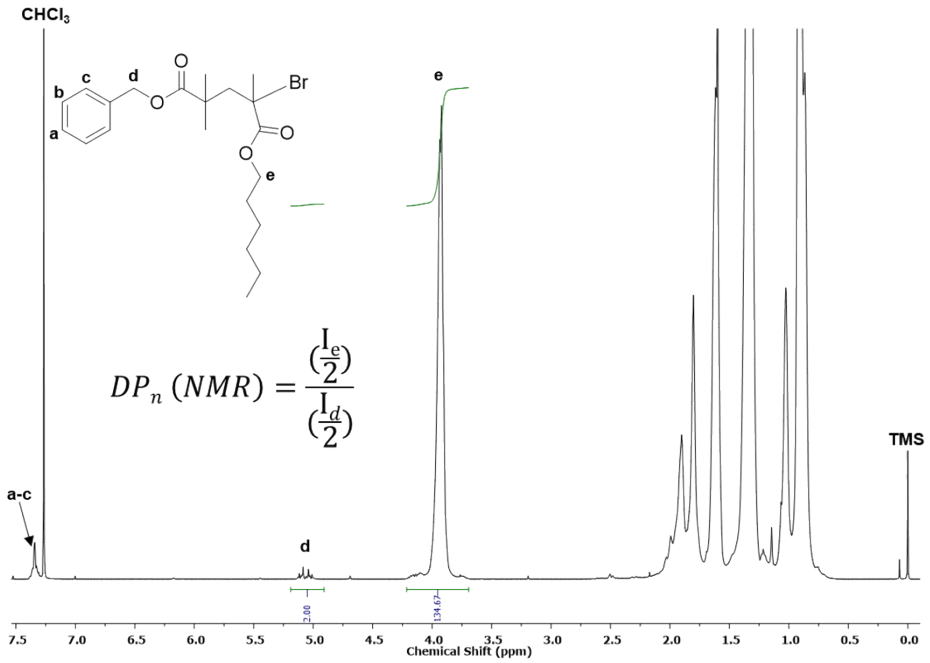


Figure S7 Quantification of the number average degree of polymerisation of p(*n*HMA) by analysis of the purified p(*n*HMA) using ^{1}H NMR spectroscopy ($CDCl_3$, 400 MHz).

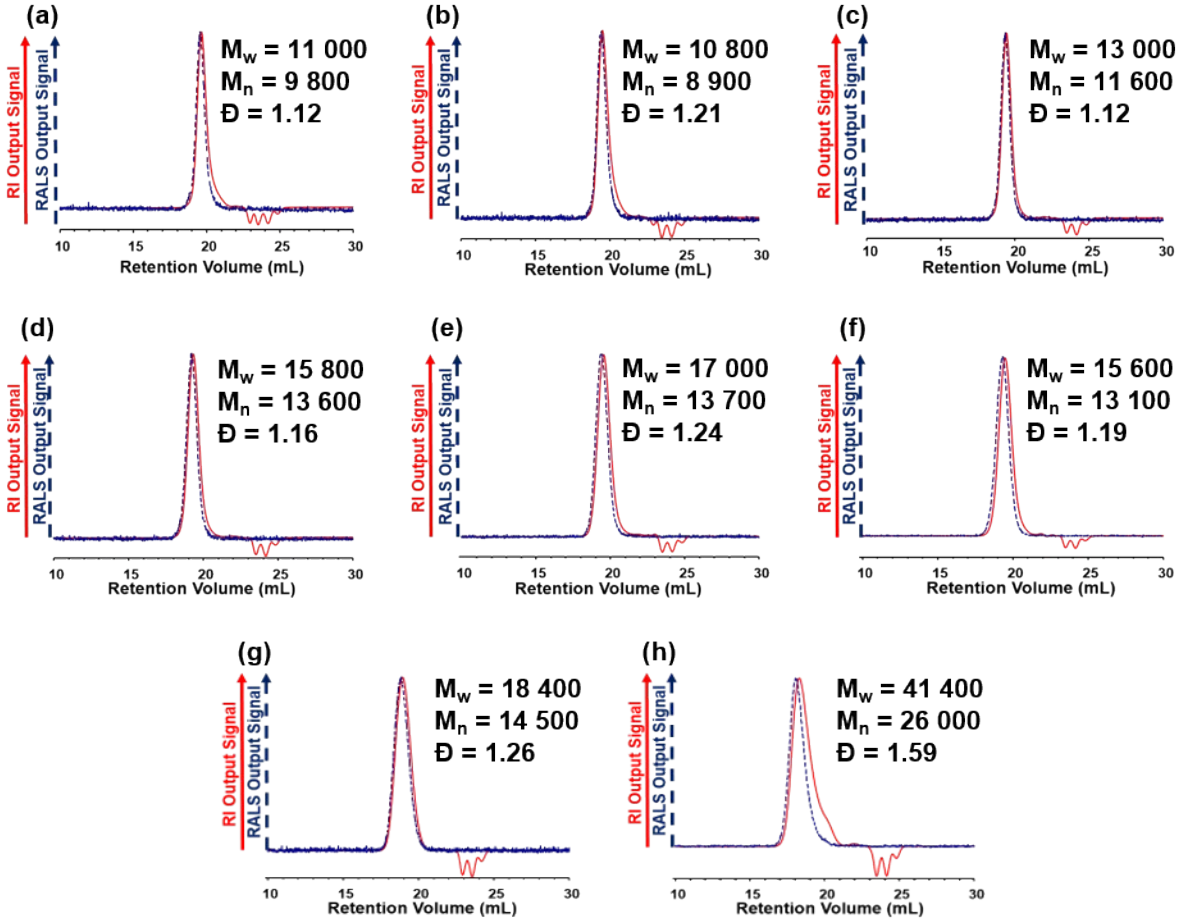


Figure S8 TD-SEC analysis of linear homopolymers generated using Cu-catalysed RDRP at 60 °C in MeOH. Overlaid refractive index (RI, red solid lines) and right-angle light scattering (RALS, blue dotted lines)

chromatograms obtained from (a) p(MMA), (b) p(EMA), (c) p(*n*BMA), (d) p(*n*HMA), (e) p(CHMA) (f) p(BzMA) (g) p(EHMA) and (h) p(LMA).

