

## Synthesis of Branched and Hyperbranched Polystyrenes

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Dendrimers have recently received much attention as materials with novel physical properties.<sup>1,2</sup> These polymers have viscosities lower than linear analogs of similar molecular weight, and the resulting macromolecules can be highly functionalized. However, because the synthesis of dendrimers is not trivial and requires multistep syntheses, their commercial development has been limited to only a few structures.

The synthesis of hyperbranched polymers has been explored to develop dendritic molecules in a single, one-pot reaction. These polymers are obtained by the reaction of AB<sub>2</sub> monomers in which A and B are functional groups capable of reacting with each other to form stable bonds. Because of the AB<sub>2</sub> structure, reaction between two monomers results in the formation of a dimer with one A group and three B groups. This process repeats itself by reaction with either monomer, dimer, trimer, etc., as in step-growth polymerizations. The resulting macromolecules have one A group and  $n + 1$  B groups, where  $n$  is the number of repeat units. Although these dendritic polymers are highly functionalized like dendrimers, they are of irregular shapes, not perfectly symmetrical as dendrimers are. The irregular structure is due to uneven growth of the macromolecule in various directions. Consequently, hyperbranched polymers have some of the qualities of dendrimers but also lack some properties of perfect dendrimers. Polymers consisting of hyperbranched phenylenes,<sup>3–5</sup> aromatic esters,<sup>6</sup> aliphatic esters,<sup>7</sup> siloxanes,<sup>8</sup> amines,<sup>9</sup> and liquid crystals<sup>10</sup> have been synthesized in the past few years.

Recently, Frechet has described a method by which functionalized vinyl monomers could be used to synthesize hyperbranched polymers with a carbon backbone by a cationic polymerization.<sup>11</sup> In the method described by Frechet, 3-[(1-chloroethyl)ethenyl]benzene was used as the monomer and was cationically polymerized in the presence of SnCl<sub>4</sub>. The monomer satisfies the AB<sub>2</sub> requirements for formation of hyperbranched polymers as the vinyl group acts as the difunctional B group and an additional alkyl halide functional group acts as the A group. By activation of the A group, by the Lewis acid, polymerization through the double bond occurred cationically.

This process differs from previous syntheses of hyperbranched polymers in two ways. The first is that the resulting functional groups in the macromolecule are described by the formula A<sub>*n*</sub>B<sub>2</sub>, where  $n$  is the number of repeat units in the polymer. Secondly, the backbone of the macromolecule is made up entirely of carbon atoms; there are no heteroatoms resulting from condensation reactions, as in previously described syntheses of hyperbranched polymers.

In this communication, we describe the formation of hyperbranched polymers by a one-pot, atom transfer radical polymerization (ATRP),<sup>12,13</sup> using commercially

available, *p*-(chloromethyl)styrene (CMS), in the presence of Cu(I) and 2,2'-bipyridyl (bpy). The synthesis of branched polystyrene by copolymerization of CMS (2%) with styrene will also be discussed.

The homopolymerization<sup>14</sup> of CMS, by ATRP, was performed with CMS acting as both initiator and monomer. The chlorine atom at the benzylic position is abstracted by Cu(I) homolytically, forming Cu(II)Cl and a benzyl radical capable of initiating the polymerization of monomer through the double bonds, Scheme 1. The propagating chain is reversibly deactivated by Cu(II)Cl. This results in the formation of a polymer chain with pendent groups consisting of *p*-benzyl chloride, with a double bond at one chain end and a chlorine atom at the other. Both of these chlorine atoms can be abstracted to form radicals which can reinitiate the polymerization.

The double bond at the chain end can be incorporated into a growing polymer chain, resulting in a branch point. Incorporation of polymer chains into one another results in molecular weight growth similar to step-growth polymerizations. That is, each of the polymer chains can react with monomers, dimers, trimers, etc.

