Supplementary Information (SI) for Polymer Chemistry.

Investigating the solubility of new branched polymers and copolymers synthesised using transfer-dominated branching radical telomerisation (TBRT) of dimethacrylates.

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Materials

1-dodecanethiol (DDT, >98%), 1- thioglycerol (TG, >98%), 2,2'-azobis(2-methylpropionitrile) (AIBN, 98%), 2-N-morpholinoethyl methacrylate (MEMA, 95%), 4-tert-butylbenzyl mercaptan (*t*BuBzM, >90%), acetone-d_6 ($(CD_3)_2CO$, 99.9%), bisphenol A dimethacrylate (BPADMA, >98 %), deuterated chloroform ($CDCl_3$, 99.8 atom% D), deuterated dichloromethane (CD_2Cl_2, 99.5 atom% D), dichloromethane (DCM, anhydrous), dimethyl-sulfoxide-d_6 (d-DMSO), methanol-d_4 (CD_3OD, >99%), triethylamine (TEA, anhydrous, 99.5 %), and 4-methoxyphenol (MeHQ, 99%) were purchased from Sigma Aldrich. Glycerol dimethacrylate (GDMA, >90.0%), glycidyl methacrylate (GlyMA, > 95 %, 100 ppm MEHQ), and isobornyl methacrylate (IBOMA, >85.0%) were purchased from Tokyo Chemical Industry UK Ltd. Acetone (analytical grade), ethyl acetate (EtOAc, analytical grade), dichloromethane (analytical grade), diethyl ether (HPLC-grade), dimethylformamide (HPLC-grade), n-hexane (HPLC-grade), methanol (MeOH, analytical grade), N.N- petroleum ether (Pet. Ether, analytical grade), propanol-2-ol (IPA, analytical grade), tetrahydrofuran (THF, HPLC-grade), magnesium sulfate, toluene (reagent grade), and xylene (HPLC-grade) were purchased from Fischer. All materials were used as received unless otherwise stated.

Characterisation

Nuclear magnetic resonance (NMR) spectroscopy

^1H and quantified ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer (^1H 400 MHz; ^{13}C 100 MHz). For photosensitive compounds, including those containing photoinitiator moieties, spectra were acquired on a Bruker AMX500 spectrometer (^1H 500 MHz; ^{13}C 126 MHz), with samples prepared in amberised NMR tubes to minimise light exposure. Samples were measured at room temperature in deuterated solvents as specified, including chloroform-d ($CDCl_3$), dichloromethane-d_2 (CD_2Cl_2), methanol-d_4 (CD3OD), acetone-d_6 ($(CD_3)_2CO$), and dimethyl sulfoxide-d_6 ($(CD_3)_2SO$). Chemical shifts (δ) are reported in parts per million (ppm) relative to the known signal. Samples were prepared at polymer concentrations of 10 mg mL^{-1} and 75 mg mL^{-1} for ^1H and ^{13}C experiments, respectively.

Triple-detection size exclusion chromatography (TD-SEC)

TD-SEC analysis of branched TBRT homo- and copolymers was performed using an Agilent 1260 Infinity II instrument equipped with an autosampler, two Agilent PLgel 10 µm mixed bed columns (and a guard column), coupled to a multi-detector suite, equipped with a dual angle light scattering detector (90:15), refractive index (RI) detector and viscometer. Two different mobile phase systems were used as specified: the primary method employed a 0.5% v/v TEA in THF operating at 40 °C with a flow rate of 1 mL min^{-1}. For select copolymers requiring higher solubility, N,N-dimethylformamide (DMF) was used as an alternative mobile phase with a system calibration against narrow and broad poly(methyl methacrylate) standards.

All polymer samples were prepared at a concentration of 5 mg mL^{-1} and filtered through a 0.2 µm PTFE syringe filter before injection (100 µL). From the resulting TD-SEC data, number-average molecular weight (M_n), weight-average molecular weight (M_w), dispersity ($Đ$), refractive index increment (dn/dc), and Mark-Houwink parameters (α) were determined. Data analysis was performed using Agilent GPC/SEC software, with method validation using polystyrene standards at 2 mg mL^{-1} (narrow PS standard: M_p: 87,200 g mol^{-1}, dn/dc: 0.185 mL g^{-1}, $[\eta]$: 0.3778 dL g^{-1}).

Synthesis of glycerol methacrylate (GMA)

Glycidyl methacrylate (20.00 g, 0.14 mol), and 4-methoxyphenol (0.25g, 0.0014 mol), were dissolved in 200 mL of distilled water in a round bottom flask fitted with a magnetic stirrer bar and an air condenser. The reaction flask was heated to 80 °C with stirring. After approximately 6 hours of stirring, the reaction mixture transitioned from turbid to clear, indicating complete hydrolysis. The crude product was extracted with diethyl ether (1× 250mL) to remove un-reacted glycidyl methacrylate. Sodium Chloride was added until saturation. Glycerol methacrylate was extracted using diethyl ether (3 × 250mL). Combined organic extracts were dried with MgSO4 and diethyl ether was removed by rotary evaporation to give GMA as a viscous colourless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.10 (s, 1H), 5.51 (s, 1H), 4.15 (m, 2H), 3.87 (m, 1H), 3.54 (m, 1H), 1.84 (s, 3H).

