Electronic Supplementary Material (ESI) for Polymer Chemistry.

RAFT Polymerisation of Renewable Terpene (Meth)acrylates and the Convergent Synthesis of Methacrylate-Acrylate-Methacrylate Triblock Copolymers – Electronic Supplementary Information

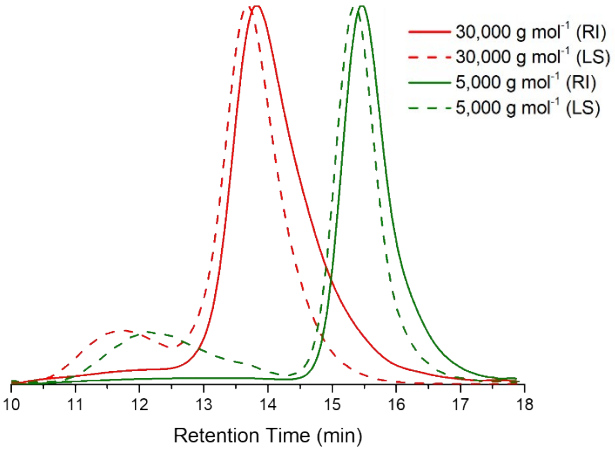

Figure S1: GPC traces for LiMA polymers produced using RAFT polymerisation, targeting 5,000 and 30,000 g mol^{-1}. RI traces are indicated by a solid line, and LS traces by a dashed line.

Table S1: GPC results for the synthesis of PMMA macro-RAFT agents (top) and for each of the diblock copolymers (bottom).

Macro RAFT	Target M_n (g mol^{-1})	Time (h)	Conv.[a] (%)	M_n (th) (g mol^{-1})	M_n[b] (g mol^{-1})	M_w[b] (g mol^{-1})	Đ[b]
PMMA1	30,000	7	50	15,000	16,400	19,500	1.19
PMMA2	40,000	7h30	36	14,400	18,700	23,600	1.27

Macro-RAFT	Monomer	Target M_n B2 (g mol^{-1})	Conv.[a] (%)	M_n (th) (g mol^{-1})	M_n[b] (g mol^{-1})	M_w[b] (g mol^{-1})	Đ[b]
PMMA 1	**αPMA**	16,400	83	30,000	24,000	28,900	1.20
PMMA 1	**αPA**	16,400	76	28,900	19,500*	25,500	1.31
PMMA 2	**βPMA**	18,700	88	35,200	29,200	36,700	1.26
PMMA 2	**βPA**	18,700	75	32,700	19,200*	28,500	1.48
PMMA 2	**LiMA**	18,700	84	34,400	25,200	31,600	1.25
PMMA 2	**LiA**	18,700	65	30,900	23,700	29,400	1.28

[a]Measured by ^{1}H NMR, [b] measured by GPC (RI detector). *Mn values reduced due to presence of low molecular weight tailing. M_n(th) values obtained from the target Mn (block 2) x conversion + measured Mn of macro-RAFT agent. The M_n values for the diblock copolymers are consistently low, despite the low dispersities, which may indicate a systematic issue with the GPC, or that the PMMA macro-RAFT agent measurements were too high.

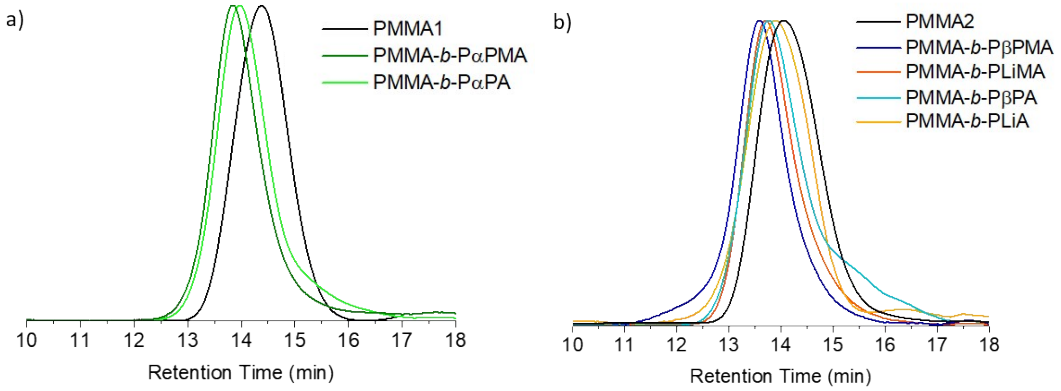

Figure S2: GPC traces showing PMMA macro RAFT agents and subsequent diblock copolymers with (a) PαPMA and PαPA, (b) PβPMA, PβPA, PLiMA and PliA.

