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Accessing new and scalable high molecular weight branched copolymer structures using transfer-dominated branching radical telomerisation (TBRT)[†]

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Academic and commercial branched polymer synthesis very commonly relies upon a repeating chemistry derived from a single monomer. Literature reports of branched homopolymers often rely upon chemistries that are difficult to scale. Step-growth polymerisations are widely utilised which also limit the molecular weight of resulting branched macromolecules. The recent reports of Transfer-dominated Branching Radical Telomerisation (TBRT) provide readily accessible routes to a range of previously inaccessible macromolecular architectures utilising free radical reactions but resulting in step-growth-like backbones. Here we show how TBRT may be used to form branched statistical copolymers with step-growth backbone chemistries using facile free radical reaction conditions through three novel synthesis strategies leading to new materials with readily tunable physical properties. The strategies are outlined conceptually, exemplified by experimental examples and determination of glass transition temperatures provides clear evidence of homogeneous statistical copolymer formation.

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Introduction

Complex macromolecular architectures have fascinated academic and industrial polymer chemists for decades. Products that benefit from branched architectures have created business opportunities that include collective global market values of >US\$1bn^{1,2} annually with considerable growth predicted in coming years. Ideally branched polymers (dendrimers) have found application in a small number of niche areas where the costs of iterative syntheses may be justified;^{3,4} however, non-ideal hyperbranched polymers have generally shown performance benefits without the need for perfect architecture control or monodisperse molecular weight distributions.^{5–8} In most cases, the chemistry employed uses conventional step-growth processes (*e.g.* formation of esters, amides and urethanes),^{9,10} the use of ring-opening reactions (*e.g.* aziridine reactions)¹¹ or the formation of lightly crosslinked vinyl polymers with carbon-carbon backbones (*e.g.* manufacture of Carbopol/Carbomer).¹²

In an orthogonal field of chemical research, radical chemistry has been used to form telomers to improve the value and application of natural feedstocks.^{13,14} Telomers are small molecules resulting from the limited addition of unsaturated compounds (taxogens), controlled by the presence of a telogen. Typically, telomerisation aims to restrict the number of taxogens that are reacted together to 2–5 molecules; however, dimerisation is often the target.¹⁵ When utilised within polymer chemistry, telomerisation will form very short chains, shorter than oligomers, with a number average degree of polymerisation (DP_n) of <5 monomer repeat units per chain.^{16,17}

We recently employed radical telomerisation concepts, using widely available conventional free radical chemistry feedstocks, to generate high molecular weight complex macromolecular architectures and present a new polymer synthesis concept named Transfer-dominated Branching Radical Telomerisation (TBRT), Fig. 1.^{18,19}

The approach utilised alkyl thiol telogens (also known as chain transfer agents, CTAs, when used at low concentration relative to mono-vinyl monomers),²⁰ multi-vinyl taxogens (MVTs; monomers that contain more than one vinyl double bond) and sources of free radicals that are generated by thermal decomposition (azo initiators). By establishing free radical telomerisation conditions,^{21–23} propagation of the MVT is restricted on average to a $DP_n < 2$ vinyl groups and gelation is avoided. Essentially, the telomers that are formed by highly

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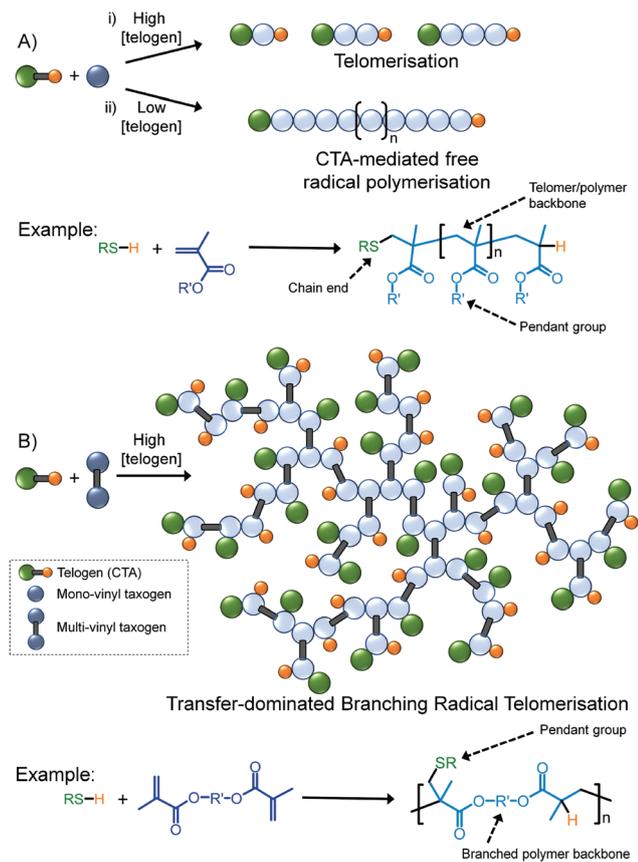


Fig. 1 Schematic representation and comparison of (Ai) linear telomerisation; (Aii) chain transfer agent-mediated free radical polymerisation; and (B) transfer-dominated branching radical telomerisation (TBRT). Examples show C–C backbone formation and telogens acting as chain ends in both conventional telomerisation and CTA-mediated free radical polymerisation; telogens become pendant groups within branched TBRT polymers and extended polymer chains are derived from taxogen chemistry.

restricted propagation are joined together *via* the linking chemistry within the MVT (*i.e.* the chemistry between the vinyl functional groups) and high molecular weight branched macromolecules are formed with complete conversion of vinyl groups at high solids concentrations.

As the C–C bond forming reactions are highly limited to combining on average <2 vinyl groups, extended chains within the branched polymers do not contain long sequences resulting from extensive propagation reactions, but rather TBRT joins together segments of backbone that were defined during MVT monomer synthesis; therefore, the polymerisation of a dimethacrylate MVT leads to a predominantly *polyester backbone* and the thiol telogen becomes a *pendant group*, Fig. 1B. This is fundamentally different to reports of CTA-mediated free radical polymerisations (for example the “Strathclyde” approach) that incorporate low concentrations of multi-vinyl monomers into copolymerisations that create long primary chains formed from mono-vinyl monomers.^{24–27}

In these cases, the thiol CTA is incorporated at low molar ratios as the primary chain end, the primary chains contain

C–C backbones and the pendant groups are defined by the mono-vinyl monomer, Fig. 1A. TBRT is also distinct from controlled radical polymerisations that aim to homopolymerise multi-vinyl monomers, at relatively low concentrations, but fail to prevent gelation at medium-high vinyl group conversions (>70%).^{28–30} Structurally, the products of TBRT are highly unusual. As the ratio of MVT to telogen is 1/1 in the final polymer, the telogen is incorporated into the final polymer as a key *structural unit* and the nominal repeating structure is formed *during* TBRT by combination of telogen and MVT, Fig. 1B. Pendant groups are known to highly influence the physical properties of polymers, therefore *telogen selection* dictates the chemistry of the final branched polymer and not solely the MVT.^{18,19} Again, this is fundamentally different to previous multi-vinyl monomer copolymerisations with low mono-vinyl monomer concentrations that incorporate CTAs solely as primary chain ends with little impact on polymer structure or properties.^{31–33}

Polymer chemistry benefits considerably from the synthesis and use of copolymer structures.^{34–37} Statistical copolymers are widely used to modify and direct polymers towards properties that are not achievable from the individual constituent monomers. For example, varying degrees of hydrophilicity may be introduced into hydrophobic polymers by copolymerisation with appropriate concentrations of hydrophilic monomers. Equally, the introduction of controlled numbers of functional groups within target structures is often achieved by varying the molar ratio of functional and non-functional monomers within copolymer chains.³⁸ Behaviour such as crystallisation,³⁹ self-assembly,⁴⁰ nanoprecipitation⁴¹ and surface activity^{42,43} may be readily controlled in this manner.