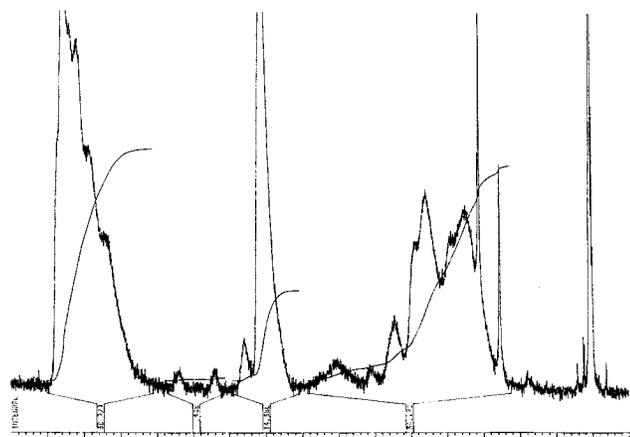
The amount of Cu(I) used in the homopolymerizations was 1 mol % relative to CMS. Increasing the amount of Cu(I) resulted in an acceleration of the polymerization. If greater than 10 mol % Cu(I) was used, the reaction mixture became a gel within 30 min and a hard insoluble solid at longer reaction times. The higher [Cu(I)] leads to an increase in [R<sup>•</sup>] and results in bimolecular coupling, yielding a cross-linked polymer. This supports a radical mechanism for ATRP as opposed to a transition metal mediated insertion mechanism.

According to the process described above, each polymer chain should have one double bond and a number of chlorine atoms equal to the number of repeat units. Two sets of signals are observed in the <sup>1</sup>H NMR spectra, Figure 1. The first set of signals, at 5.2 and 5.7 ppm, arises from the two methylene protons of the remaining double bond; the methine proton absorbs at ≈6.6 ppm and is obscured by the signal from the aromatic protons. The second set of signals is due to the methylene and methine protons adjacent to the chlorine atoms, 4.3–4.9 ppm. The peak is broad due to the various microstructures of the polymer.

By comparison of the integration of the signals from the double bond to those of the aromatic region, one can determine the number of aromatic rings per unreacted double bond. Assuming that there is one double bond per polymer chain, this provides the degree of polymerization.

The ratio of the integration of the signals attributed to the CH<sub>*n*</sub>-Cl protons to that of the aromatic protons provides some information as to the degree of branching. This ratio should be 2:4 for linear poly(CMS) prepared by conventional radical polymerization and 1.5:4 for a perfect dendritic structure. The experimentally observed ratio of 1.6:4 indicates an imperfect structure. However, due to the various possible structures in the macromolecules, the precise determination of the degree of branching has not yet been successful and requires detailed NMR studies, which are in progress.

Table 1 lists results obtained by homopolymerization of CMS by ATRP. Both bulk and solution homopolymerizations gave hyperbranched polymers in high yield. <sup>1</sup>H NMR indicates higher values of molecular weight than GPC, confirming a hyperbranched structure.



**Figure 1.**  $^1\text{H}$  NMR spectrum of homopolymerization of CMS.  $M_n = 6280$  ( $^1\text{H}$  NMR),  $M_n = 2510$  (GPC).

Instead of hyperbranched homopolymers, branched copolymers can be synthesized by copolymerization of CMS with styrene (Sty), by ATRP.<sup>15</sup> The degree of branching can be controlled by adjusting the amount of CMS used and the reaction time. The subsequent discussion covers the copolymerization system.

In the presence of Cu(I), CMS initiates the polymerization of styrene, similar to the manner described above. Because the growing polystyrene has a double bond at the chain end, it can also be incorporated into another growing macromonomer, forming a branch point. Thus, the growing chain can either add additional monomer units or other chains of polystyrene.