Table S2: Table of T_g data for the terpene (meth)acrylate homopolymers from DSC and DMA, with corresponding molecular weights Higher T_g values have generally been observed for the DMA measurements, but at higher molecular weights (e.g. PαPMA above 100,000 g mol^{-1}) this difference appears to be less pronounced.

Polymer	M_n (g mol^{-1})[a] /Đ	T_g (DSC)[b]	M_n (g mol^{-1})[a] /Đ	T_g (DMA)
PαPMA	22,0000 /1.85	142	26,000 /1.45	158
	109,000 /1.95	164*	196,000 /2.18	168
PαPA	23,0000 /2.20	71	46,000 /2.04	84
PβPMA	21,000 /1.53	115	29,000 /1.65	121
PβPA	32,02,000 / 2.06	41	-	-
PLiMA	-	-	29,000 /1.21	51
PLiA	17,000 /2.23	-5	160,000 /3.96	-3

[a]Measured by GPC, [b]DSC results obtained from reference.[5] 0.5 wt% CTA used in each case. *This result was obtained in this work, broad DSC transition observed.

Table S3: Detailed results for the syntheses of monofunctional RAFT agents PαPMA1, PαPMA2, PβPMA1 and PβPMA2, used in the synthesis of diblock copolymers.

Polymer	Monomer	Target M_n (g mol^{-1})	Time (h)	Conv. (%)	M_n(th) (g mol^{-1})	M_n (g mol^{-1})	M_w (g mol^{-1})	Đ**
PαPMA1	αPMA	30,000	5h30*	58	17,400	19,000	24,000	1.26
PαPMA2	αPMA	30,000	2h30*	62	18,600	18,500	23,700	1.28
PβPMA1	βPMA	30,000	6	65	19,500	22,100	17,800	1.26
PβPMA2	βPMA	30,000	4	58	17,400	24,100	27,600	1.15

Molecular weights and dispersities measure using GPC.*PαPMA1 carries out at 65 °C PαPMA2 carrried out at 75 °C leading to a difference in reaction time

**Đ values for PαPMA slightly elevated relative to others due to using RI detector rather than LS for the GPC measurement

Table S4: Results for the initial polymerisations of αPMA using BDAT as a RAFT agent, and results for three repeats targeting molecular weights of 10,000 and 12,000 g mol^{-1}, showing the range of molecular weights obtained.

Entry	Target M_n (g mol^{-1})	Time (h)	Conv.[a] (%)	M_n (th) (g mol^{-1})	M_n[b] (g mol^{-1})	M_w[b] (g mol^{-1})	Đ[b]
1	5,000	26	97	4,900	8,100	12,600	1.55
2	10,000	1h30	58	5,800	20,900	35,700	1.71
3	50,000	2	41	20,500	42,200	70,200	1.66
4	10,000	50min	53	5,300	17,100	27,200	1.58
5	10,000	30	38	3,800	15,600	24,400	1.56
6	12,000	1	49	5,900	18,100	30,000	1.60
7	12,000	1	60	7,200	16,100	25,000	1.55
8	12,000	1	59	7,100	15,300	23,400	1.53

[a]Calculated from ^{1}H NMR measurements, [b]calculated from GPC measurements.

Table S5: Results for the polymerisation of βPMA using BDAT as the RAFT agent.

Entry	Temp (°C)	Target M_n (g mol^{-1})	Time (h)	Conv.[a] (%)	M_n (th) (g mol^{-1})	M_n[b] (g mol^{-1})	M_w[b] (g mol^{-1})	Đ[b]
1	65	10,000	23	74	7,400	24,600	45,400	1.84
2	75	10,000	2	81	8,100	15,800	25,200	1.59
3	75	10,000	1h15	59	5,900	9,000	13,300	1.47
4	75	10,000	1h30	54	5,400	17,100	28,400	1.66
5	75	20,000	1h15	62	12,400	19,000	28,500	1.50

[a]Calculated from ^{1}H NMR measurements, [b]calculated from GPC measurements. *Carried out using the same ratios as seen in the paper by Ma et al.[15]

Table S6: Results for the synthesis of difunctional PαPMA and PαβPMA macro-RAFT agents using BDAT RAFT agent, used in the synthesis of triblock copolymers.