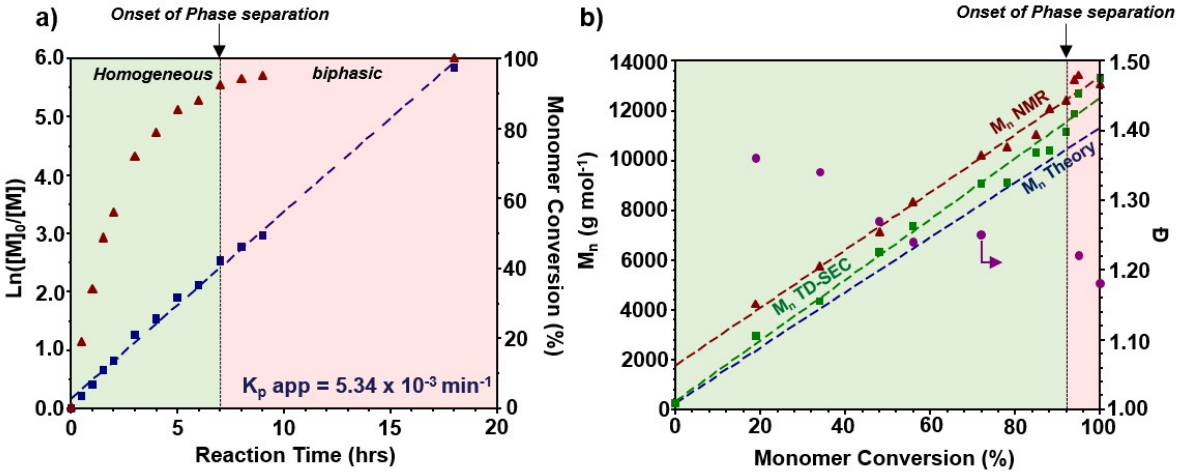


Figure S9 Kinetic studies on the Cu-catalysed RDRP of *n*HMA at 60 °C in anhydrous methanol. a) Monitoring the rate of polymerisation using ^{1}H NMR spectroscopy to construct plots of monomer conversion and semi-logarithmic plots against time. b) Analysis of the evolution of number average molecular weight (M_n) and polymer dispersity (Đ) with monomer conversion.

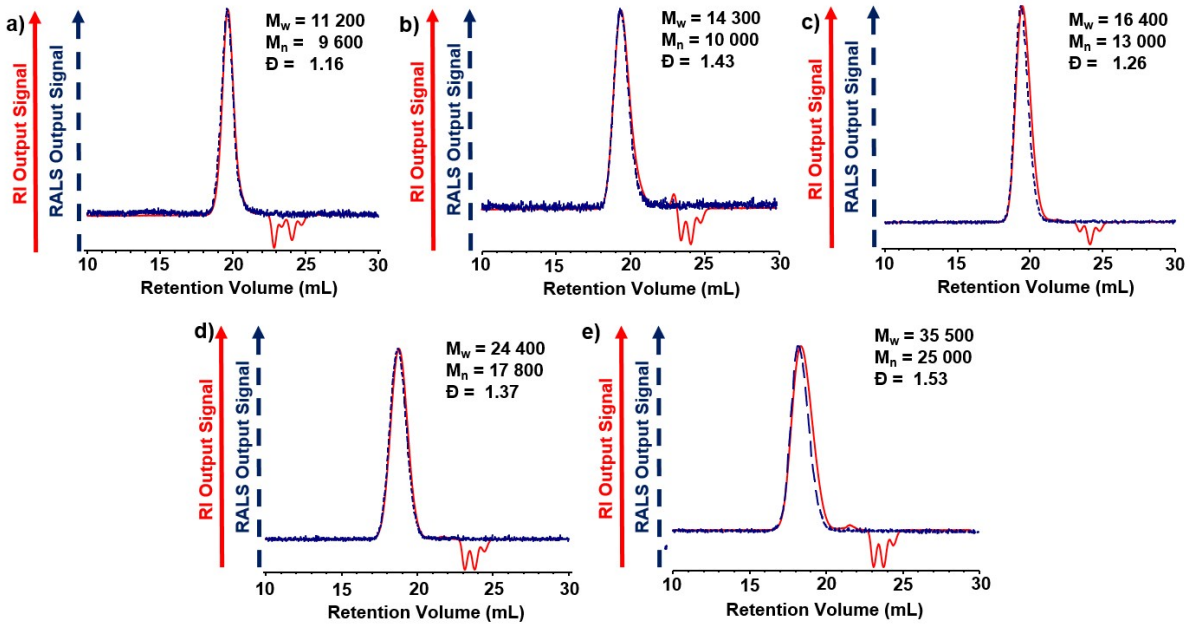


Figure S10 TD-SEC analysis of linear homopolymers generated using Cu-catalysed RDRP at 60 °C in IPA. Overlaid refractive index (RI, red solid lines) and right-angle light scattering (RALS, blue dotted lines) chromatograms obtained from (a) p(MMA), (b) p(*t*BMA), (c) p(CHMA), (d) p(LMA), (e) p(SMA).

