

## Preparation of Hyperbranched and Star Polymers by a “Living”, Self-Condensing Free Radical Polymerization

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Free radical polymerization remains one of the most widely used carbon–carbon bond-forming industrial processes, with millions of tons of polymers being produced annually. Unlike other vinyl polymerizations, it can be used with a broad variety of monomers and is also synthetically much less demanding than anionic or cationic processes. Despite these advantages and its tremendous commercial significance, free radical polymerization still lacks versatility in terms of its ability to control polymer architecture. Recent advances in “living” free radical polymerizations,<sup>1</sup> notably the work of Georges et al., have allowed the preparation of narrow polydispersity linear polymers and some block copolymers, but dendritic structures such as hyperbranched polymers have remained elusive.

This is unfortunate since 3-dimensional dendritic polymers,<sup>2</sup> such as dendrimers and hyperbranched polymers, have been noted for their unusual properties.<sup>3</sup> Their shape- and functionality-related properties<sup>4</sup> can be exploited to design materials that have unique viscoelastic properties,<sup>5</sup> can form unusual blends,<sup>6</sup> or even act as size- and shape-selective carrier molecules.<sup>7</sup> In this report, we detail the first approach to hyperbranched and other complex macromolecular architectures based on living free radical polymerizations. This work is based on two recent developments in vinyl polymerizations. The first is the discovery by Hawker<sup>8</sup> that well-defined unimolecular initiators can be used to initiate radical polymerizations with accurate control over molecular weights and chain ends.<sup>8,9</sup> The second is the report by Fréchet et al.<sup>10</sup> of a novel “self-condensing” vinyl polymerization which, under cationic conditions, affords hyperbranched polymers with a broad polydispersity.

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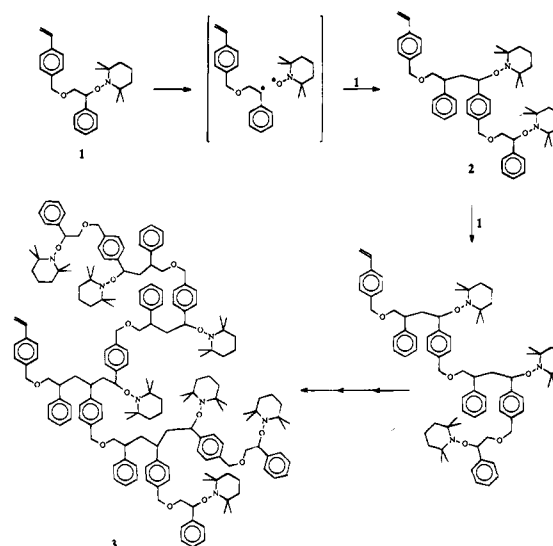
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### Scheme 1



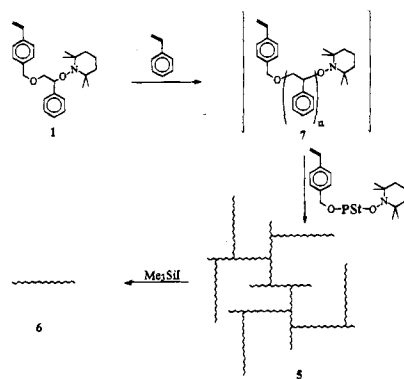
Our approach, which combines the two concepts, significantly extends their usefulness because it involves highly controlled and experimentally forgiving living free radical processes while providing facile access to a variety of previously inaccessible molecular architectures derived from commodity vinyl monomers.

To test our design for the preparation of hyperbranched polymers by living free radical polymerization, the monomer **1** was selected as starting material.<sup>9</sup> The structure of **1** is interesting since it contains a polymerizable styrene group and an initiating/propagating moiety consisting of a nitroxide linked to a substituted benzylic carbon atom. Because of the low bond dissociation energy of the carbon–oxygen bond linking the nitroxide group to the **1**, thermal activation of the self-condensing free radical polymerization is possible.<sup>11</sup> In such a process, thermolysis of **1** leads to a propagating benzylic radical, which can add to the vinyl group of a second molecule of **1** to afford the dimer **2** after thermally reversible recombination with the otherwise inactive TEMPO “counter” radical. The dimer **2** is now an AB<sub>2</sub> monomer with one polymerizable double bond and two initiating/propagating sites. Further additions involving **2** and other molecules of **1**, **2**, or oligomers proceed to form higher oligomers and finally the hyperbranched polymer **3**, which contains a single vinyl group (Scheme 1). As the concentration of vinyl groups decreases, the rate of polymerization also decreases; however, the hyperbranched product **3** remains living, as the reactivity of its numerous terminal benzylic nitroxide moieties is retained. Overall, the polymerization involves the stepwise coupling of monomers and oligomers, a process that is typical of polycondensation reactions, yet it proceeds by living free radical vinyl chemistry.