Polymer	Monomer	Target M_n (g mol^{-1})	Time (h)	Conv.[a] (%)	M_n (th) (g mol^{-1})	M_n[b] (g mol^{-1})	M_w[b] (g mol^{-1})	Đ[b]
PαPMA3	αPMA	10,000	50 min	53	5,300	17,100	27,200	1.58
PαPMA4	αPMA	12,000	1	59	7,100	15,300	23,400	1.53
PαPMA5	αPMA	12,000	1	49	5,900	18,100	30,000	1.60
PαPMA6	αPMA	50,000	2	41	20,500	42,200	70,200	1.66
PβPMA3	βPMA	10,000	1h30	54	5,400	17,100	28,400	1.66
PβPMA4	βPMA	10,000	1h15	59	5,900	9,000	13,300	1.47

[a]Calculated from ^{1}H NMR measurements, [b]calculated from GPC measurements.

Table S7: Results for the chain extensions of each of the difunctional macro-RAFT agents with BuA or LiA.

Polymer	Mon.	RAFT Agent	Target M_n (B2) (g mol^{-1})	Time (h)	Conv.[a] (%)	M_n (th) (g mol^{-1})	M_n[b] (g mol^{-1})	M_w[b] (g mol^{-1})	Đ[b]	Wt%[a]	Dn/dc[c]
αBα-74-23	BuA	PαPMA3	59,000	24 h	97	74,300	73,800	96,900	1.31	23	0.0760
αLα	LiA	PαPMA4	30,000	28	63	34,500	45,600	91,400	2.01	47	-
αBα-64-28	BuA	PαPMA5	46,000	24 h	97	62,400	64,400	87,000	1.35	28	0.0780
αBα-60-33	BuA	PαPMA5	37,000	24 h	96	53,200	60,200	79,900	1.34	33	0.0799
αBα-91-42	BuA	PαPMA6	73,000	24 h	76	98,100	91,400	149,700	1.63	42	0.0834
βBβ-67-25	BuA	PβPMA3	50,000	72	96	65,100	66,800	92,400	1.38	25*	0.0770
βBβ-46-23	BuA	PβPMA4	30,000	28	98	38,400	46,100	66,200	1.44	23*	0.0762
βLβ	LiA	PβPMA3	30,000	28	67	29,100	21,200*	67,800*	3.21	31*	-

[a]Calculated from ^{1}H NMR measurements, [b]calculated from GPC measurements, [c]calculated from the molar fractions of each block and homopolymer dn/dc values using Equation 2.1.

*Wt% estimated from the theoretical molecular weight, due to some overlap of the PβPMA and PLiA/PBuA polymer peaks in the ^{1}H NMR spectrum.

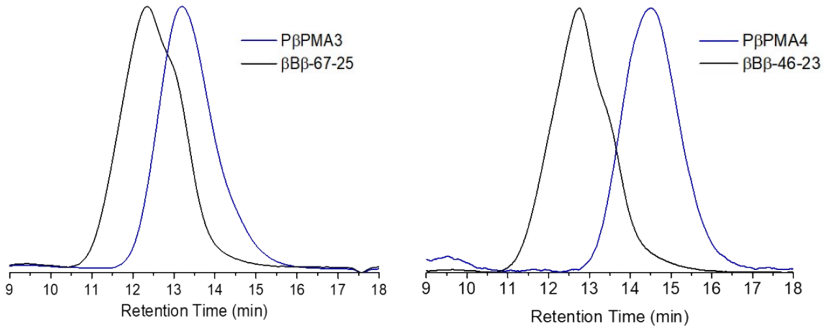

Figure S3: GPC traces for each of the PβPMA-*b*-PBuA-*b*-PβPMA triblock copolymers and their corresponding macro-RAFT agents.