There are relatively few reports of readily accessible branched and hyperbranched copolymer structures with step-growth backbone chemistries and reports of mixtures of AB_n monomers are very rare;⁴⁴ however, many opportunities exist to create previously inaccessible branched macromolecules using TBRT. With the nominal repeating structure being formed during the TBRT reaction, polymers of differing chemistry may be created using a single MVT and different telogens. The variation within commercially available and bespoke MVTs and telogens is considerable and the availability of entirely novel copolymer structures is significant. Here, we present an overview of three conceptually new synthetic strategies, available *via* TBRT, to produce novel branched copolymers with polyester backbones. The structural implications of the TBRT methodologies are highlighted and explored through careful and detailed characterisation including the measurement and remarkable control of the thermal properties of the resulting complex macromolecules.

Results and discussion

Calculation of chain transfer constants

TBRT requires the addition of a telogen at a concentration conventionally applied to telomerisation of small molecules; nor-



mally a molar excess relative to vinyl group is used. This allows transfer reactions between active free radicals and unreacted telogen to dominate the reaction mechanism^{45,46} and avoids multiple addition reactions (propagation). Understanding the chain transfer rates of different telogens is, therefore, important^{47,48} to establish appropriate TBRT reaction conditions and avoid gelation when using an MVT. A series of model polymerisations were undertaken with methyl methacrylate (MMA) and a series of structurally diverse thiols. Five thiol telogens were selected, namely benzyl mercaptan (BzM), phenyl ethyl mercaptan (PhEM), *t*-butyl benzyl mercaptan (*t*BuBzM), cyclohexanethiol (CHT) and dodecanethiol (DDT), Fig. 2A.

Each reaction was initiated with 2,2'-azobis(2-methylpropionitrile) (AIBN; 1.5 mol% with respect to MMA double bonds) at 70 °C, carried out at 50 wt% solids content in ethyl acetate, and terminated after 15 minutes to ensure low conversion (<10% vinyl consumption).⁴⁹ The products were purified and analysed using triple-detection size exclusion chromatography (TD-SEC), Fig. 2B, to determine DP_n. The data generated was used to determine the chain transfer coefficients

from the gradient of the subsequent Mayo plots,^{20,50} Fig. 2C (Table S1, Fig. S1 and eqn (S1)†).

Across the structurally diverse telogens studied, a noticeable variation in chain transfer constant (C_T) was clearly observed. DDT and *t*BuBzM displayed very similar behaviour with calculated $C_T = 0.45$ and 0.42 and were, therefore, selected for further study in order to simplify later reaction conditions. Telomerisation studies were conducted that allowed high conversion of MMA using either DDT or *t*BuBzM to compare the species formed during these reactions. Time of Flight – Matrix Assisted Laser Desorption-Ionisation mass spectrometry and oligomer size exclusion chromatography was conducted on the products and the DP_n values of the species identified were very similar, again confirming the similar chain transfer behaviour of these telogens (Fig. S2–S5, Tables S2–S3 and eqn (S2)†).

TBRT homopolymer structures

Our recent report of high molecular weight branched polymer synthesis *via* TBRT utilised ethylene glycol dimethacrylate (EGDMA) as the MVT and DDT as the telogen,¹⁸ Fig. 3A. Here we have repeated this using near identical conditions to those used during the elucidation of C_T values above (1.5% AIBN; 50 wt% solids content in ethyl acetate; 70 °C) but with an initial MVT/telogen ratio ($[MVT]_0/[Tel]_0$) of 0.850 and allowing the reaction to reach >99% conversion of vinyl groups (determined by ¹H NMR of the crude reaction mixture) over a 24-hour timescale (Fig. S6 and 7†). The MVT/telogen ratio was selected as the highest observed value able to maintain telomer formation and avoid gelation. After precipitation into methanol at ambient temperature, the recovered *p*(DDT-EGDMA) homopolymer was characterised by TD-SEC, ¹H and ¹³C NMR spectroscopy; number-average molecular weight (M_n) = 19 395 g mol⁻¹, weight-average molecular weight (M_w) = 2 803 000 g mol⁻¹, a Mark–Houwink–Sakurada (MHS) α value = 0.361 and an MVT/telogen ratio in the final structure ($[MVT]_f/[Tel]_f$) of 1.02 (Fig. S8–10†) were found. Removal of impurities by precipitation was important to allow detailed measurement of glass transition temperature (T_g) using differential scanning calorimetry (DSC) and it is possible that some low molecular weight material was also removed during this process.

TBRT conducted under near identical conditions but using *t*BuBzM at an $[MVT]_0/[Tel]_0$ ratio of 0.825, also led to >99% vinyl group conversion; purified polymer characterisation showed $[MVT]_f/[Tel]_f = 1.06$, $M_n = 20 150$ g mol⁻¹ and $M_w = 575 540$ g mol⁻¹, MHS $\alpha = 0.342$, Fig. 3B (Fig. S11–17†). The variation in purified polymer molecular weight, particularly M_w , when using the different telogens is an indication of the impact of telogen structure and the initial MVT/telogen ratio on the extent of branching that occurs during TBRT.⁵¹ Additionally, removal of low molecular weight species by reprecipitation may also be impacted by differences in solubility driven by telogen chemistry.

The schematic representation of the TBRT homopolymers derived from EGDMA, Fig. 3A+B, demonstrates the structural

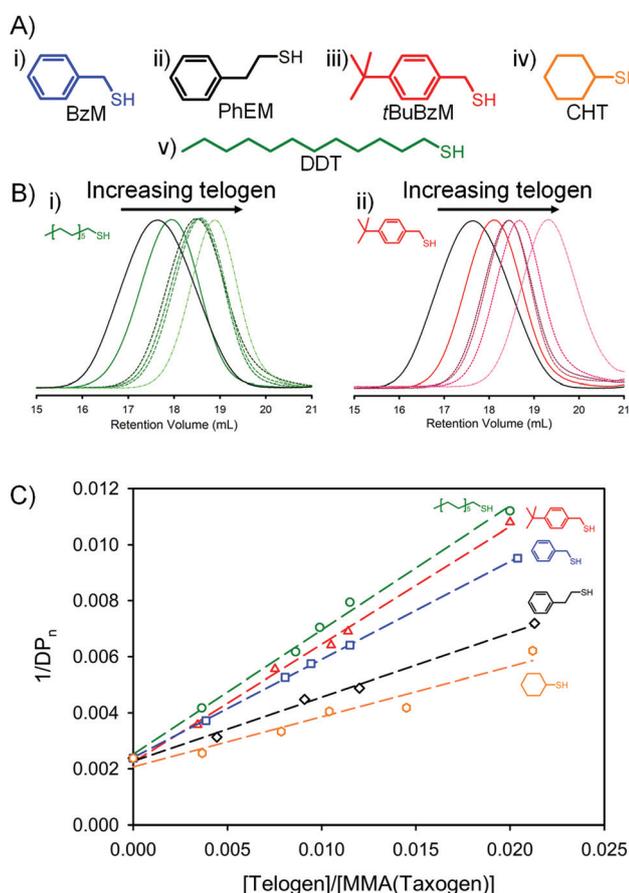


Fig. 2 Study of chain transfer using (Ai) benzyl mercaptan, (Aii) phenyl ethyl mercaptan, (Aiii) *t*-butyl benzyl mercaptan, (Aiv) cyclohexanethiol and (Av) dodecanethiol. (B) Examples of *p*(methyl methacrylate) distributions from Mayo plot studies. (C) Comparison of Mayo plots for each chain transfer agent.