General procedure for the homopolymerisation of GDMA with DDT

In a typical TBRT experiment targeting a $[GDMA]_0/[DDT]_0$ ratio of 0.60:1.00, GDMA (3.00 g, 13.14 mmol, 0.60 equiv), DDT (4.43 g, 21.9 mmol, 1.00 equiv), AIBN (0.06 g, 0.39 mmol, 1.5 mol% versus vinyl bonds) and ethyl acetate (7.50 g, 85.1 mmol, 50 wt%) were loaded into a 50 mL round-bottomed flask equipped with a magnetic stirrer bar. The solution was homogenised by agitation and a sample was extracted for ^{1}H NMR spectroscopic analysis prior to initiation to determine accurate starting ratios. The solution was deoxygenated whilst stirring for 20 minutes using a nitrogen purge. The solution was then heated to 70 °C with stirring and the reaction allowed to proceed for 24 hours under a nitrogen atmosphere. The reaction was ceased by exposure to air and cooling to ambient temperature. A sample of the crude reaction mixture was extracted for ^{1}H NMR spectroscopic analysis. The remaining sample was diluted with ethyl acetate (< 10 mL) to reduce the viscosity, and precipitated into methanol (10× v/v excess) at ambient temperature, affording a white precipitate and cloudy dispersion. The precipitate was washed further with fresh methanol (3 × 50 mL) and subsequently dried *in vacuo* overnight at 40 °C. Finally, samples of the purified polymer were taken for ^{1}H NMR and TD-SEC analysis.

General polymerisation of copolymerisation of BPADMA and IBOMA with *t*BuBzM,

In a typical TBRT experiment targeting a $[BPADMA]_0/[IBOMA]_0/[t\text{BuBzM}]_0$ ratio of 0.43:0.43:1.00, BPADMA (1.00 g, 2.74 mmol, 0.425 equiv), IBOMA (0.61 g, 2.74 mmol, 0.425 equiv), *t*BuBzM (1.16 g, 6.46 mmol, 1.00 equiv), AIBN (0.02 g, 0.13 mmol, 1.5 mol% versus vinyl bonds) and toluene (2.80 g, 30.3 mmol, 50 wt%) were loaded into a 25 mL round-bottomed flask equipped with a magnetic stirrer bar. The solution was homogenised by agitation and a sample was extracted for ^{1}H NMR spectroscopic analysis prior to initiation to determine accurate starting ratios. The solution was deoxygenated whilst stirring for 20 minutes using a nitrogen purge. The solution was then heated to 90 °C with stirring and the reaction allowed to proceed for 24 hours under a nitrogen atmosphere. The reaction was ceased by exposure to air and cooling to ambient temperature. A sample of the crude reaction mixture was extracted for ^{1}H NMR spectroscopic analysis. The remaining sample was diluted with toluene (< 5 mL) to reduce the viscosity, and precipitated into methanol (10× v/v excess) at ambient temperature, affording a white precipitate and cloudy dispersion. The precipitate was washed further with fresh methanol (3 × 50 mL) and subsequently dried *in vacuo* overnight at 40 °C. Finally, samples of the purified polymer were taken for ^{1}H NMR and TD-SEC analysis.

Polymerisations were conducted according to general procedures applicable across all TBRT homo- and copolymers, with specific reaction parameters adjusted based on the desired polymer architecture and functionality. Table S1 summarises the solvent systems, reaction temperatures, and antisolvents used for each target polymer within the TBRT homo-and copolymer library.

Table S1 Reaction conditions and precipitation antisolvents used to synthesise the TBRT homo-and copolymer library used within this study