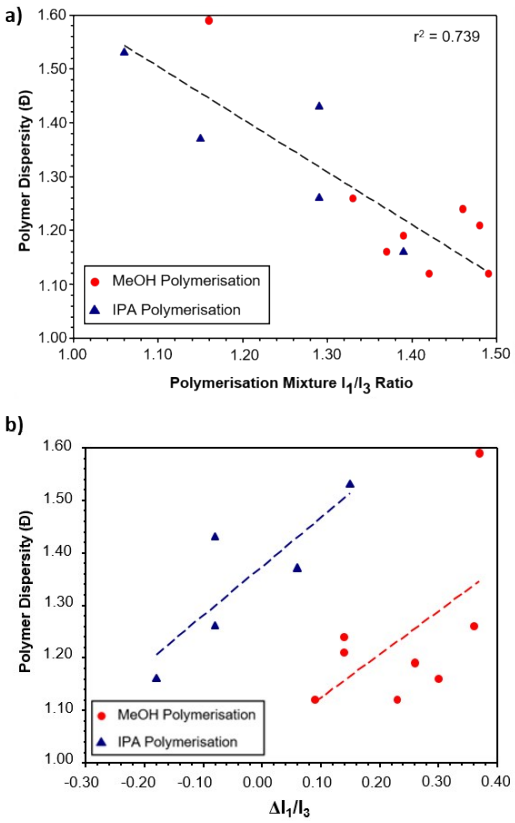
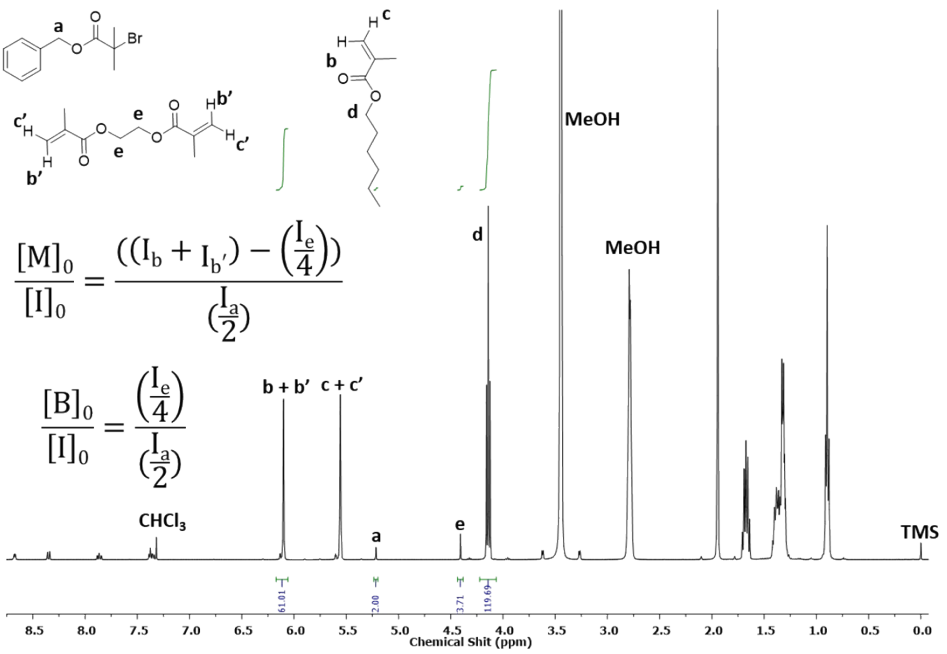


Figure S11 Graphical representation of the relationship between polymerisation mixture polarity and the resulting polymer dispersity. a) Plots of polymer dispersity *vs.* the absolute polarity of monomer-alcohol mixtures. b) Plots showing the net impact of monomer on mixture polarity (*vs*. neat alcohol) against the resulting polymer dispersity.

General procedure for the branched statistical copoylmers by Cu-Catalysed RDRP (MMA, *n*BMA, *t*BMA, nHMA, CHMA, EHMA, LMA and SMA)

In a typical branching statistical copolymerisation of *n*HMA and EGDMA targeting a primary chain DP_n of 60 monomer units and a branching ratio ($[B]_0/[I]_0$) of 0.90, *n*HMA (5.00 g, 29.4 mmol), EGDMA (87.3 mg, 0.441 mmol), bpy (153 mg, 0.978 mmol) and BzBiB (126 mg, 0.489 mmol) were added to an oven dried round bottom flask (25 mL) equipped with a magnetic stirrer bar. The reaction solvent, either anhydrous methanol (6.84 mL, 50 wt %) or anhydrous IPA (6.86 mL, 50 wt %) was added and the resulting solution was purged with N_2 for a further 15 minutes. At this point a sample was withdrawn (*ca.* 100 µL) and diluted in $CDCl_3$ allowing quantification of $[M]_0/[I]_0$ (Figure S5) and $[B]_0/[I]_0$ (Figure S12) by ^{1}H NMR spectroscopy.



$$\frac{[M]_0}{[I]_0} = \frac{((I_b + I_{b'}) - (\frac{I_e}{4}))}{(\frac{I_a}{2})}$$

$$\frac{[B]_0}{[I]_0} = \frac{(\frac{I_e}{4})}{(\frac{I_a}{2})}$$

Figure S12 Quantification of $[B]_0/[I]_0$ for the polymerisation of *n*HMA by analysis of the reaction mixture at t_0 using ^{1}H NMR spectroscopy ($CDCl_3$, 400 MHz).

Cu(I)Cl (48.5 mg, 0.978 mmol) was added rapidly to the flask, instantly forming a brown coloured solution. The reaction was purged with N_2 for a further 60 seconds and quickly submerged into an oil bath preheated at 60 ° C. The reaction was stopped after 24 hours by dilution with $CDCl_3$ until a homogeneous blue/green solution was obtained, at this point a sample (ca. 500 µL) was taken for quantification of monomer conversion by ^{1}H NMR (Figure S6). The solution was further diluted in $CHCl_3$, passed over a neutral alumina column to remove the copper catalyst and dried *in vacuo*. The polymer was re-dissolved in a minimum amount of THF and precipitated twice from THF into cold methanol to give a viscous clear liquid. Polymers were then dried *in vacuo* at 40 ° C for 48 hours and characterised by ^{1}H NMR in $CDCl_3$ (Figure S7) and triple detection SEC using a THF/TEA eluent (98/2 v/v %) using a narrow poly(styrene) standard calibration.

