

Transfer-dominated branching radical telomerisation (TBRT): studying the impact of multi-vinyl taxogen dimensions on the branching behaviour of high molecular weight polymers

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The creation of complex macromolecular architectures *via* branching polymerisation strategies offers opportunities for innovation through the formation of polymers with novel physical and chemical behaviour. Transfer-dominated branching radical telomerisation (TBRT) employs conventional free radical chemistries to achieve the homopolymerisation of multi-vinyl taxogens (MVTs) to high vinyl conversion (>99%) by including an excess of thiol-based telogen to enforce telomerisation conditions upon the system. This dominant chain transfer mechanism effectively restricts the telomeric number-average degree of polymerisation and affords polymers with taxogen and telogen-derived functionality pervading throughout the macrostructure. It follows that the outcomes of TBRT are highly dependent on the selection of the MVT and telogen.

Here, the impact of MVT dimensions on hyperbranched polymers formed *via* TBRT is examined. A series of branched polymers has been prepared using three chemically comparable MVTs with varying physical dimensions. Initial polymerisations, conducted under identical reaction conditions, present starkly contrasting gelation behaviours with varying taxogen dimensions. Through a series of model reactions, the intimate branching behaviour of the MVTs is investigated. Kinetic studies and Mayo experiments highlight variations in the chain transfer ability of a common telogen with each MVT, leading to notable differences in the primary chain length of sub-structural telomers within each polymer. However, the telomeric primary chain length is found not to correlate with trends in gelation behaviour, exposing a more dominant factor: the physical dimensions of the MVT. With the aid of a ‘transfer perimeter’ model, supported by TD-SEC and NMR analyses, the dimensions of the MVT is proposed to alter the branching efficiency of the MVT through changes to the molecular volume of polymers formed, and by shifting the balance of intermolecular and intramolecular branching processes during TBRT.

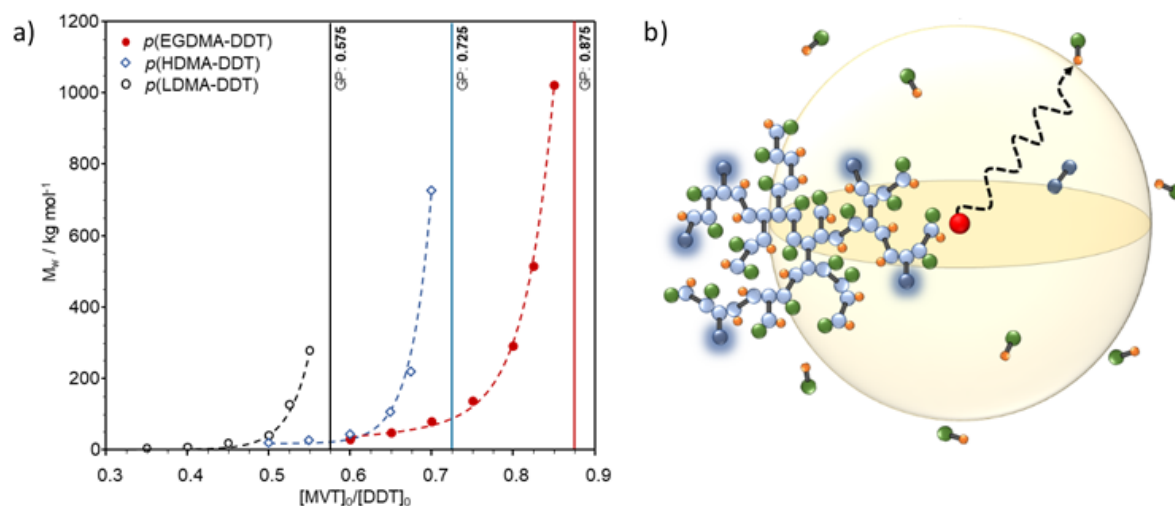


Figure 1 a) The evolution of weight-average molecular weight with varying feedstock $[MVT]_0/[DDT]_0$ ratio. b) Schematic representation of the ‘transfer perimeter’ model.