Polymer	Reaction Solvent	Reaction Temperature (°C)	Solids Content (wt%)	Antisolvent
Homopolymers				
p(DDT-GDMA)	Ethyl acetate	70	50	Methanol
p(*t*BuBzM-GDMA*)*	Ethyl acetate	70	50	Petroleum Ether
p(TG-GDMA)	Ethanol	70	50	50:50 Petroleum Ether: Isopropanol
p(DDT-BPADMA)	Toluene	90	50	Methanol
p(*t*BuBzM-BPADMA*)*	Toluene	90	50	Methanol
p(TG-BPADMA)	Ethyl acetate	70	25	50:50 Petroleum Ether:Isopropanol
Statistical Copolymers				
p([DDT-GDMA]-*stat*-GMA)	Ethanol	70	50	Petroleum Ether
p([*t*BuBzM-GDMA]-*stat*-GMA)	Ethanol	70	50	Petroleum Ether
p([TG-GDMA]-*stat*-GMA)	Ethanol	70	50	Ethyl acetate
p([DDT-GDMA]-*stat*-GlyMA)	Ethyl acetate	70	50	Petroleum Ether
p([*t*BuBzM-GDMA]-*stat*-GlyMA)	Ethyl acetate	70	50	Petroleum Ether
p([TG-GDMA]-*stat*-GlyMA)	Ethanol	70	50	Ethyl acetate
p([DDT-GDMA]-*stat*-IBOMA)	Ethyl acetate	70	50	Methanol
p([*t*BuBzM-GDMA]-*stat*-IBOMA)	Ethyl acetate	70	50	Methanol
p([TG-GDMA]-*stat*-IBOMA)	Ethanol	70	50	50:50 Petroleum Ether:Isopropanol
p([DDT-GDMA]-*stat*-MEMA)	Ethyl acetate	70	50	Petroleum Ether
p([*t*BuBzM-GDMA]-*stat*-MEMA)	Ethyl acetate	70	50	Petroleum Ether
p([TG-GDMA]-*stat*-MEMA)	Ethanol	70	50	50:50 Petroleum Ether:Isopropanol
p([DDT-BPADMA]-*stat*-GMA)	Ethyl acetate	70	50	Methanol
p([*t*BuBzM-BPADMA]-*stat*-GMA)	Ethyl acetate	70	50	Methanol
p([TG-BPADMA]-*stat*-GMA)	Butyl acetate	90	25	50:50 Petroleum Ether:Isopropanol
p([DDT-BPADMA]-*stat*-GlyMA)	Ethyl acetate	70	50	Methanol
p([*t*BuBzM-BPADMA]-*stat*-GlyMA)	Toluene	90	50	Methanol
p([TG-BPADMA]-*stat*-GlyMA)	Ethyl acetate	70	25	50:50 Petroleum Ether:Isopropanol
p([DDT-BPADMA]-*stat*-IBOMA)	Toluene	90	50	Methanol
p([*t*BuBzM-BPADMA]-*stat*-IBOMA)	Toluene	90	50	Methanol
p([TG-BPADMA]-*stat*-IBOMA)	Ethyl acetate	70	25	50:50 Petroleum Ether:Isopropanol
p([DDT-BPADMA]-*stat*-MEMA)	Toluene	90	50	Methanol
p([*t*BuBzM-BPADMA]-*stat*-MEMA)	Toluene	90	50	Methanol
p([TG-BPADMA]-*stat*-MEMA)	Ethyl acetate	70	25	50:50 Petroleum Ether:Isopropanol

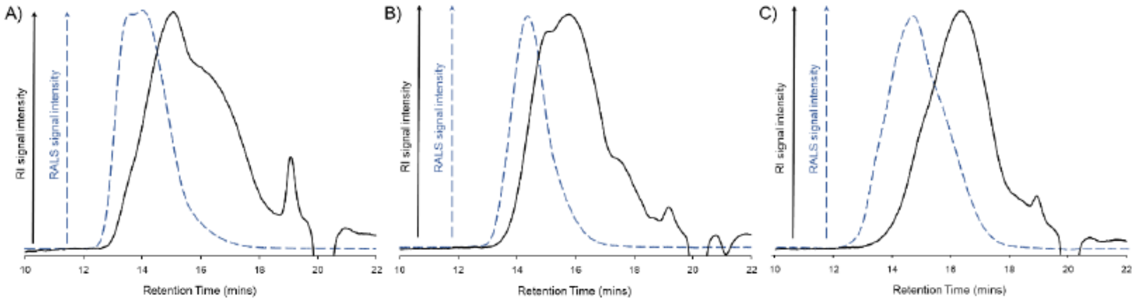


Figure S1 Examples of TD-SEC analysis of homopolymers and statistical copolymer samples synthesised during this study. A) Homopolymer p(DDT-GDMA); B) Homopolymer p(TG-GDMA); and C) Statistical copolymer *p*([DDT-GDMA]-*stat*-GlyMA). Solid black lines indicate RI signal; Dotted blue lines indicate RALS signal (THF eluent with a 0.5% v/v TEA) .