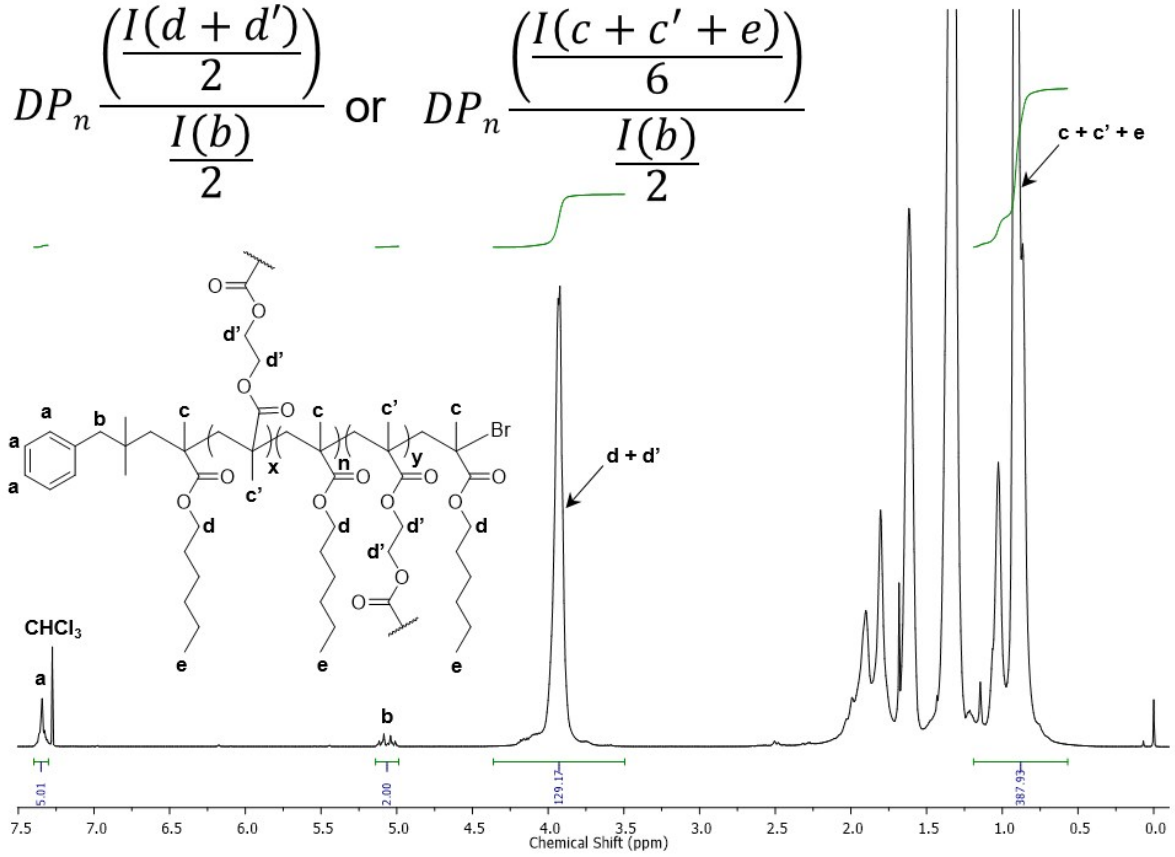


Figure S13 Quantification of the DP_n of the primary chains of which branched statistical copolymers, in this case p(*n*HMA$_{65}$-*co*-EGDMA$_{0.98}$), are constructed. Analyses were conducted *via* ^{1}H NMR spectroscopy of branched copolymers following purification ($CDCl_3$, 400 MHz). The M_n of constituent primary chains (M_n(pc)) were subsequently calculated as M_n(pc) = (DP_n x Mr(monomer)) + Mr (Initiator).

Table S3 Good and bad solvents identified for purification of linear homopolymers and branched statistical copolymers.

Polymer	Polymer Good Solvents	Polymer Bad Solvent(s)
p(MMA)^{B,L}	**Acetone**, THF, DCM	MeOH^c, **MeOH/H$_2$O^{c*}**, Hexane^c
p(EMA)^{B,L}	**Acetone**, THF, DCM	MeOH^c, **MeOH/H$_2$O^{c*}**, Hexane^c
p(*n*BMA)^{B,L}	Acetone, **THF**, DCM	MeOH^c, **MeOH/H$_2$O^{c*}**, Hexane^c
p(*t*BMA)^{B,L}	Acetone, **THF**, DCM	MeOH^c, **MeOH/H$_2$O^{c*}**
p(*n*HMA)^{B,L}	Acetone, **THF**, DCM	**MeOH,**
p(CHMA)^{B,L}	Acetone, **THF**, DCM	**MeOH^c,**
p(BzMA)^{B,L}	Acetone, **THF**, DCM	**MeOH^c,**
p(EHMA)^{B,L}	**THF**, DCM	**MeOH,**
p(LMA)^{B,L}	**THF**, DCM	**MeOH,** IPA
p(SMA)^{B,L}	**THF**, DCM	MeOH, EtOH, IPA, **Acetone**

Solvent used for polymer purification by precipitation highlighted in bold. ^{B} Branched copolymer. ^{L} Linear homopolymer. ^{c} Precipitation conducted in a solid CO_2 ice bath. * Conducted at a MeOH/H_2O composition of 80/20 (v/v %).