The polymerization of the self-condensing monomer **1** was conducted using bulk polymerization conditions at 130 °C under argon for 72 h. Close monitoring of this polymerization by size exclusion chromatography (SEC) at various stages during the reaction support the hybrid polycondensation and living free radical vinyl polymerization mechanism shown in Scheme 1. In the initial stages of the reaction, a gradual buildup of dimer, trimers, tetramers, etc. is observed, and as time progresses, these oligomers decrease in concentration and a corresponding increase in polymeric material is observed; thus, molecular weight evolves with conversion in a step growth pattern. Precipitation of the reaction mixture after 72 h gave the hyperbranched macromolecule **3** as a light yellow solid in 51%

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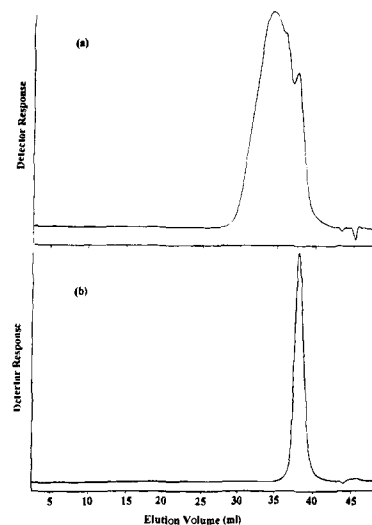
## Scheme 2



yield which was shown to have a polystyrene equivalent molecular weight,  $M_w$ , of 6000 (PD = 1.40) and a glass transition temperature of 45 °C. Significantly, no insoluble or cross-linked material was observed, which provides further support for the absence of significant termination reactions in living free radical polymerizations mediated by nitroxides. The structure of the hyperbranched macromolecule 3 was confirmed by a combination of infrared and <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

The presence of bound nitroxide functionalities at the chain ends of 3 affords interesting opportunities for the preparation of alternate molecular architectures such as hyperbranched stars. In this process, the living chain ends are used to initiate the polymerization of vinyl monomers, such as styrene. Hyperbranched macromolecules, such as 3, can therefore be thought of as multifunctional hyperbranched initiating cores for the formation of multiarm star polymers. To demonstrate the feasibility of this approach, the bulk polymerization of 3 with styrene (300 equiv per chain end) was conducted at 130 °C. Again no evidence of cross-linking was observed, and a soluble hyperstar macromolecule 4 was obtained in 88% yield after purification. As expected, the molecular weight increased substantially, from  $M_w$  = 6000 (PD = 1.40) for the starting hyperbranched macromolecule 3, to  $M_w$  = 300 000 (PD = 4.35) for 4. This demonstrates that the chain ends of 3 can initiate the polymerization of vinyl monomers to give hyperstar macromolecules 4. The number of arms in 4 varies due to the polydisperse nature of 3, and this results in the observed increase in polydispersity. Examination of the <sup>1</sup>H and <sup>13</sup>C NMR spectra of 4 showed the expected resonances for the polystyrene arms, and exchange of deuterated styrene for styrene in the above reaction allowed the presence of the hyperbranched core in 4 to be confirmed. Because the monomer 1 includes a cleavable benzyl ether group, further insight into the presence and nature of the branching in 4 and the polydispersity of the introduced arms can be gained by cleavage of the hyperstar at its branch points. This is accomplished using trimethylsilyl iodide, and analysis of the cleaved material showed a decrease in the molecular weight of the polymer, from  $M_w$  = 300 000 (PD = 4.35) for 4, to  $M_w$  = 65 000 (PD = 1.57) for the cleaved product.

The ability to use living free radical polymerization to form complex polymeric architectures can also be extended to the formation of polymers with controlled branch densities and lengths. This is achieved by copolymerization of vinyl monomers with specific amounts of monomers, such as 1, which act as both the initiating group and branch points in the final macromolecule. To demonstrate this concept, the living free radical polymerization of 1 with 25, 50, and 100 equiv of styrene was performed under the conditions defined above. In each case, a high yield of polymer 5 was obtained (>85%), with no evidence of cross-linked or insoluble material (Scheme 2). <sup>1</sup>H NMR spectroscopy allowed the presence of repeat units derived from 1 to be confirmed, and their level of incorporation was essentially the same as the feed ratio. GPC analysis of the



**Figure 1.** Comparison of GPC traces for the branched polymer 5 (a) from the reaction of 1 and styrene (100 equiv) with the cleaved product 6 and (b) after reaction with trimethylsilyl iodide.

polymers showed a regular increase in molecular weight with increasing number of equivalents of styrene, which is consistent with a larger number of repeat units between the branch points. For the reaction involving 100 equiv of styrene, the polystyrene equivalent  $M_w$  was found to be 54 000 (PD = 2.45). Again, the presence and nature of the branching can be examined by cleavage of the benzyl ether linking groups of 5 with trimethylsilyl iodide. Interestingly, for each of the above copolymer ratios, a similar picture of the polymerization process emerged from an analysis of the cleavage results. In each case, the cleaved product was found to have a very low polydispersity (1.1–1.2), with a molecular weight similar to that expected from the ratio of 1 to styrene. For example, the molecular weight of the 1:100 branched copolymer 5 decreased from  $M_w$  = 50 000 (PD = 2.45) to  $M_w$  = 11 000 (PD = 1.17) for the cleaved product 6 (Figure 1). These results correlate with the *in situ* generation of macromonomers, such as 7, which contain a polymerizable styrene group and a propagating nitroxide group at the chain ends. As the reaction proceeds, coupling of these macromonomers with each other and any remaining monomer leads to the branched polymer 5. The independent nature of these propagating chain ends and the uniformity of the linear polymer segments is demonstrated by the very low polydispersity of the cleaved polystyrene 6 and the close agreement of the experimentally determined molecular weight,  $M_n$  = 9500 for 6, with the theoretical value of 10 500.<sup>12</sup>

Because the control of the ultimate physical and chemical properties is so important for the practical use of commodity polymers, the self-condensing living free radical chemistry we have described significantly expands the usefulness of free radical polymerization techniques and the range of dendritic structures which can be produced. It is likely that the high functionality and desirable physical properties of hyperbranched polymers, combined with the robustness and ease of polymerization of vinyl monomers, will make this new approach attractive for the preparation of novel materials. We are currently extending this concept to other reactive processes and monomers, as well as other copolymers with branched architectures.

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(12) Theoretical value calculated from ratio of initiator and monomer, assuming no branching or coupling reactions.