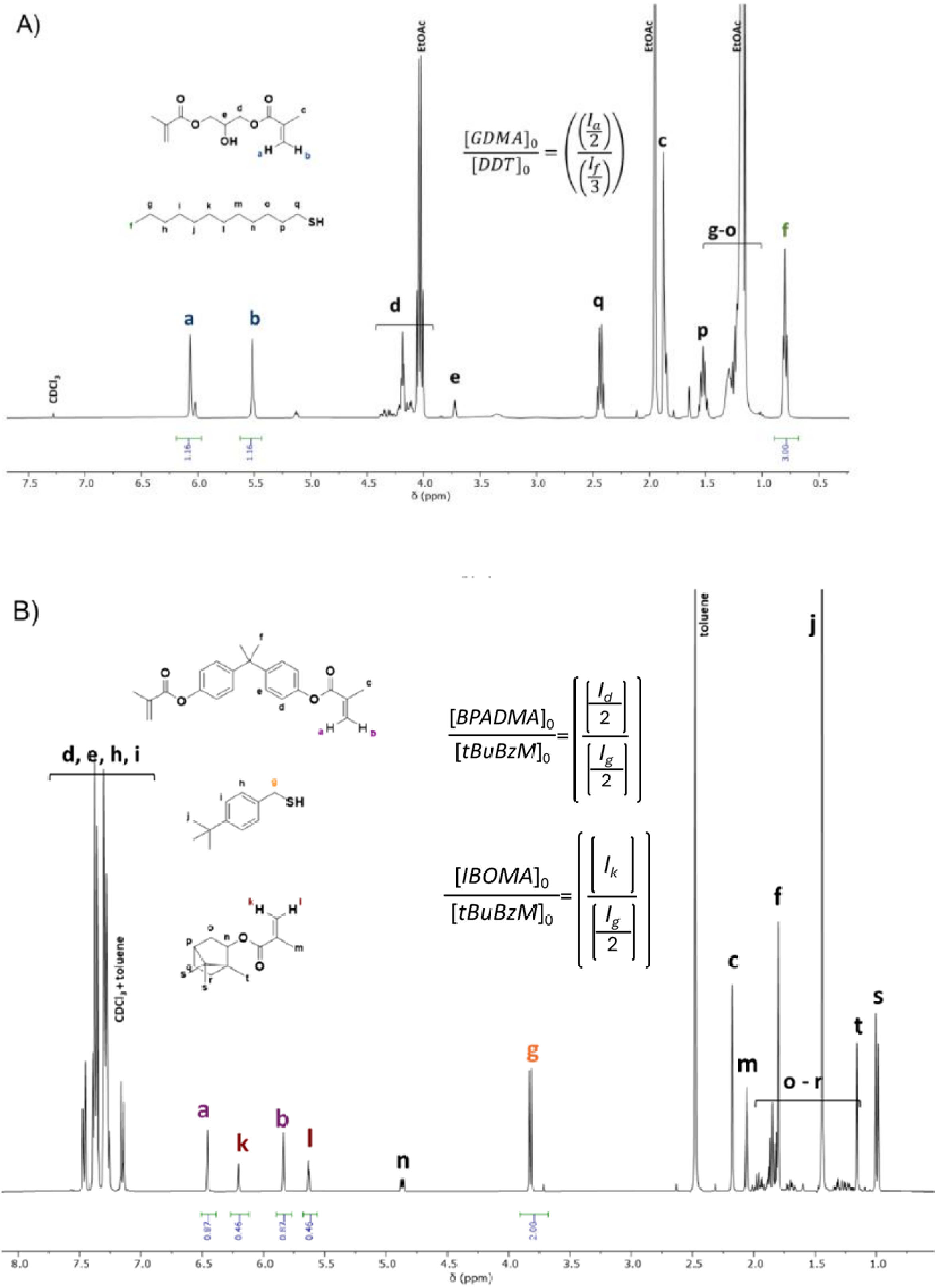


Figure S2 Examples of typical ^{1}H NMR (400 MHz, CDCl$_3$) spectra used to obtain accurate multi-vinyl taxogen/mono-vinyl taxogen/telogen ratios prior to thermal initiation (t = 0). A) Reaction mixture sample utilised for the homopolymerisation of *p*(DDT-GDMA), and B) Reaction mixture sample utilised for the copolymerisation of *p*([*t*BuBzM-BPADMA]-*stat*-IBOMA).