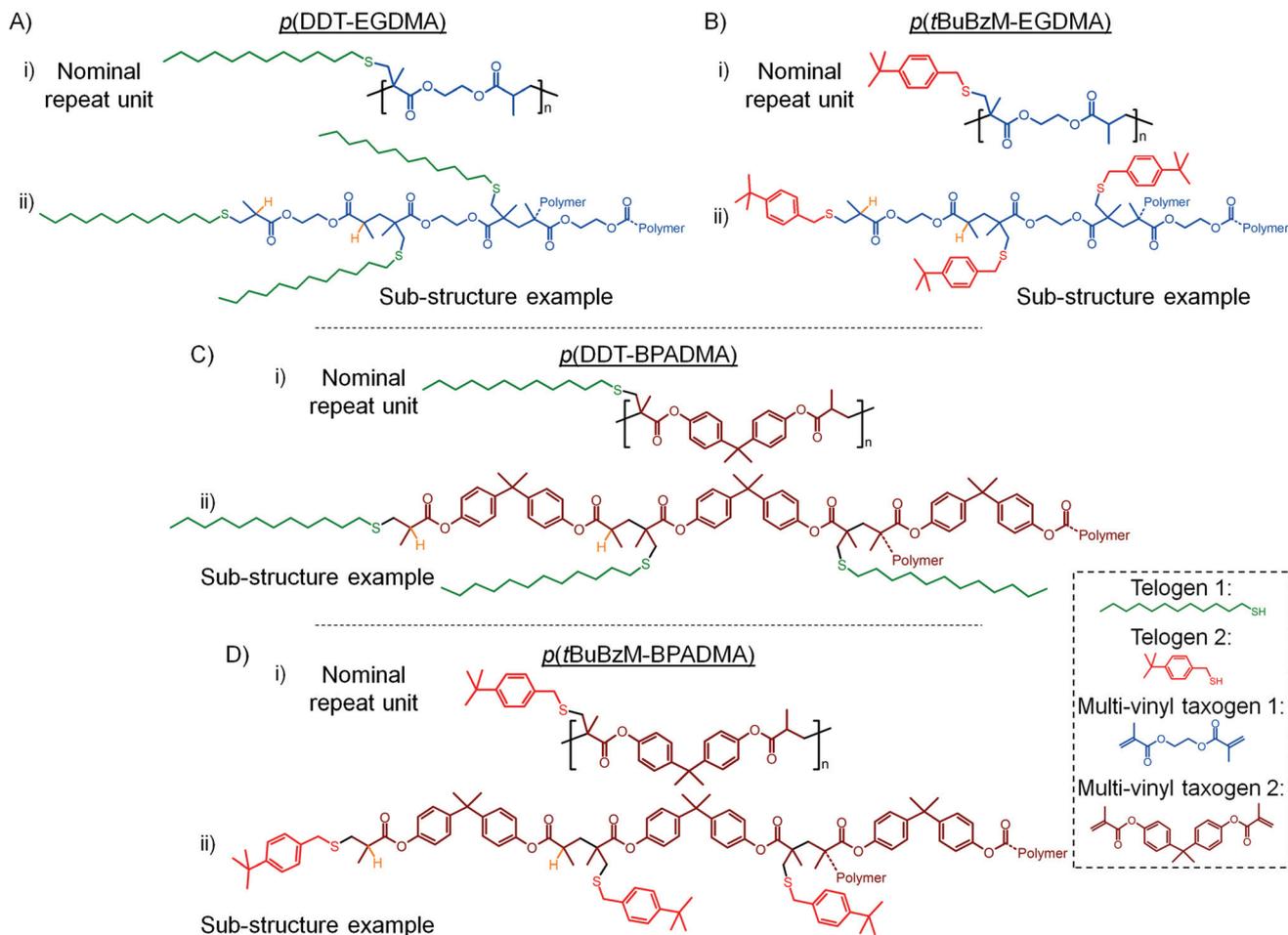


Fig. 3 Schematic representation of branched homopolymers available using combinations of two telogens and two multi-vinyl taxogens (MVT). (A) Structure of p(DDT-EGDMA): (Ai) Nominal repeat unit shown as 1/1 adduct of telogen and MVT; and (Aii) example sub-structure unit showing polyester backbone and pendant telogen groups. (C) Structure of p(DDT-BPADMA): (Ci) Nominal repeat unit shown as 1/1 adduct of telogen and MVT; and (Cii) example sub-structure unit showing polyester backbone and pendant telogen groups. (D) Structure of p(tBuBzM-BPADMA): (Di) Nominal repeat unit shown as 1/1 adduct of telogen and MVT; and (Dii) example sub-structure unit showing polyester backbone and pendant telogen groups. Bonds formed during TBRT in black, coloured groups indicate reactant residues.

impact of telogen selection as the nominal repeating structures have different pendant groups, Fig. 3Ai+Bi, with the substructure examples showing the same extended polyester backbone, Fig. 3Aii+Bii. Utilising a different MVT, bisphenol-A dimethacrylate (BPADMA), with the same telogens under similar conditions produces a predominantly aromatic polyester backbone with structural variation from aliphatic, Fig. 3C, to aromatic pendant groups, Fig. 3D (Fig. S18–31†). When using this MVT, the highest $[MVT]_0/[Tel]_0$ ratios that were accessible before gelation were 0.400 and 0.425 for DDT or *t*BuBzM respectively. Variation in TBRT reaction conditions may be derived from differing complex reaction kinetics such as combinations of transfer kinetics, intramolecular branching and telomer chain length distributions. The impact of different telogen chemistry on the purified polymer molecular weight was also seen within the TD-SEC analysis when using BPADMA, Table 1. Additionally, $[MVT]_f/[Tel]_f$ ratios are ≈ 1 , suggesting minimal/comparable cyclisation, possibly due to a combi-

nation of MVT dimensions and TBRT reaction conditions employed.^{19,51}

Mixed telogen TBRT copolymers

As mentioned above, small molecule telomers are often synthesised using telogens at relatively high concentration. Conversely, telogens are utilised at low concentration as CTAs to limit the propagation of relatively high molecular weight linear polymers under conventional free radical polymerisation conditions. Normally, within macromolecular chemistry, there would be limited, if any, reason to mix CTAs within a conventional free radical polymerisation as this would create a product under varying chain transfer conditions leading to a complex molecular weight distribution of mixed chain ends. In one specific example within the patent literature, a mixture of isomeric C_{10} thiol-based CTAs was shown to produce very similar products, but with reduced residual odour, when compared to using *n*-decyl mercaptan alone within free radical



Table 1 Characterisation of branched homopolymers and statistical copolymers synthesised via TBRT