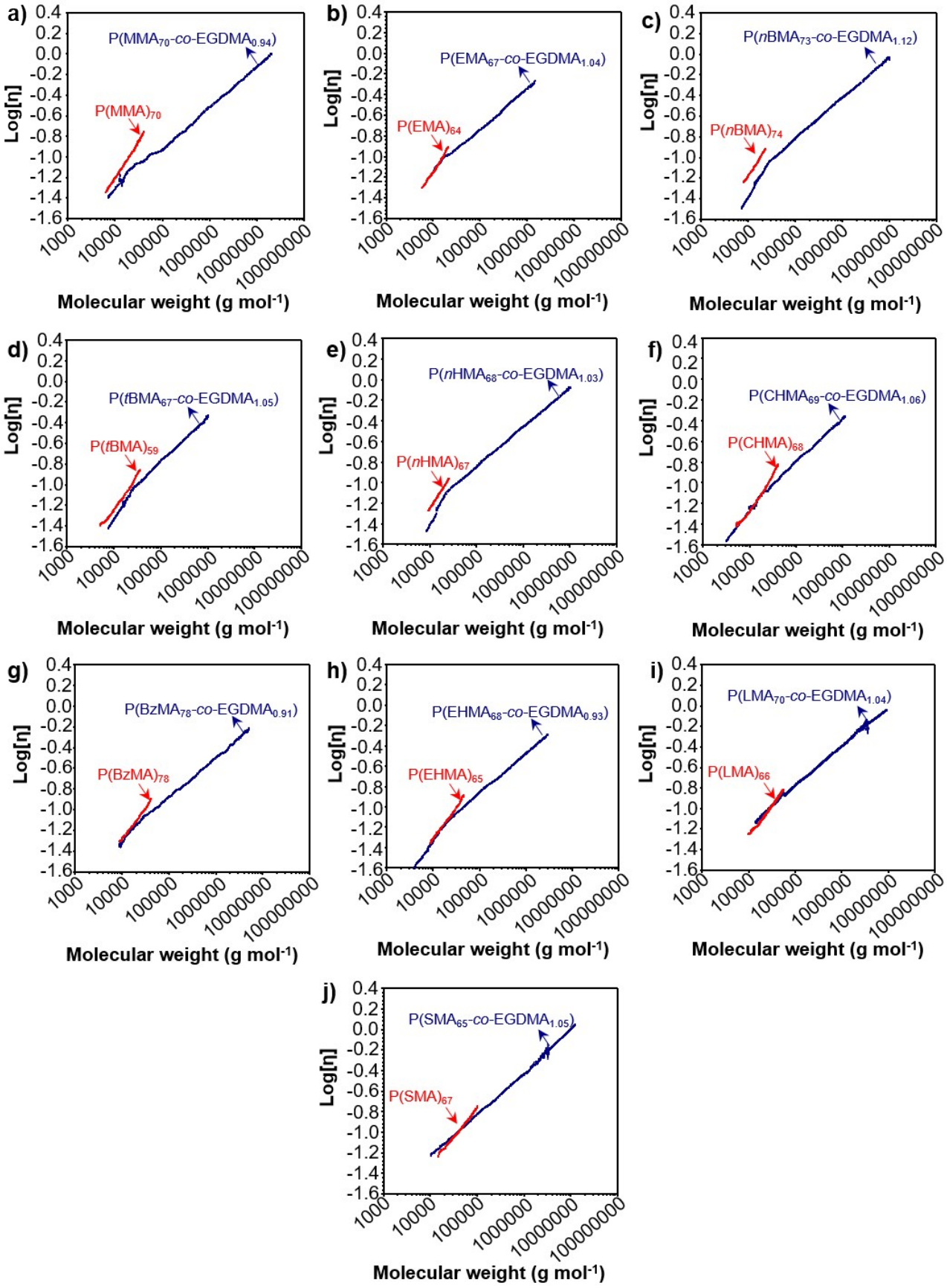


Figure S14 Overlaid Mark-Houwink-Sakurada (MHS) plots obtained for linear homopolymers and branched statistical copolymers consisting of a) p(MMA), b) p(EMA), c) p(*n*BMA), d) p(*t*BMA), e) p(*n*HMA), f) p(CHMA), g) p(BzMA), h) p(EHMA), i) p(LMA), j) p(SMA) produced *via* Cu-catalysed RDRP.