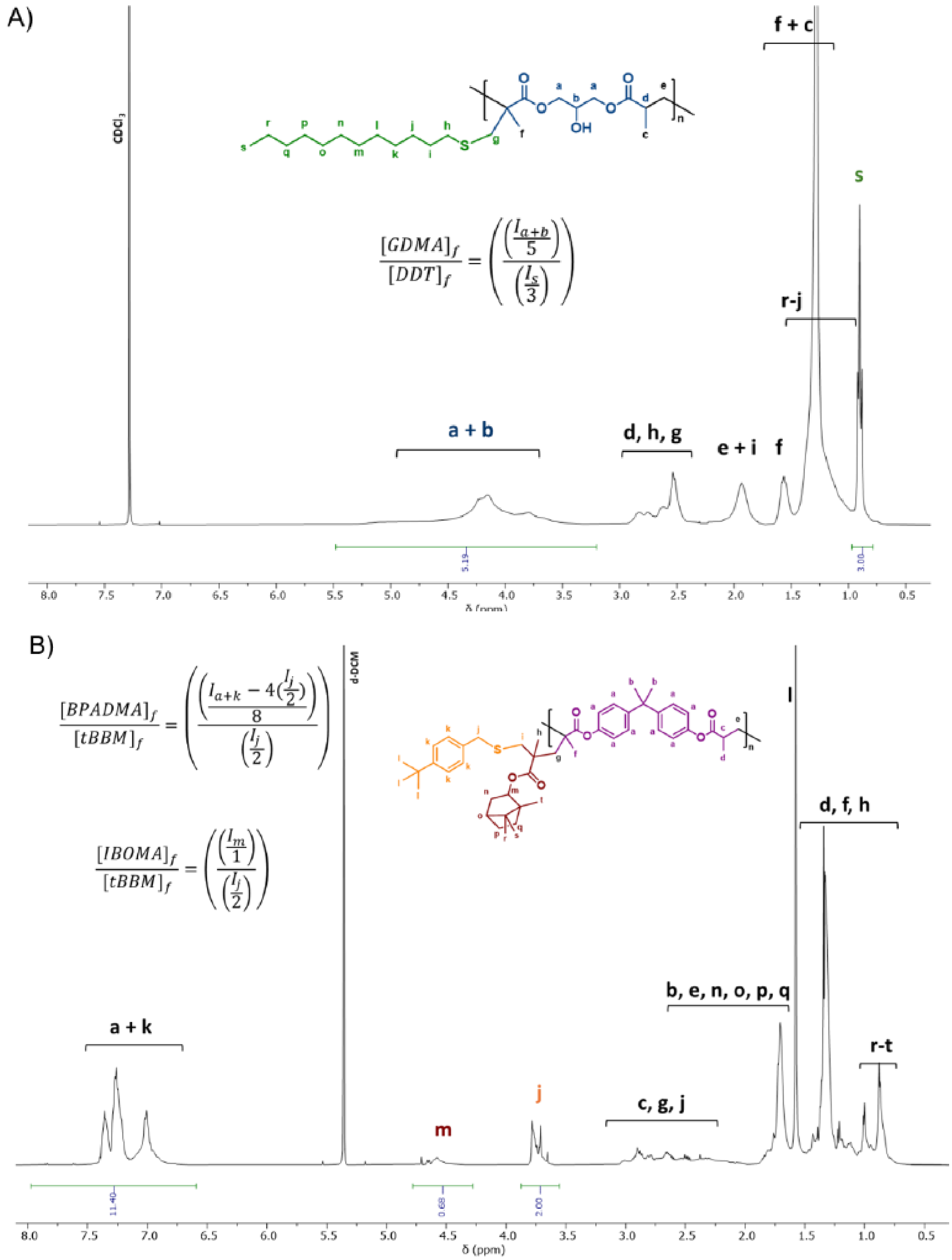
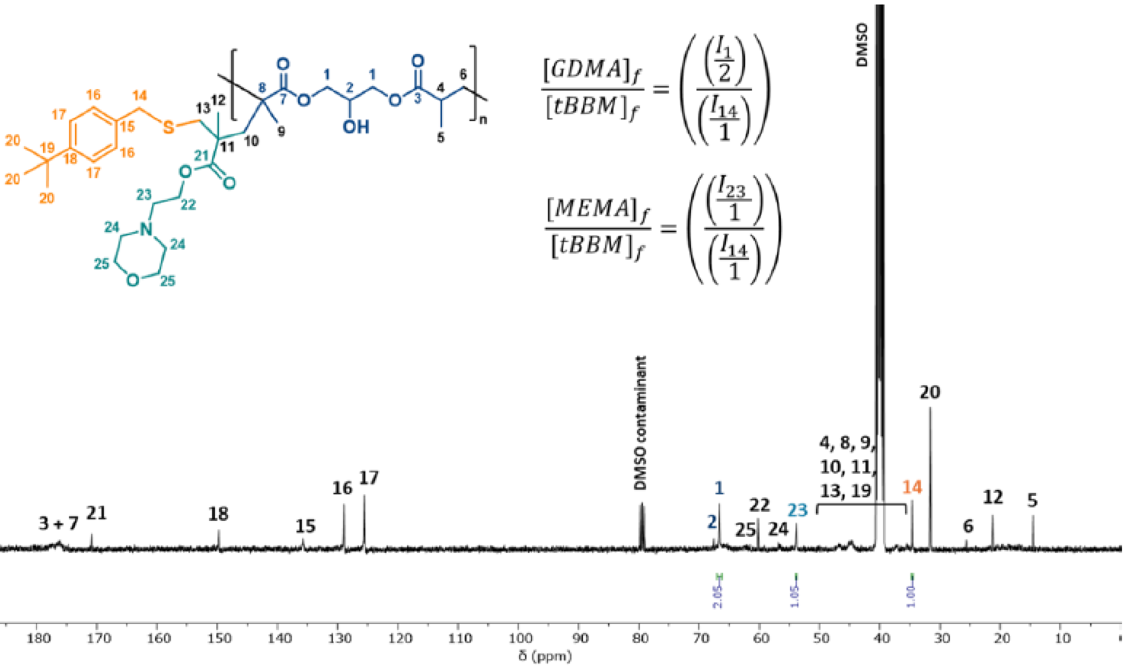


Figure S3 Examples of typical ^{1}H NMR (400 MHz, CDCl$_3$) spectra used to obtain accurate compositions from purified polymer and statistical copolymer samples. A) Homopolymer p(DDT-GDMA), and B) Copolymer *p*([*t*BuBZM-BPADMA]-*stat*-IBOMA)



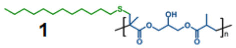
$$\frac{[GDMA]_f}{[tBBM]_f} = \left(\frac{\left(\frac{I_1}{2}\right)}{\left(\frac{I_{14}}{1}\right)}\right)$$

$$\frac{[MEMA]_f}{[tBBM]_f} = \left(\frac{\left(\frac{I_{23}}{1}\right)}{\left(\frac{I_{14}}{1}\right)}\right)$$

Figure S4 Example of the use of inverse gated ^{13}C NMR (100 MHz, DMSO-d$_6$) spectroscopy (statistical copolymer *p*([*t*BuBzM-GDMA]-*stat*-MEMA)) to obtain accurate compositions from purified polymers.