Polymer ^a (telogen-MVT)	¹ H NMR		TD-Size exclusion chromatography ^b				Differential scanning calorimetry
	[MVT] ₀ /[Tel] ₀ (initial reaction)	[MVT] _f /[Tel] _f (purified polymer)	M _w (g mol ⁻¹)	M _n (g mol ⁻¹)	D	MHS α	T _g (°C)
Homopolymers							
p(DDT-EGDMA)	0.850	1.02	1 803 000	19 395	92.98	0.361	-48
p(<i>t</i> BuBzM-EGDMA)	0.825	1.06	575 540	20 150	28.57	0.342	28
p(DDT-BPADMA)	0.400	1.08	2 414 000	55 545	43.46	0.397	11
p(<i>t</i> BuBzM-BPADMA)	0.425	1.05	845 135	32 400	26.09	0.372	69
Statistical copolymers							
<i>Mixed telogen copolymers</i>							
p([<i>t</i> BuBzM-EGDMA]- <i>stat</i> -[DDT-EGDMA])	0.825	1.04	578 000	13 550	42.67	0.351	-1
p([<i>t</i> BuBzM-BPADMA]- <i>stat</i> -[DDT-BPADMA])	0.400	1.14	441 020	12 080	36.50	0.333	39
<i>Mixed MVT copolymers</i>							
p([DDT-BPADMA]- <i>stat</i> -[DDT-EGDMA])	0.500	1.06	1 557 000	31 900	49.78	0.369	-13
p([<i>t</i> BuBzM-BPADMA]- <i>stat</i> -[<i>t</i> BuBzM-EGDMA])	0.550	1.05	5 326 000	56 720	93.90	0.496	48
<i>Mixed mono-vinyl taxogen/MVT copolymers</i>							
p([DDT-EGDMA]- <i>stat</i> -BzMA)	0.925	1.19	2 149 000	27 700	77.59	0.401	12
p([<i>t</i> BuBzM-EGDMA]- <i>stat</i> -BzMA)	0.925	1.05	361 200	8150	16.47	0.340	33

^a Polymers are derived from either 100 mol% MVT, 1/1 molar ratios of mixed MVTs, or 1/1 molar ratios of mixed mono-vinyl taxogen/MVTs. Telogens are present as either 100 mol% or 1/1 molar ratios. ^b TD-SEC conducted using THF eluent.

initiated emulsion polymerisation;⁵² no structural or chemical benefits were described.

As the telogen is a key structural component of the branched polymers synthesised here, TBRT offers a unique opportunity to form copolymer structures through the use of *mixed telogens*; mixed telogens create a combination of different nominal repeating units even when employing a single MVT. Essentially, the telogen creates a pendant group to the MVT-derived backbone and this would be expected to impact branched polymer properties in a manner that is analogous to the impact of side chains in chain-growth polymers derived from the extended propagation of different mono-vinyl monomers under conventional free radical conditions.

The two telogens utilised in homopolymer syntheses above, have similar chain transfer constants, Fig. 2C, and a combination within the reaction would be expected to generate high molecular weight polymers, containing a statistical mixture of nominal repeat units. Indeed, when an equimolar ratio of DDT/*t*BuBzM was utilised within the TBRT of EGDMA under identical conditions to those described above, >99% vinyl conversion was again achieved (Fig. S32 and S33†). TD-SEC analysis of the recovered and purified polymer gave M_n = 13 550 g mol⁻¹, M_w = 578 000 g mol⁻¹ (Table 1, Fig. S34†). ¹H NMR analysis also showed that the final ratio of MVT/telogen in the purified polymer was 1.04/1.00; NMR spectra were further resolved to determine a final DDT/*t*BuBzM ratio of 0.51/0.49 showing near ideal incorporation of the different telogens (Fig. S35†). The structure of this branched TBRT copolymer is represented in Fig. 4A.

The near ideal mixing of the telogens within the final polymer, facilitated by the very similar C_T values, suggests limited reactivity differences or steric constraints during branched polymer formation. Structurally, the mixed telogen TBRT copolymer has several features unique to this synthetic

strategy. Maintaining propagation to a DP_n < 2 units within the structure is highly dependent on the formation of a large number of DP₁ units,^{18,19} Fig. 4Ai-ii; the same 1/1 MVT/telogen 'nominal' repeating structures from the homopolymer structures, Fig. 3Ai+Bi, may also be considered as being present within the copolymer. When using a mixture of telogens the chemistry of the DP₁ substructures would be expected to be statistically distributed, especially when the C_T values are so well matched. Equally, the distribution of telogens throughout the DP ≥ 2 units would also be expected to be statistical.

Evidence of DP₁ structural units containing either DDT or *t*BuBzM was provided by ¹³C NMR spectroscopy (Fig. S36–39†). Resonances of the carbons α (3°) and β (2°) to the DP₁ ester were identified for units bearing either the DDT or *t*BuBzM telogen (DDT-EGDMA: α carbon = 40.3 ppm, β carbon = 36.0 ppm; *t*BuBzM-EGDMA: α carbon = 40.0 ppm, β carbon = 34.6 ppm). Inverse-gated ¹³C NMR spectroscopy showed near equimolar ratios of DP₁ units bearing each telogen, matching the initial feed ratio (Fig. S40†). ¹³C chemical shifts were also identified for telomer substructures with ≥2 vinyl residues bearing either a DDT or *t*BuBzM as the telogen. Both telogens appear to be equally distributed across the broad range of telomer subunits within the branched architecture suggesting a statistical p([*t*BuBzM-EGDMA]-*stat*-[DDT-EGDMA]) copolymer has been formed, Fig. 4A.

The TBRT of BPADMA was also conducted with an equimolar DDT/*t*BuBzM ratio and ¹H NMR analysis of the resulting p([*t*BuBzM-BPADMA]-*stat*-[DDT-BPADMA]) copolymer showed a [MVT]_f/[Tel]_f ratio of 1.14/1.00 (Fig. S41–44†). An overall DDT/*t*BuBzM of 0.47/0.53 was determined for the polymer sample which matched the telogen ratio within DP₁ substructures. A number of resonances were readily observed by ¹³C NMR analysis of the mixed telogen copolymer, Fig. 5A, that were unique to each single-telogen homopolymer, Fig. 5Ai-iv; DDT and



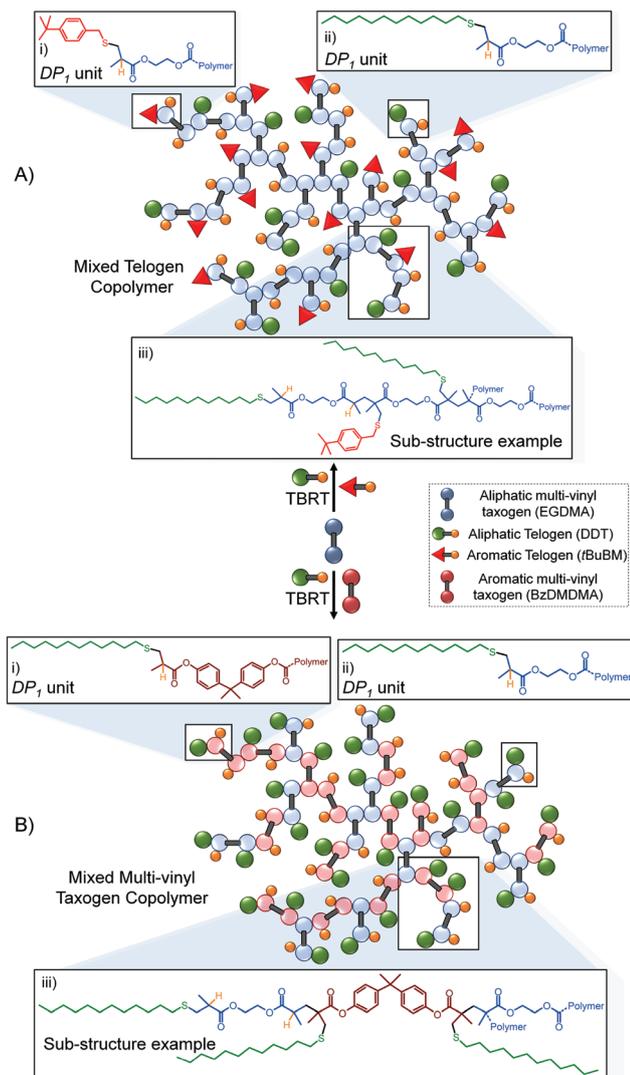


Fig. 4 Schematic representation of strategies for synthesising statistical TBRT copolymers using multi-vinyl taxogens and telogens. (A) a mixed Telogen TBRT Copolymer with, (i) DP_1 substructure units derived from *t*BuBzM-EGDMA reaction and (ii) DP_1 substructure units derived from DDT-EGDMA reaction; (iii) representation of highlighted sub-structure showing polyester backbone and variation of telogen derived pendant units. (B) a mixed Multi-vinyl Taxogen TBRT Copolymer with (i) DP_1 substructure units derived from DDT-BPADMA reaction and (ii) DP_1 substructure units derived from DDT-EGDMA reaction; (iii) representation of highlighted sub-structure showing polyester backbone and variation of taxogen derived backbone units.