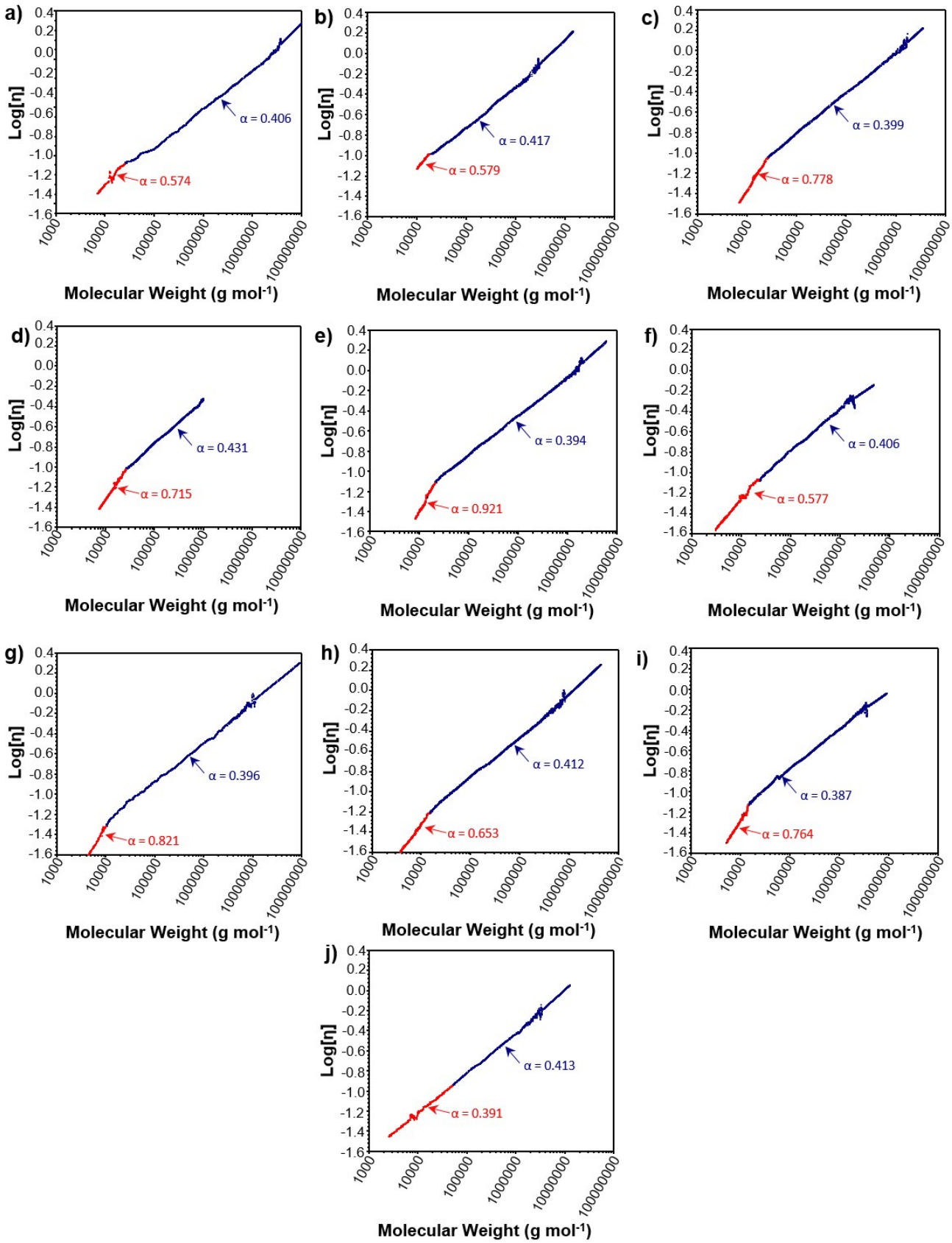


Figure S15 Deconvolution of MHS plots obtained for branched statistical copolymers consisting of a) p(MMA$_{66}$-*co*-EGDMA$_{0.90}$), b) p(EMA$_{66}$-*co*-EGDMA$_{0.90}$), c) p(*n*BMA$_{66}$-*co*-EGDMA$_{0.90}$), d) p(*t*BMA$_{66}$-*co*-EGDMA$_{0.90}$), e) p(*n*HMA$_{66}$-*co*-EGDMA$_{0.90}$), f) p(CHMA$_{66}$-*co*-EGDMA$_{0.90}$), g) p(BzMA$_{66}$-*co*-EGDMA$_{0.90}$), h) p(EHMA$_{66}$-*co*-EGDMA$_{0.90}$), i) p(LMA$_{66}$-*co*-EGDMA$_{0.90}$), j) p(SMA$_{66}$-*co*-EGDMA$_{0.90}$) produced *via* Cu-catalysed RDRP.

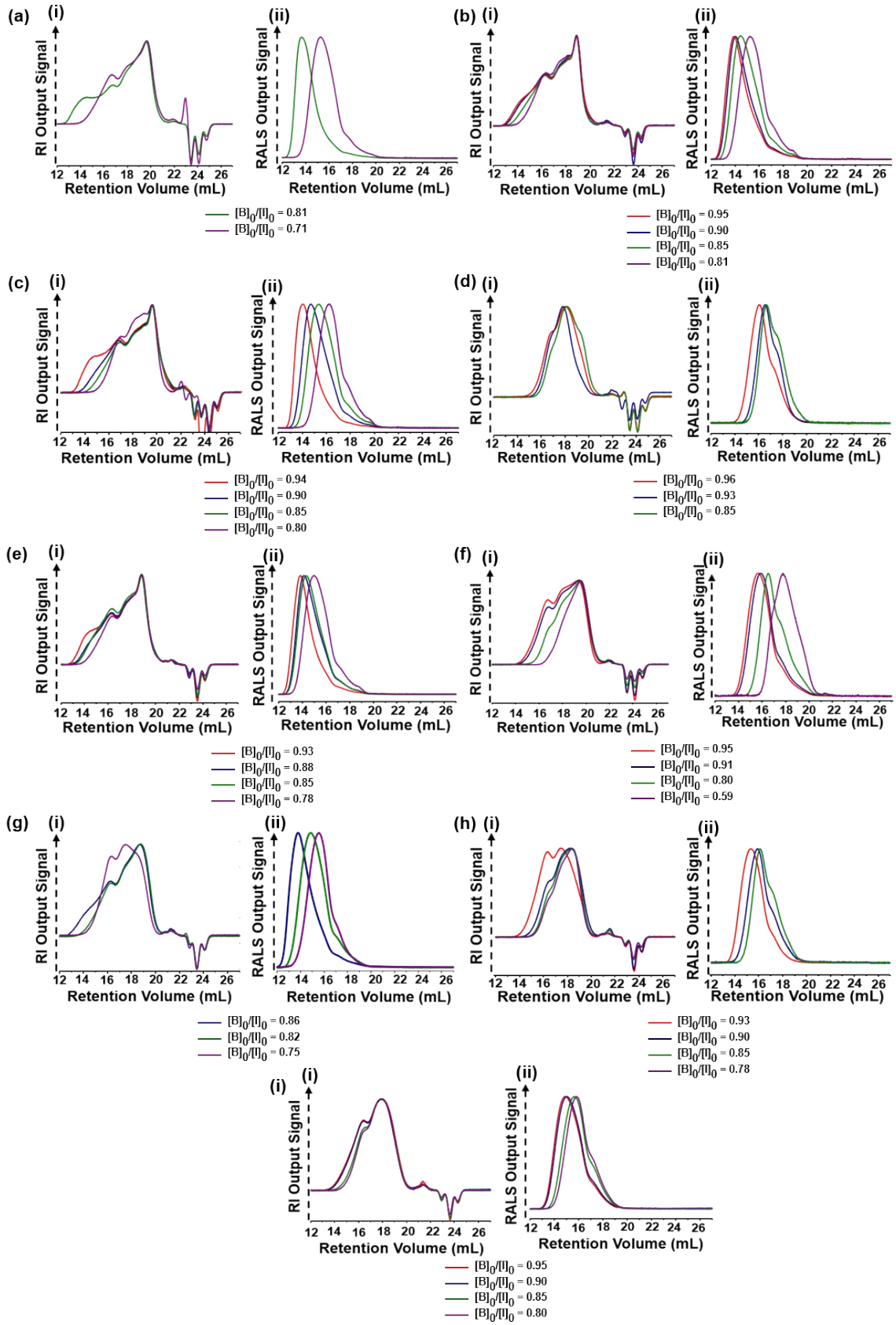


Figure S16 Overlaid (i) RI and (ii) RALS chromatograms for branched copolymers obtained from statistical copolymerisations of EGDMA with (a) MMA, (b) EMA, (c) *n*BMA, (d) *t*BMA, (e) *n*HMA, (f) CHMA, (g) BzMA (h) EHMA, (i) LMA and (j) SMA produced *via* Cu-catalysed RDRP at varied $[B]_0/[I]_0$ ratios.