Table S2 Experimental results of solubility of varying study polymers and copolymers across seven common solvents

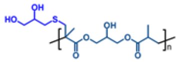
	Solubility (mg mL^{-1})						
Polymer	Water	Methanol	Acetone	THF	Diethyl ether	Xylene	Hexane
Homopolymers							
p(DDT-GDMA)	0.0	1.0	87.8	90.4	7.1	89.8	0.0
*p(t*BuBzM-GDMA*)*	0.3	20.0	94.9	102.5	2.0	92.9	1.3
p(TG-GDMA)	9.1	79.3	16.3	64.2	0.1	1.3	1.1
p(DDT-BPADMA)	0.1	1.4	38.9	91.4	7.5	91.2	28.2
*p(t*BuBzM-BPADMA*)*	0.0	4.3	87.8	100.6	2.0	100.4	5.2
p(TG-BPADMA)	0.0	3.0	58.2	93.9	0.1	0.2	1.8
Statistical Copolymers							
p([DDT-GDMA]-*stat*-GMA)	0.0	90.1	90.9	94.6	0.2	2.1	1.3
p([*t*BuBzM-GDMA]-*stat*-GMA)	0.9	93.3	113.6	102.5	0.0	1.0	0.0
p([TG-GDMA]-*stat*-GMA)	25.2	77.4	14.8	25.1	0.1	0.6	0.2
p([DDT-GDMA]-*stat*-GlyMA)	0.0	46.6	79.9	87.9	4.9	88.0	1.2
p([*t*BuBzM-GDMA]-*stat*-GlyMA)	0.5	35.8	83.8	95.1	3.9	89.0	2.3
p([TG-GDMA]-*stat*-GlyMA)	43.0	115.1	11.5	33.0	0.0	0.1	0.0
p([DDT-GDMA]-*stat*-IBOMA)	0.0	6.5	90.0	93.3	7.5	101.4	84.3
p([*t*BuBzM-GDMA]-*stat*-IBOMA)	0.0	4.9	77.5	85.0	7.7	83.4	1.5
p([TG-GDMA]-*stat*-IBOMA)	0.3	84.7	86.8	91.4	0.0	2.8	0.4
p([DDT-GDMA]-*stat*-MEMA)	0.9	4.5	86.9	89.7	4.0	80.0	0.8
p([*t*BuBzM-GDMA]-*stat*-MEMA)	0.1	4.8	85.6	87.4	0.2	80.9	1.2
p([TG-GDMA]-*stat*-MEMA)	18.0	52.5	21.5	104.1	0.0	0.0	0.0
p([DDT-BPADMA]-*stat*-GMA)	0.7	1.2	92.9	86.6	4.2	91.6	4.0
p([*t*BuBzM-BPADMA]-*stat*-GMA)	0.0	1.7	95.3	103.4	0.9	97.3	0.5
p([TG-BPADMA]-*stat*-GMA)	0.7	65.6	92.6	102.9	0.0	0.0	0.0
p([DDT-BPADMA]-*stat*-GlyMA)	2.2	7.6	89.3	90.4	7.3	91.4	25.3
p([*t*BuBzM-BPADMA]-*stat*-GlyMA)	6.2	8.9	89.1	99.1	2.3	96.6	6.6
p([TG-BPADMA]-*stat*-GlyMA)	38.7	77.8	74.4	107.8	0.2	0.9	0.7
p([DDT-BPADMA]-*stat*-IBOMA)	0.2	5.8	36.8	91.8	8.0	85.7	50.3
p([*t*BuBzM-BPADMA]-*stat*-IBOMA)	0.6	7.5	71.9	100.1	3.6	99.6	17.6
p([TG-BPADMA]-*stat*-IBOMA)	0.9	9.3	82.8	88.1	0.3	1.8	0.6
p([DDT-BPADMA]-*stat*-MEMA)	0.0	5.5	80.6	31.7	4.8	79.9	2.3
p([*t*BuBzM-BPADMA]-*stat*-MEMA)	0.0	5.1	94.4	103.0	1.6	101.9	3.8
p([TG-BPADMA]-*stat*-MEMA)	18.9	18.1	55.5	106.6	0.2	1.0	0.1



1

p(DDT-GDMA)

CCCCCCCCCCCCSCC(C)(C)C(=O)OCC(O)COC(=O)C(C)C



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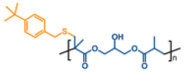
p(*t*BuBzM-GDMA)