*t*BuBzM-bearing telomer substructures were clearly present indicating statistical copolymer formation (Fig S45–49†).

The statistical nature of mixed telogen incorporation leads to a range of expected sub-structures within the branched polymer, Fig. 4iii. As mentioned above, the telogens introduce thioether groups that are pendant to the polyester backbone and these may be incorporated singly on each MVT residue or the residue may bear two telogens; in the case of a mixed telogen copolymer, these may either be the same or of

different chemical nature, Fig. 4A. Some MVTs that bridge between telomers with $DP \geq 3$ units may have no telogen pendant group. The complexity of the substructure and ordering of units is analogous to sequencing of monomer residues within statistical copolymers^{53–55} and copolymer physical properties would be expected to vary with telogen composition and display behaviours that lay between those of the relevant homopolymers.^{56–60}

Mixed multi-vinyl taxogen TBRT copolymers

TBRT also offers a conventional route to copolymer structures that is more familiar to chain-growth copolymerisations *via* the combination of MVTs. To the best of our knowledge, the reaction of mixed multi-vinyl monomers to complete vinyl conversion to form soluble branched copolymers using conventional, or controlled, free radical chemistries has not been reported previously. To investigate the potential of mixed MVT copolymers, EGDMA and BPADMA were combined in an equimolar ratio and TBRT was conducted in the presence of either DDT or *t*BuBzM telogens under the conditions described above to form either $p([DDT-BPADMA]-stat-[DDT-EGDMA])$ or $p([tBuBzM-BPADMA]-stat-[tBuBzM-EGDMA])$. It is important to emphasise again that the use of different telogens fundamentally creates different copolymer structures *via* the presence of varied pendant group functionality within polyester repeat units.

$p([DDT-BPADMA]-stat-[DDT-EGDMA])$ was synthesised using the highest MVT/telogen ratio at which soluble branched copolymers were formed when using equimolar MVT mixtures ($[MVT]_0/[Tel]_0 = 0.500$); this was again accompanied by >99% vinyl conversion and yielded very high molecular weight branched copolymers, Table 1 (Fig. S50–52†). In an ideal scenario, the resulting copolyester backbone comprises a statistical mixture of aliphatic and aromatic units that is more readily associated with step-growth strategies using mixed diols, Fig. 4B. The incorporation of BPADMA within the mixed MVT copolymerisation provides an opportunity to introduce backbone chemistry variation and rigidity into the extended branched polyester, which would be expected to impact the physical properties. ¹H NMR analysis confirmed the near-equimolar ratio of BPADMA and EGDMA residues in the final copolymer structure (0.48/0.52 respectively, Fig. S53†) and an $[MVT]_f/[Tel]_f$ ratio of 1.06/1.00. In a similar manner to the characterisation of mixed telogen copolymers, ¹³C NMR analysis identified the vinylic residues of both BPADMA and EGDMA taxogens within DP_1 substructures, Fig. 4Bi+ii, and telomers with ≥ 2 units (Fig. S54–58†). Similar results were obtained from the copolymerisation of BPADMA and EGDMA in the presence of *t*BuBzM ($[MVT]_0/[Tel]_0 = 0.550$, Fig. S59–61†) to form $p([tBuBzM-BPADMA]-stat-[tBuBzM-EGDMA])$ at >99% vinyl conversion. ¹H NMR analysis of the purified copolymer again showed a BPADMA/EGDMA molar ratio of 0.52/0.48 respectively and a final $[MVT]_f/[Tel]_f$ ratio of 1.05/1.00 (Fig. S62†). ¹³C NMR analysis also demonstrated the formation of both BPADMA and EGDMA repeat unit structures contain-