In the early stages of the copolymerization, the growth of molecular weight is linear with conversion, which is consistent with a "living" linear polymerization, Figure

**Table 1. Homopolymerization of *p*-(Chloromethyl)styrene in the Presence of Cu<sup>I</sup>Cl and 2,2'-Bipyridyl<sup>a</sup>**

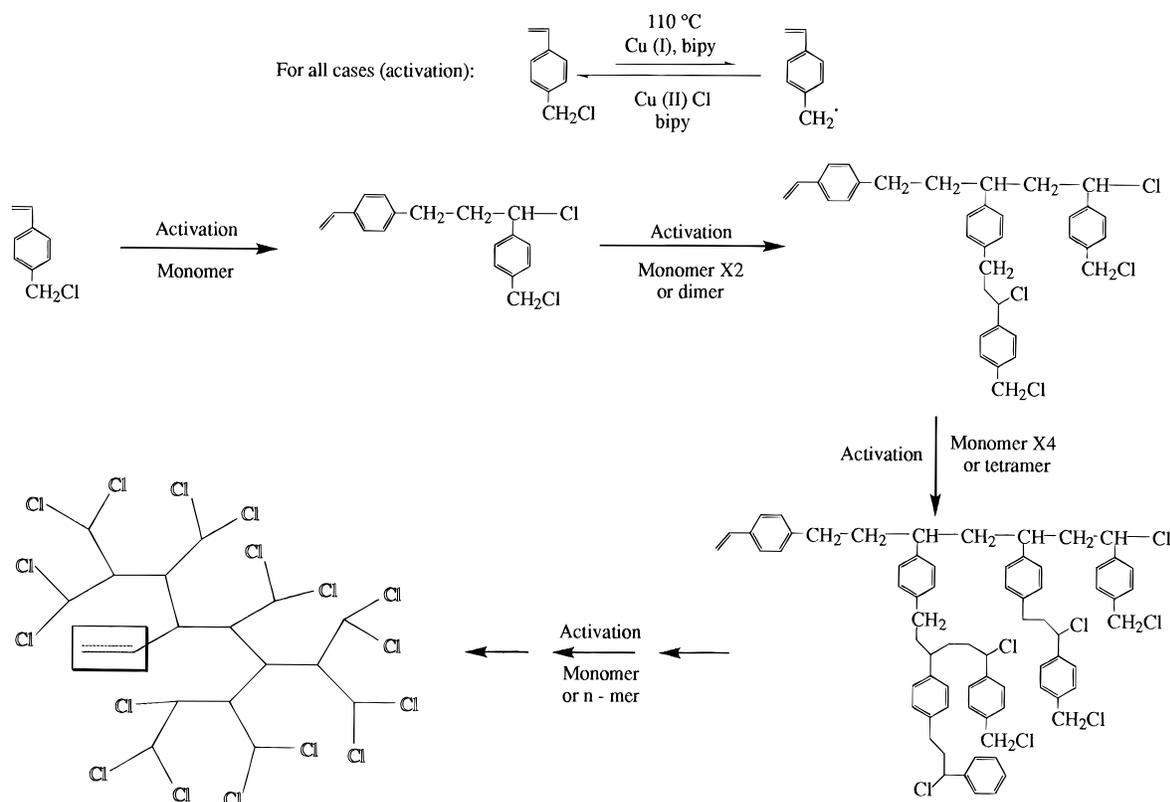
temp (°C)	time (h)	conversion (%) <sup>c</sup>	$M_n^d$	$M_n^e$	$M_w/M_n^e$	$M_n^f$
125	0.5	67	1900	1160	1.8	1070
	1.0	75	2250	1780	2.1	1870
	1.5	90	2940	2410	2.1	2480
	2.0	92	6280	2510	2.5	2750
110 <sup>b</sup>	24.0	96	2420	2100	1.3	