CC(C)C(=O)OCC(O)COC(=O)C(C)(C)CSCc1ccc(cc1)C(C)(C)C



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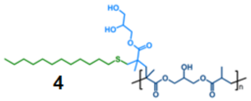
p(TG-GDMA)

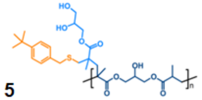
CC(C)C(=O)OCC(O)COC(=O)C(C)(C)CSCC(O)CO



4

p([DDT-GDMA]-*stat*-GMA)

CCCCCCCCCCCCSCC(C)(CC(C)(C)C(=O)OCC(O)COC(=O)C(C)C)C(=O)OCC(O)CO



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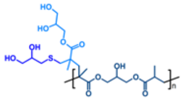
p([*t*BuBzM-GDMA]-*stat*-GMA)

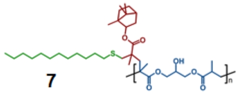
CC(C)C(=O)OCC(O)COC(=O)C(C)(C)CC(C)(CSCc1ccc(cc1)C(C)(C)C)C(=O)OCC(O)CO



6

p([TG-GDMA]-*stat*-GMA)

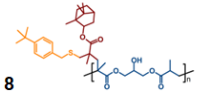
CC(C)C(=O)OCC(O)COC(=O)C(C)(C)CC(C)(CSCC(O)CO)C(=O)OCC(O)CO



7

p([DDT-GDMA]-*stat*-IBOMA)

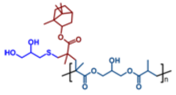
CCCCCCCCCCCCSCC(C)(CC(C)(C)C(=O)OCC(O)COC(=O)C(C)C)C(=O)OC1CC2CCC1(C)C2(C)C



8

p([*t*BuBzM-GDMA]-*stat*-IBOMA)

CC(C)C(=O)OCC(O)COC(=O)C(C)(C)CC(C)(CSCc1ccc(cc1)C(C)(C)C)C(=O)OC2CC3CCC2(C)C3(C)C



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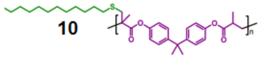
p([TG-GDMA]-*stat*-IBOMA)

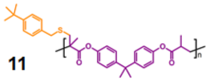
CC(C)C(=O)OCC(O)COC(=O)C(C)(C)CC(C)(CSCC(O)CO)C(=O)OC1CC2CCC1(C)C2(C)C



10

p(DDT-BPADMA)

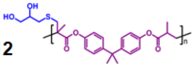
CCCCCCCCCCCCSCC(C)(C)C(=O)Oc1ccc(cc1)C(C)(C)c2ccc(OC(=O)C(C)C)cc2



11

p(*t*BuBzM-BPADMA)

CC(C)C(=O)Oc1ccc(cc1)C(C)(C)c2ccc(OC(=O)C(C)(C)CSCc3ccc(cc3)C(C)(C)C)cc2



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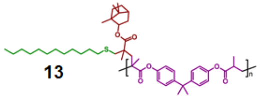
p(TG-BPADMA)

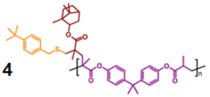
CC(C)C(=O)Oc1ccc(cc1)C(C)(C)c2ccc(OC(=O)C(C)(C)CSCC(O)CO)cc2



13

p([DDT-BPADMA]-*stat*-IBOMA)

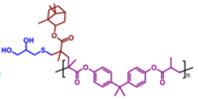
CCCCCCCCCCCCSCC(C)(CC(C)(C)C(=O)Oc1ccc(cc1)C(C)(C)c2ccc(OC(=O)C(C)C)cc2)C(=O)OC3CC4CCC3(C)C4(C)C



14

p([*t*BuBzM-BPADMA]-*stat*-IBOMA)

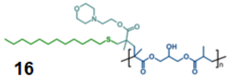
CC(C)C(=O)Oc1ccc(cc1)C(C)(C)c2ccc(OC(=O)C(C)(C)CC(C)(CSCc3ccc(cc3)C(C)(C)C)C(=O)OC4CC5CCC4(C)C5(C)C)cc2



15

p([TG-BPADMA]-*stat*-IBOMA)

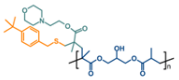
CC(C)C(=O)Oc1ccc(cc1)C(C)(C)c2ccc(OC(=O)C(C)(C)CC(C)(CSCC(O)CO)C(=O)OC3CC4CCC3(C)C4(C)C)cc2



16

p([DDT-GDMA]-*stat*-MEMA)

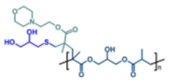
CCCCCCCCCCCCSCC(C)(CC(C)(C)C(=O)OCC(O)COC(=O)C(C)C)C(=O)OCCN1CCOCC1



17

p([*t*BuBzM-GDMA]-*stat*-MEMA)

CC(C)C(=O)OCC(O)COC(=O)C(C)(C)CC(C)(CSCc1ccc(cc1)C(C)(C)C)C(=O)OCCN2CCOCC2

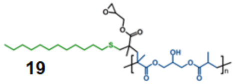


18

p([TG-GDMA]-*stat*-MEMA)

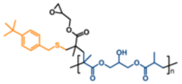
CC(C)C(=O)OCC(O)COC(=O)C(C)(C)CC(C)(CSCC(O)CO)C(=O)OCCN1CCOCC1

Figure S5 Structures and associated SMILES strings for polymers and copolymers **1**-**18** synthesised during this study.