Analysis of Branched Copolymer Architecture by TD-SEC

Plots of cumulative weight fraction (cum. ω_f) *vs.* number of primary chains per macromolecule were constructed by modification of the cum. ω_f *vs.* molecular weight plots generated *via* TD-SEC. the absolute molecular weights (M) obtained were divided by the M_n of their linear homologues, generated in the absence of EGDMA under identical polymerisation conditions, which provides suitable representation of the primary chains from which the branched copolymers are constructed (Equation S1). For example, the modification of the cum. ω_f *vs.* M plot obtained for *p*(MMA_{70}-*co*-$EGDMA_{0.94}$), calculation of the number of primary chains per macromolecule was achieved by dividing each incremental increase in M by the M_n of $p(MMA)_{67}$ obtained from the homopolymerisation of MMA in anhydrous IPA. Similar modifications were made to generate plots of cumulative mol fraction (X_f) vs. number of pimary chains per macromolecule (Figure S16).

$$Primary\ chains\ per\ macromolecule = \frac{M}{Mn\ (LH)}$$

Equation S1 Calculation of the number of primary chains per macromolecule where M = absolute molecular weight of the species contributing towards the cum. ω_f and M_n (LH) = the number average molecular weight of the linear homopolymer generated in the absence of EGDMA under identical polymerisation conditions.

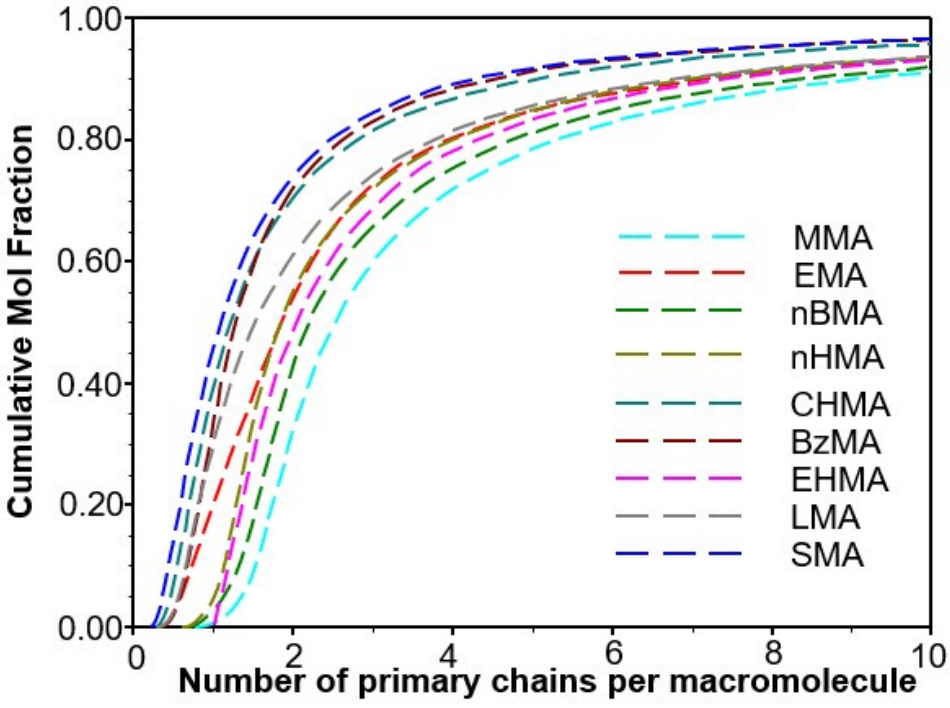


Figure S17 Plots of primary chains per macromolecule *vs.* cumulative mol fraction (cum. x_f) for branched statistical copolymers: a) p(MMA_{66}-*co*-$EGDMA_{0.90}$), b) p(EMA_{66}-*co*-$EGDMA_{0.90}$), c) p(*n*BMA_{66}-*co*-$EGDMA_{0.90}$), d) p(*t*BMA_{66}-*co*-$EGDMA_{0.90}$), e) p(*n*HMA_{66}-*co*-$EGDMA_{0.90}$), f) p($CHMA_{66}$-*co*-$EGDMA_{0.90}$), g) p($BzMA_{66}$-*co*-$EGDMA_{0.90}$), h) p($EHMA_{66}$-*co*-$EGDMA_{0.90}$), i) p(LMA_{66}-*co*-$EGDMA_{0.90}$), j) p(SMA_{66}-*co*-$EGDMA_{0.90}$) produced *via* Cu-catalysed RDRP.

Table S4 Calculation of the differences in initiator ($[I]_0$) and methacrylate group ($[M]_0$) concentrations which arises as a result of the increased contribution of the pendant side group to the overall monomer mass.

			Monomer			Initiator		EGDMA	
Monomer	M_r	Side Chain	Mass (g)	mmol	Volume (mL)	Mass (mg)	mmol	Mass (mg)	mmol
MMA	100	14	1.000	9.99	1.06	42.80	0.166	29.70	0.150
EMA	114	28	1.000	8.76	1.09	37.55	0.146	26.05	0.131
*n*BMA	142	56	1.000	7.03	1.12	30.14	0.117	20.91	0.105
*t*BMA	142	56	1.000	7.03	1.14	30.14	0.117	20.91	0.105
*n*HMA	170	84	1.000	5.87	1.16	25.17	0.098	17.46	0.088
CHMA	168	82	1.000	5.94	1.04	25.47	0.099	17.67	0.089
BzMA	176	90	1.000	5.68	0.96	24.32	0.095	16.87	0.085
EHMA	198	112	1.000	5.04	1.13	21.61	0.084	14.99	0.076
LMA	254	168	1.000	3.93	1.15	16.84	0.066	11.69	0.059
SMA	339	253	1.000	2.95	1.16	12.66	0.049	8.78	0.044