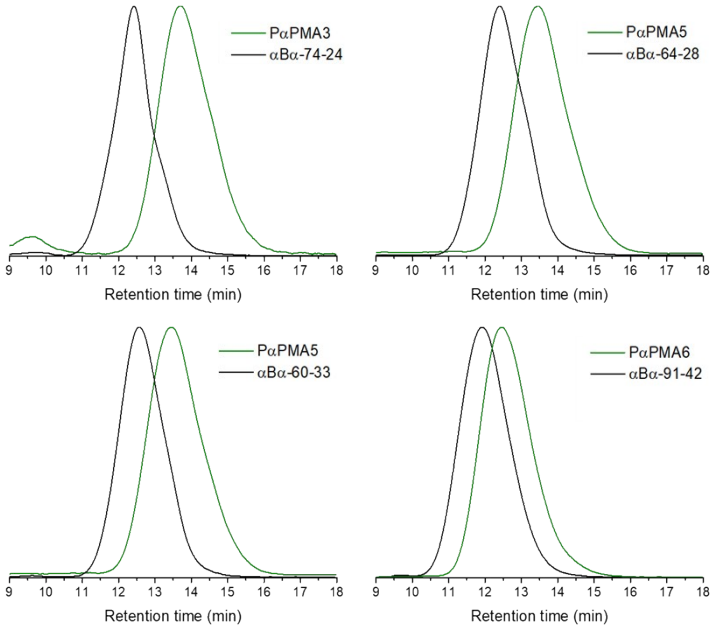

Figure S4: GPC traces for each of the PαPMA-*b*-PBuA-*b*-PαPMA triblock copolymers and their corresponding macro-RAFT agents.

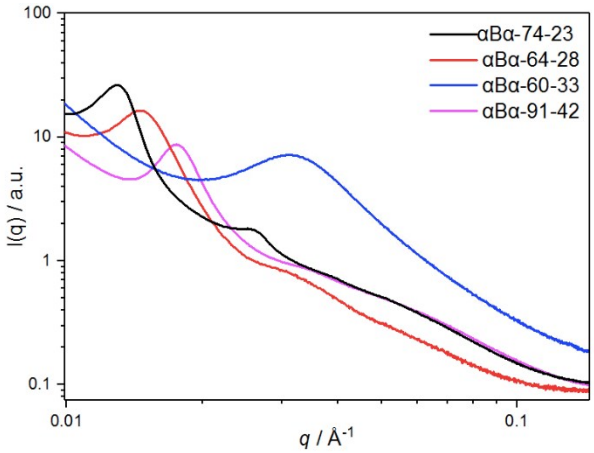

Figure S5: 1D radially integrated SAXS profiles of triblock copolymers αBα-[74-23 (black), 64-28 (red), 60-33 (blue) & 91-42 (magenta)].

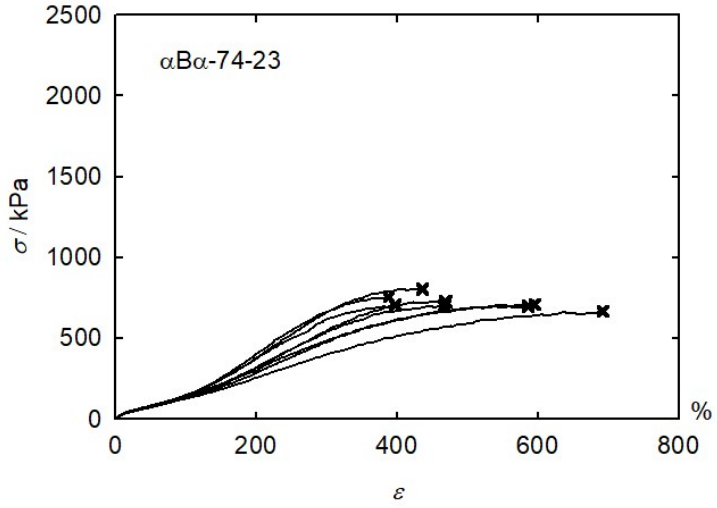

Figure S6: Repeat measurements for the tensile testing of αBα-74-23.

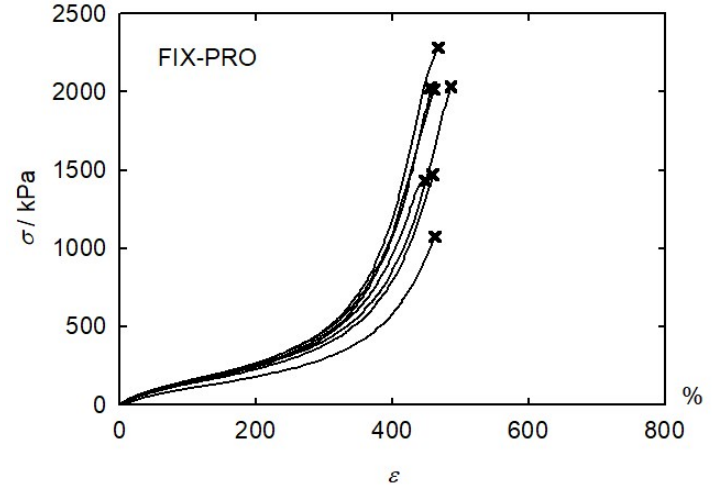

Figure S7: Repeat measurements for the tensile testing of FIX-PRO**.**