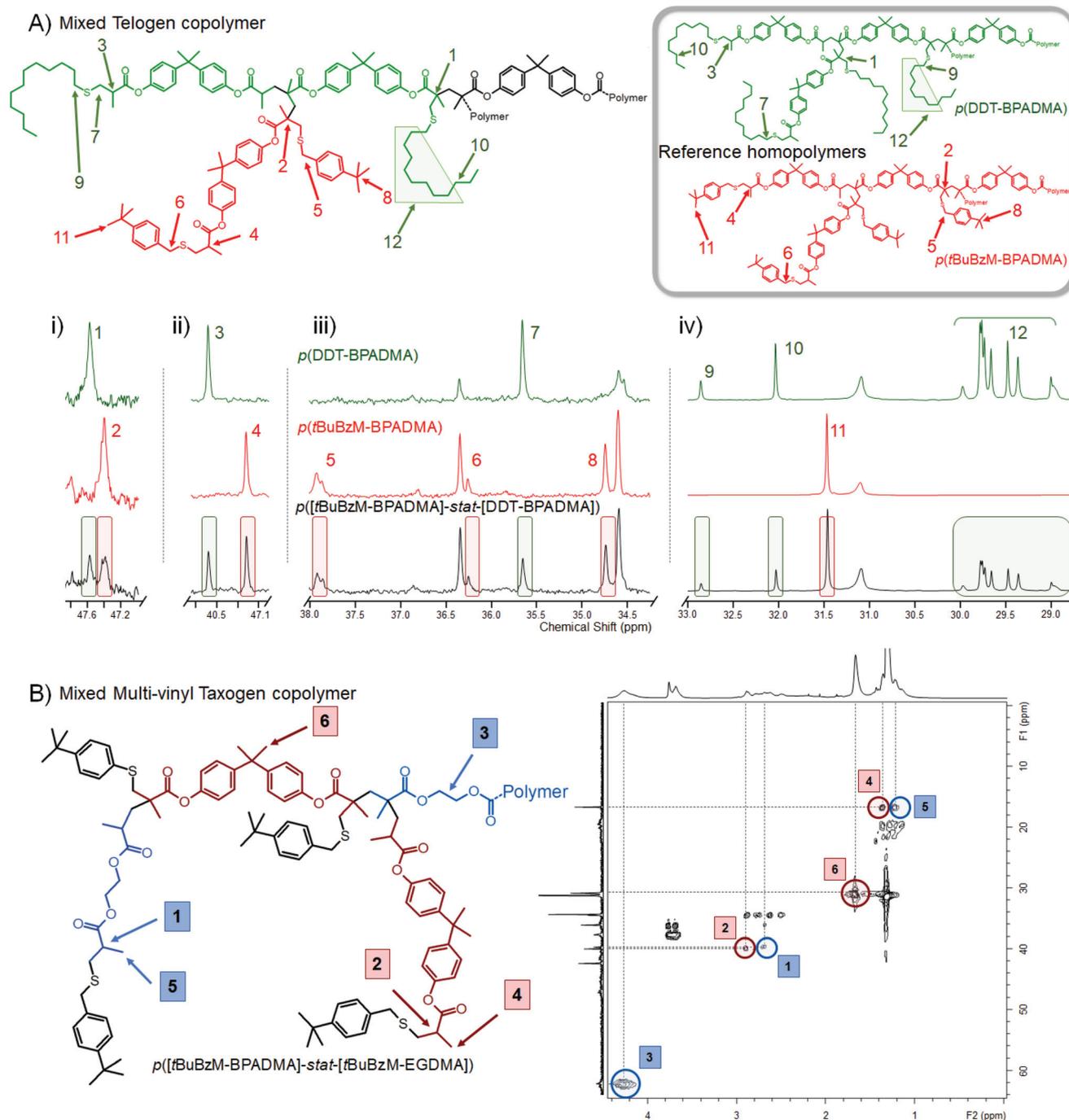


Fig. 5 Nuclear magnetic resonance studies of TBRT copolymers. (A) ^{13}C NMR Comparisons of p(DDT-BPADMA), p(tBuBzM-BPADMA) and p([tBuBzM-BPADMA]-stat-[DDT-BPADMA]) showing incorporation of both telogens within the mixed telogen copolymer; (B) Heteronuclear single quantum coherence spectrum of p([tBuBzM-BPADMA]-stat-[tBuBzM-EGDMA]) showing the combination of multi-vinyl taxogens within this copolymer structure.

ing varied DP values (Fig. S63–67 and Table S4†) with assignment facilitated by heteronuclear single quantum coherence spectroscopy, Fig. 5B.

Collectively, the characterisation suggests a statistical reaction of each telogen with the different MVTs and incorporation of the MVT mixture into the final copolymers. No difference in reactivity or steric hindrance constraining one MVT to occupy

more peripheral sites within each branched architecture is observed. The mixed MVT statistical copolymers formed here would be relatively difficult to synthesise using conventional step-growth chemistries as the mixed backbone, Fig. 4Biii, contains both phenyl and aliphatic ester links and facile high yielding reaction conditions common to both chemistries may not be readily achievable.⁶¹



Mixed mono/multi-vinyl taxogen TBRT copolymers

A third synthesis strategy is also available through TBRT, namely the combination of mono-vinyl taxogens within the MVT reaction. As mentioned above, low concentrations of multi-vinyl monomers have been previously incorporated into polymerisations of mono-vinyl monomers to form lightly branched polymers with extended C–C backbones. Here, we incorporate low concentrations of mono-vinyl monomers into TBRT reactions and form extended branched step-growth backbones, Fig. 6.

To investigate the potential for copolymer synthesis through the inclusion of low concentrations of mono-vinyl taxogens, the TBRT homopolymer syntheses forming p(DDT-EGDMA) and p(*t*BuBzM-EGDMA) were modified to include an equimolar ratio of benzyl methacrylate (BzMA) to EGDMA (Fig. S68–83 and Table S5†). The inclusion of BzMA has a number of potential structural impacts on the architecture of the TBRT copolymers and these are schematically highlighted in Fig. 6. Firstly, BzMA may be included in the peripheral units of the architecture which would be normally considered as a DP₁ structure in TBRT polymers comprised solely of MVTs, Fig. 6A. Inclusion of BzMA in the peripheral units clearly modifies the chemistry through the addition of an aromatic pendant group; however, these regions are still DP₁ units with respect to the propagation of MVT and it is unlikely that all of the DP₁ units will have a BzMA residue, Fig. 6B.

It is also hypothetically possible that peripheral units incorporate more than one BzMA unit and that there may be considerable variation in the sequence of MVT and BzMA at these

sites (*e.g.* telogen-MVT, telogen-BzMA-MVT; telogen-MVT-BzMA; telogen-BzMA-MVT-BzMA). In each case, a DP₁ unit with respect to MVT is still present but varying chemistry and averaged behaviour would be expected. ¹³C NMR studies showed clear evidence of DP₁ units derived solely from MVT (*i.e.* without BzMA; telogen-MVT) being generated in copolymers formed using each telogen (Fig. S75 & 83†); this correlated with resonances identified during analysis of p(*t*BuBzM-EGDMA) and p(DDT-EGDMA) corresponding to the 3° carbon α to the DP₁ ester at approximately 40 ppm in each case (Fig. S10 & S15†). Although accurate quantification was not possible, the intensities of the resonances corresponding to these DP₁ units (telogen-MVT) appeared to be reduced, relative to total telogen, for the copolymers containing BzMA when compared to the corresponding homopolymers. This would be expected if statistical incorporation of BzMA at a fraction of the DP₁ units (relative to MVT) altered the chemical environment of some peripheral units and the resulting resonances were more akin to those seen for DP ≥ 2 units (relative to MVT).

Additionally, the inclusion of BzMA within the internal telomer structures (DP ≥ 2 with respect to MVT) extends the telomer length without contributing to branching, Fig. 6C. This is analogous to BzMA addition at DP = 1 units (with respect to MVT). Again, there will be MVT-derived telomers that have a statistical distribution of BzMA incorporation, therefore telomers without BzMA will be expected to be present at this mono-vinyl telogen/MVT ratio. The inclusion of BzMA to form p([DDT-EGDMA]-*stat*-BzMA) and p([*t*BuBzM-EGDMA]-*stat*-BzMA) allowed a higher taxogen/telogen ratio within the reaction mixture in the formation of high molecular weight copolymers, than used in the formation of the p(DDT-EGDMA) and p(*t*BuBzM-EGDMA) respectively. This also suggests incorporation within the internal telomer distribution as non-branching units will impact the gelation point.

Characterisation of thermal behaviour of TBRT copolymers

Conventional homopolymers, generated either by step-growth or chain-growth polymerisation, would be expected to present differing T_g behaviour based on the varying structures of their component monomers. Step-growth polymers formed using combinations of A_n and B_n monomers have varying monomer-dependent backbone mobility and interchain interactions that exhibit different thermal responses and observable T_g values (*e.g.* poly(ethylene adipate), $T_g = -40$ °C; poly(ethylene terephthalate), $T_g = 72$ °C).⁶² For chain-growth homopolymers (and a small example set of step-growth macromolecules), the introduction of flexible or space-filling pendant groups to the same C–C backbone will also lead to T_g modification primarily through free volume effects (*e.g.* poly(dodecyl methacrylate), $T_g = -55$ °C; poly(methyl methacrylate), $T_g = 105$ °C; poly(phenyl methacrylate), $T_g = 120$ °C).⁶² Importantly, the T_g behaviour of *monodisperse linear polymers* is also known to be inversely related to molecular weight *via* the Flory-Fox relationship,⁶³ with a $T_{g\infty}$ plateau at a theoretical infinite molecular weight