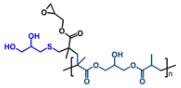
19

p([DDT-GDMA]-*stat*-GlyMA)
CCCCCCCCCCCCSCC(C)(CC(C)(C)C(=O)OCC(O)COC(=O)C(C)C)C(=O)OCC1CO1



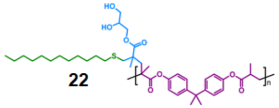
20

p([*t*BuBzM-GDMA]-*stat*-GlyMA)
CC(C)C(=O)OCC(O)COC(=O)C(C)(C)CC(C)(CSCc1ccc(cc1)C(C)(C)C)C(=O)OCC2CO2



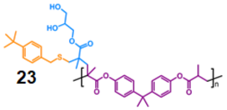
21

p([TG-GDMA]-*stat*-GlyMA)
CC(C)C(=O)OCC(O)COC(=O)C(C)(C)CC(C)(CSCC(O)CO)C(=O)OCC1CO1



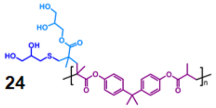
22

p([DDT-BPADMA]-*stat*-GMA)
CCCCCCCCCCCCSCC(C)(CC(C)(C)C(=O)Oc1ccc(cc1)C(C)(C)c2ccc(OC(=O)C(C)C)cc2)C(=O)OCC(O)CO



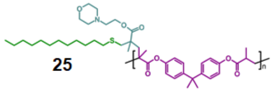
23

p([*t*BuBzM-BPADMA]-*stat*-GMA)
CC(C)C(=O)Oc1ccc(cc1)C(C)(C)c2ccc(OC(=O)C(C)(C)CC(C)(CSCc3ccc(cc3)C(C)(C)C)C(=O)OCC(O)CO)cc2



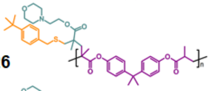
24

p([TG-BPADMA]-*stat*-GMA)
CC(C)C(=O)Oc1ccc(cc1)C(C)(C)c2ccc(OC(=O)C(C)(C)CC(C)(CSCC(O)CO)C(=O)OCC(O)CO)cc2



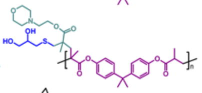
25

p([DDT-BPADMA]-*stat*-MEMA)
CCCCCCCCCCCCSCC(C)(CC(C)(C)C(=O)Oc1ccc(cc1)C(C)(C)c2ccc(OC(=O)C(C)C)cc2)C(=O)OCCN3CCOCC3



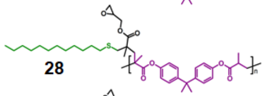
26

p([*t*BuBzM-BPADMA]-*stat*-MEMA)
CC(C)C(=O)Oc1ccc(cc1)C(C)(C)c2ccc(OC(=O)C(C)(C)CC(C)(CSCc3ccc(cc3)C(C)(C)C)C(=O)OCCN4CCOCC4)cc2



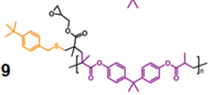
27

p([TG-BPADMA]-*stat*-MEMA)
CC(C)C(=O)Oc1ccc(cc1)C(C)(C)c2ccc(OC(=O)C(C)(C)CC(C)(CSCC(O)CO)C(=O)OCCN3CCOCC3)cc2



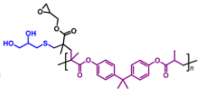
28

p([DDT-BPADMA]-*stat*-GlyMA)
CCCCCCCCCCCCSCC(C)(CC(C)(C)C(=O)Oc1ccc(cc1)C(C)(C)c2ccc(OC(=O)C(C)C)cc2)C(=O)OCC3CO3



29

p([*t*BuBzM-BPADMA]-*stat*-GlyMA)
CC(C)C(=O)Oc1ccc(cc1)C(C)(C)c2ccc(OC(=O)C(C)(C)CC(C)(CSCc3ccc(cc3)C(C)(C)C)C(=O)OCC4CO4)cc2



30

p([TG-BPADMA]-*stat*-GlyMA)
CC(C)C(=O)Oc1ccc(cc1)C(C)(C)c2ccc(OC(=O)C(C)(C)CC(C)(CSCC(O)CO)C(=O)OCC3CO3)cc2

Water: O
Methanol: CO
Acetone: CC(=O)C
THF: C1CCOC1
Diethyl Ether: CCOCC
m-Xylene: Cc1cccc(C)c1
Hexane: CCCCCC

Figure S6 Structures and associated SMILES strings for copolymers **19**-**30** synthesised during this study and associate SMILES for the seven study solvents.