	Solvent				Conc. (mol dm^{-3})		Conc (normalised)	
Monomer	Weight %	Mass (g)	Volume (mL)	Total Volume (mL)	$[I]_0$	$[M]_0$	Initiator	Monomer
MMA	50	1.07	1.35	2.42	0.069	4.131	1.00	1.00
EMA	50	1.06	1.34	2.43	0.060	3.600	0.87	0.87
*n*BMA	50	1.05	1.33	2.44	0.048	2.877	0.70	0.70
*t*BMA	50	1.05	1.33	2.47	0.047	2.847	0.69	0.69
*n*HMA	50	1.04	1.32	2.48	0.040	2.373	0.57	0.57
CHMA	50	1.04	1.32	2.35	0.042	2.525	0.61	0.61
BzMA	50	1.04	1.31	2.28	0.042	2.493	0.60	0.60
EHMA	50	1.04	1.31	2.44	0.034	2.068	0.50	0.50
LMA	50	1.03	1.30	2.45	0.027	1.604	0.39	0.39
SMA	50	1.02	1.29	2.45	0.020	1.207	0.29	0.29

Table S5 Calculation of the differences in initiator ($[I]_0$) and methacrylate group ($[M]_0$) concentrations which arises as a result of the increased contribution of the pendant side group to the overall monomer mass.

	Monomer		Initiator	EGDMA	Solvent		$[I]_0$		$[M]_0$	
Conc. (wt %)	Mass (g)	V (mL)	Mass (mg)	Mass (mg)	Mass (mg)	V (mL)	mmol dm^{-3}	Normalised	mmol dm^{-3}	Normalised
50	1.00	1.06	43	30	1.07	1.35	69	1.00	4131	1.00
40	1.00	1.06	43	30	1.61	2.03	54	0.78	3227	0.78
30	1.00	1.06	43	30	2.50	3.16	39	0.57	2365	0.57
20	1.00	1.06	43	30	4.29	5.42	26	0.37	1541	0.37
10	1.00	1.06	43	30	9.65	12.2	13	0.18	754	0.18
1	1.00	1.06	43	30	106	134	1	0.02	74	0.02

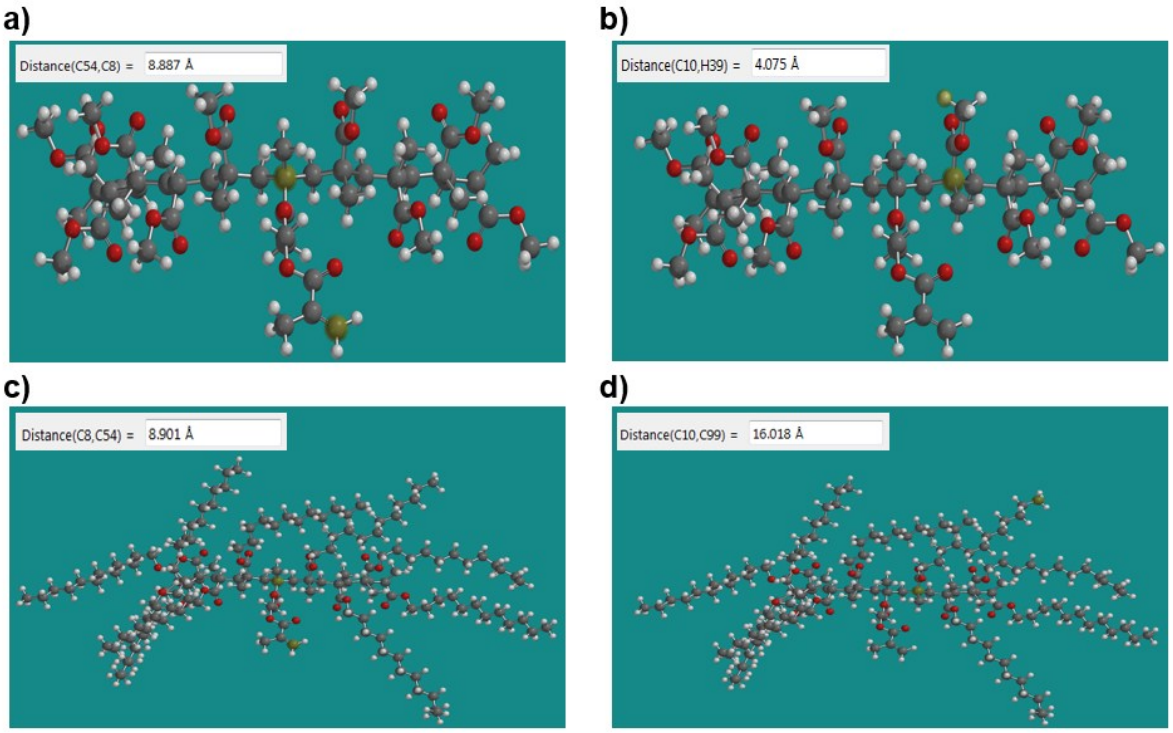


Figure S18 Spartan simulations of pendant group and repeat unit protrusion distances in p(MMA) and p(LMA) oligomers (DP = 10) containing one EGDMA unit per chain. Distances were measured between the polymer backbone and the: a) pendant methacrylate group in p(MMA_{10}-co-$EGDMA_1$), b) pendant CH_3 of a p(MMA) repeat unit, c) pendant methacrylate group in p(LMA_{10}-co-$EGDMA_1$), b) terminal CH_3 of a p(LMA) repeat unit.

Table S6 Calculated pendant group and repeat unit protrusion distances from the methacryllic polymer backbone using Spartan molecular modelling software.

Polymer	Pendant Methacrylate (Å)	Repeat Unit (Å)	Repeat Unit (Å)	Repeat Unit (Å)	Repeat Unit (Å)	Average Repeat Unit (Å)
p(MMA)	8.887	4.071	4.461	4.073	4.462	4.267
p(LMA)	8.901	16.018	16.255	15.056	17.411	16.185