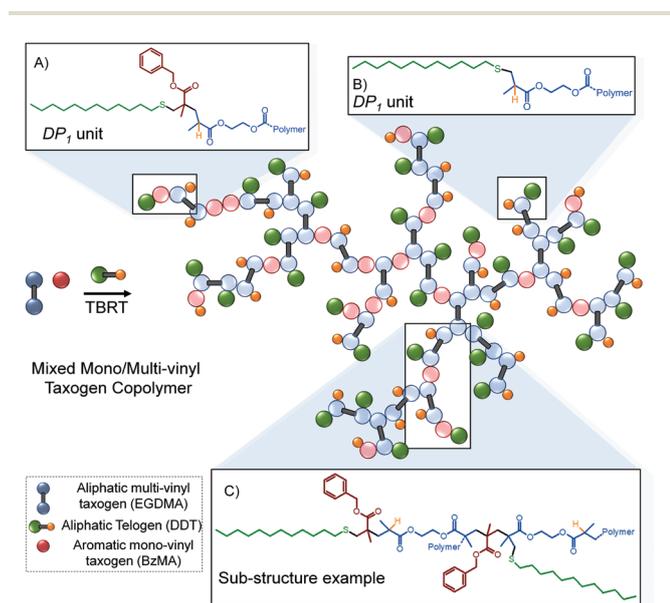


Fig. 6 Schematic representation of a mixed mono/multi-vinyl Taxogen TBRT Copolymer. (A) DP₁ substructure unit derived from *t*BuBzM-EGDMA reaction; (B) DP₁ substructure unit derived from DDT-EGDMA reaction; (C) Representation of highlighted sub-structure showing polyester backbone and variation of telogen derived pendant units.



or, experimentally, very high values of M_n (for reference, $T_{g\infty}$ is achieved at $M_n > 50\,000\text{ g mol}^{-1}$ for low dispersity linear polystyrene).⁶⁴ For polydisperse samples, this molecular weight dependence has been postulated to be better represented as inversely proportional to $(M_n \times M_w)^{1/2}$, as the presence of a high molecular weight fraction within the molecular weight distribution may dominate physical and thermal properties.⁶⁵ Additionally, modifications of relationships such as the Fox or DiMarzio-Gibbs equations, to take diad and triad sequences within statistical vinyl copolymers into consideration, have been required in order to explain well reported deviations from the predicted linear compositional relationships.⁶⁶

DSC analysis of the four TBRT homopolymers, Fig. 3 & 7A, synthesised here, showed significant T_g variation that appears to follow a rationale that combines the considerations from both conventional step-growth and chain-growth polymers, Table 1. Variation of telogen from DDT to *t*BuBzM shows an increase in observed T_g which is analogous to pendant group variation in chain-growth vinyl polymers, Table 1, with an increase of $>55\text{ }^\circ\text{C}$ in both cases of MVT. Additionally, variation of MVT from the flexible aliphatic EDGMA to the more rigid BPADMA, within the homopolymer backbone structures with each telogen, leads to an increase in T_g values of $>40\text{ }^\circ\text{C}$, Table 1, in a manner analogous to step-growth polymers.

Within the mixed telogen copolymers, DSC analysis of the $p([t\text{BuBzM-EGDMA}]\text{-stat-}[\text{DDT-EGDMA}])$ copolymer led to an observed thermal transition ($T_g = -1\text{ }^\circ\text{C}$) that lies approximately halfway between the two relevant homopolymer values namely $p(t\text{BuBzM-EGDMA})$ ($T_g = 28\text{ }^\circ\text{C}$) and $p(\text{DDT-EGDMA})$ ($T_g = -48\text{ }^\circ\text{C}$). This demonstrates thermal property modification in a manner that is analogous to chain-growth statistical copolymer strategies through variation in pendant group chemistry from a single backbone, Fig. 7B (Fig. S84†). Studies of the mixed telogen copolymer $p([t\text{BuBzM-BPADMA}]\text{-stat-}[\text{DDT-BPADMA}])$, containing the aromatic MVT, and hence a more rigid extended polyester backbone, also exhibited a thermal transition that lay between the two relevant homopolymer values ($T_g = 39\text{ }^\circ\text{C}$). In this case, the copolymer T_g is almost exactly at the midpoint value, Fig. 7B (Fig. S85†).

Our second copolymerisation strategy utilised mixed MVTs (single telogen) to influence backbone structure. DSC analysis of the two mixed MVT statistical copolymers yielded thermal transitions that, again, lay as intermediary values between the relevant homopolymers, Fig. 7C (Fig. S86 and 87†).

It is important to define the homopolymers that are relevant for comparison, and these are either $p(t\text{BuBzM-EGDMA})$ ($T_g = 28\text{ }^\circ\text{C}$) and $p(t\text{BuBzM-BPADMA})$ ($T_g = 69\text{ }^\circ\text{C}$) or $p(\text{DDT-EGDMA})$ ($T_g = -48\text{ }^\circ\text{C}$) and $p(\text{DDT-BPADMA})$ ($T_g = 11\text{ }^\circ\text{C}$) in each case.

In a similar manner to the mixed telogen copolymers, the predominantly aromatic architectures showed a near-perfect linear T_g variation with the $p([t\text{BuBzM-BPADMA}]\text{-stat-}[\text{tBuBzM-EGDMA}])$ copolymer T_g value ($48\text{ }^\circ\text{C}$) almost exactly at the midpoint of the two relevant homopolymer values, namely $p(t\text{BuBzM-EGDMA})$ ($T_g = 28\text{ }^\circ\text{C}$) and $p(t\text{BuBzM-BPADMA})$ ($T_g = 69\text{ }^\circ\text{C}$, Fig. S87†). The ability to readily influence the thermal

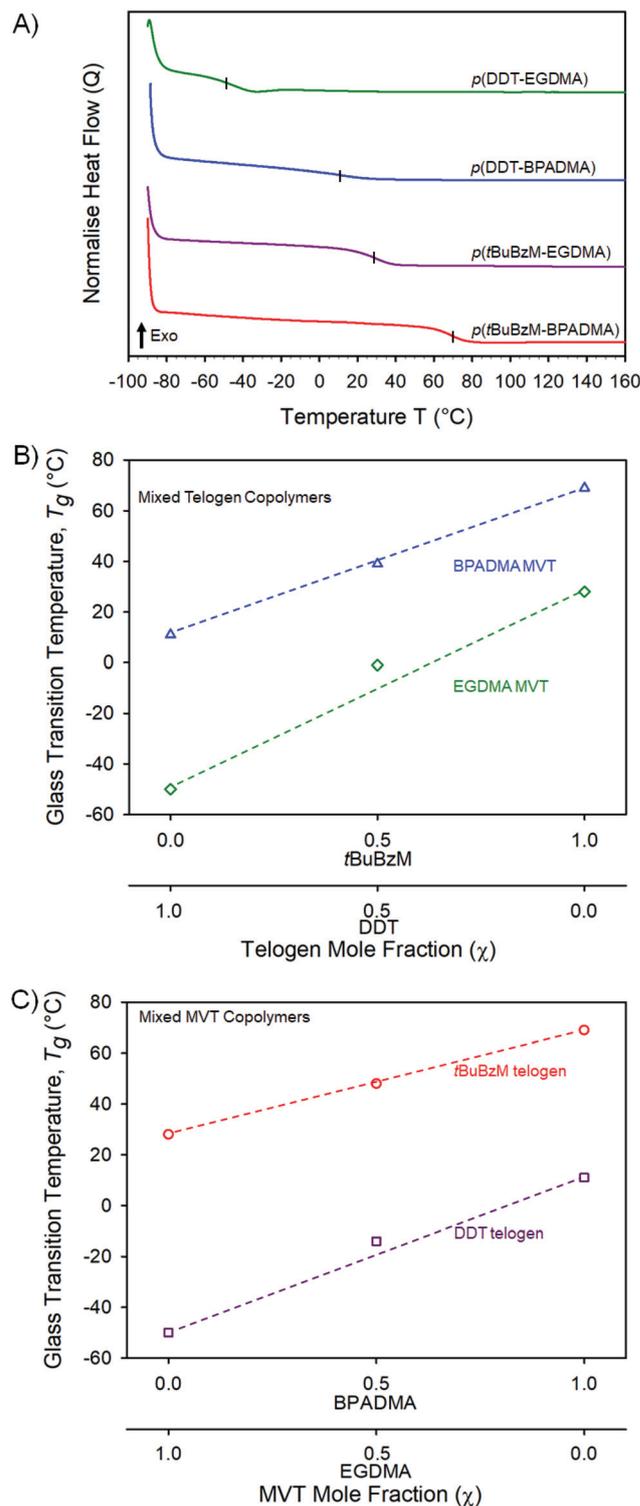


Fig. 7 Thermal analysis of homopolymers and copolymers synthesised using TBRT. (A) DSC thermograms of homopolymers; (B) comparison of T_g values of homopolymers and statistical copolymers derived using mixed telogens; (C) comparison of T_g values of homopolymers and statistical copolymers derived using mixed MVTs.



behaviour of branched polyesters *via* the judicious selection of telogen mixtures and/or backbone chemistries derived from MVTs is remarkable, especially using robust free radical telomerisation chemistries.

Finally, the inclusion of the mono-vinyl taxogen BzMA in the TBRT of a single MVT/telogen combination led to an increase in T_g values, as would be expected when viewing this approach as forming statistical copolymers with varying pendant groups. BzMA was specifically chosen as it would normally be expected to increase T_g , relative to a starting homopolymer with a low T_g value if included in a statistical chain-growth copolymerisation (Fig. S88†). Addition of another pendant group in this way would be expected to influence the thermal behaviour of copolymers.

The homopolymers that are relevant within this comparison are p(DDT-EGDMA) and p(*t*BuBzM-EGDMA). TBRT in the presence of an equimolar ratio of BzMA/MVT led to the formation of p([DDT-EGDMA]-*stat*-BzMA), with a 60 °C increase in T_g relative to p(DDT-EGDMA), and p([*t*BuBzM-EGDMA]-*stat*-BzMA) with a 5 °C increase in T_g relative to p(*t*BuBzM-EGDMA). The modified thermal behaviour is readily rationalised through considerations of significantly decreased free volume and increased restrictions to backbone mobility when BzMA repeat units are added to p(DDT-EGDMA). The additional pendant aromatic ring will hamper the mobility of the flexible aliphatic structure and the similarity of T_g values for p(*t*BuBzM-EGDMA) and p([DDT-EGDMA]-*stat*-BzMA) is noteworthy.

The much smaller increase in T_g when forming p([*t*BuBzM-EGDMA]-*stat*-BzMA) may indicate that the starting homopolymer p(*t*BuBzM-EGDMA) was already highly constrained by the presence of the *t*BuBzM pendant group derived from the telogen. A T_g value that was 76 °C higher than that of p(DDT-EGDMA) was already seen for p(*t*BuBzM-EGDMA) and the addition of further aromatic pendant groups was still able to increase this value by a further 5 °C.

All samples have broad dispersity, but it should be noted that a further sample of p(DDT-EGDMA) was isolated after repeated precipitation, with very high molecular weight. This fraction ($M_n = 1\,676\,000\text{ g mol}^{-1}$; $M_w = 10\,160\,000\text{ g mol}^{-1}$, Fig. S89†) was analysed by DSC and found to have a T_g value = -50 °C (Fig. S90†). This is almost identical to the thermal behaviour of the unfractionated p(DDT-EGDMA) with lower M_n (Table 1; $M_n = 19\,395\text{ g mol}^{-1}$). Additionally, the copolymer with the lowest M_n value (p([*t*BuBzM-EGDMA]-*stat*-BzMA)) exhibits a T_g value 81 °C higher than that of p(DDT-EGDMA) which would suggest very limited influence of the low molecular weight fraction within these samples. Despite the broad molecular weight distributions, the measured T_g values are expected to represent $T_{g\infty}$. It is also important to note that a single thermal transition was observed in all DSC analyses, Fig. 7 (Fig. S84–88 and S90†), suggesting that the structural and chemical modifications derived from the copolymerisation strategies are impacting the behaviour of the polymers homogeneously throughout the composition and no block-like or phase separated structures are present which may lead to

two or more T_g values.⁶⁷ To confirm this hypothesis, the blending of homopolymers was conducted and DSC analysis of a 1:1 blend of p(*t*BuBzM-EGDMA) and p(*t*BuBzM-BPADMA) showed two distinct T_g values that correlated directly with the values obtained for the pure homopolymers (Fig. S91†). This suggests that the homopolymers are not readily compatible and multiple transitions would be seen if the statistical copolymers were not homogeneous.

Conclusion

The formation of new polymer structures offers novel innovation opportunities within materials science and its applications. TBRT presents a new strategy for forming complex branched polymer architectures using a combination of free radical chemistries and the principles of telomerisation. We have shown here that the scope for copolymerisation is considerable even with a small number of taxogens and telogens. The copolymer strategies are easy to undertake as they utilise free radical C–C bond formation reactions and not step-growth techniques that would normally require considerable stoichiometric control and the elimination of small molecule by-products to drive the reaction to appreciable molecular weights. Unlike many branched vinyl polymerisations, the use of low molar ratios of mono-vinyl taxogens also opens considerable scope within commercially available monomer chemistries. Additionally, TBRT offers access to very high molecular weight branched homopolymers and copolymers, which are not readily available through other synthetic strategies.

We have chosen to present a relatively small number of example polymers to demonstrate the potential for the three copolymerisation strategies. Within these polymers, the variation and control of thermal properties is considerable and T_g values spanning nearly 120 °C were achieved. Remarkably, the correlation between T_g and copolymer chemical composition was highly uniform with linear, or near linear, relationships which suggest further opportunities to tune and possibly predict behaviour. A direct influence of MVT structure, and mole fraction within copolymers, on T_g may be considered predictable as backbone variation is expected to have a major influence on thermal properties; however, the direct relationship in these polymers would not have been obvious. Additionally, the considerable influence from mono-vinyl taxogen inclusion provides another variable within TBRT polymer design to direct the behaviour of the branched step-growth polymer backbones. More surprising is the close correlation with telogen structure in homopolymers, and telogen mole fraction in statistical copolymers, which strongly underlines the critical nature that the telogen plays in determining the properties of TBRT polymers. This also highlights the fundamental difference between TBRT and previous approaches that utilise telogens at low concentration and expect them to behave as trivial chain ends with little importance in final polymer structure or properties.



The materials chemical space and architectural variation available from TBRT approaches does place this chemistry as a new platform for materials scientists. There is still much to learn about TBRT including the impact of steric hindrance on chain transfer during the intermolecular branching reactions. As transfer is dominant and repeat unit structures are formed during the transfer reactions that occur throughout the polymerisation, access to unreacted vinyl groups would be expected to impact the growth of the final branched architectures. This may, potentially, already be indicated by the different outcomes when using DDT vs. *t*BuBzM under identical conditions of MVT, temperature and concentration. Future research will study routes to control dispersity to a greater extent; however, numerous industrial applications utilise polydisperse macromolecules and it is expected that synthesis optimisation will only be required in areas determined by a clear application or performance need.

Author contributions

SPR was responsible for grant funding, conceptualisation of the original research programme, supervision, writing of the original draft, editing and review. PC contributed to supervision, formal analysis, validation, and manuscript review. SRC and SF contributed to experimentation, data curation, formal analysis and manuscript review.

Conflicts of interest

The authors are co-inventors on patents that protect the TBRT chemistry; these patents have been licensed to Scott Bader and form the basis of Polymer Mimetics Ltd (Company number 12598928).

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