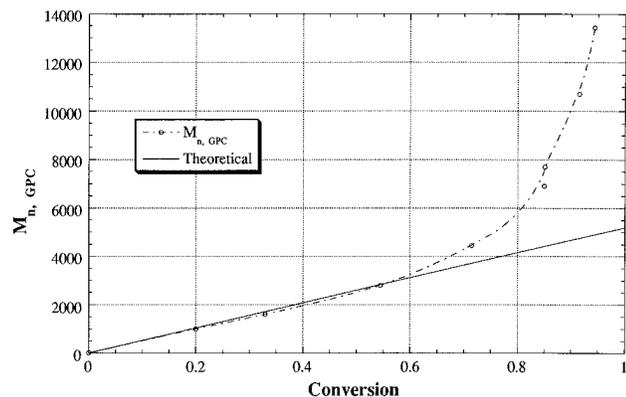
<sup>a</sup> Bulk polymerization,  $[M]_0 = 7.04$  M,  $[\text{CuCl}]_0 = 0.07$  M,  $[\text{bpy}]_0 = 0.21$  M. <sup>b</sup> Solution polymerization in benzene,  $[M]_0 = 3.52$  M,  $[\text{CuCl}]_0 = 0.035$  M,  $[\text{bpy}]_0 = 0.11$  M. <sup>c</sup> Conversion based on consumption of double bonds in the reaction mixture observed by  $^1\text{H}$  NMR. <sup>d</sup>  $M_n$  determined by  $^1\text{H}$  NMR after precipitation. <sup>e</sup>  $M_n$ ,  $M_w$  determined of entire sample, prior to precipitation, by GPC, using linear polystyrene standards. <sup>f</sup>  $M_n$  by GPC, using linear polystyrene standards, after precipitation into methanol/brine.

2. It appears that the polymer chains are not significantly incorporated into each other until later in the polymerization, where there is a significant deviation from the theoretical dependence,  $\text{DP} = \Delta[\text{Sty}]/[\text{CMS}]_0$ . This deviation reflects consumption of the double bonds at the chain end. Thus, the number of chains is significantly less than  $[\text{CMS}]_0$ .

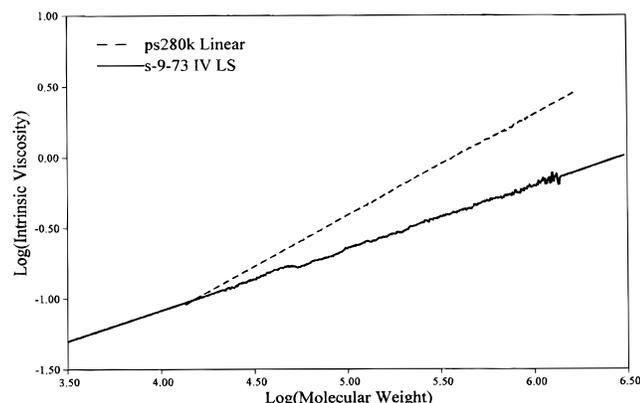
Further proof that the polymer is branched is provided by in-line light scattering and viscometry measurements.<sup>16</sup>  $M_n$  and  $M_w$ , of the final sample, as determined by viscosity measurements and light scattering, were 31 600 and 164 500, respectively. These values are in contrast to the values obtained by GPC, with calibration based on linear polystyrene standards, which gave values of 13 400 and 75 000 for  $M_n$  and  $M_w$ . This discrepancy is expected as the branched polymers should have smaller hydrodynamic volumes than a linear polymer of similar molecular weight and compo-

**Scheme 1. Schematic of the Homopolymerization of CMS by Atom Transfer Radical Polymerization To Form a Hyperbranched Polymer**





**Figure 2.**  $M_{n, \text{GPC}}$  dependence versus conversion for copolymerization of Sty and CMS.  $[\text{Sty}]_0 = 4.37 \text{ M}$ ,  $[\text{CMS}]_0 = 0.087 \text{ M}$ ,  $[\text{Cu}^{\text{I}}\text{Cl}]_0 = 0.087 \text{ M}$ ,  $[\text{bpy}]_0 = 0.26 \text{ M}$ , temperature =  $130 \text{ }^\circ\text{C}$ .



**Figure 3.** Mark-Houwink plots of a broad, linear polystyrene standard, ps280k linear, and branched polystyrene, S-9-73 IV LS.

sition, resulting in longer retention times and, therefore, a lower apparent molecular weight. The broad polydispersities are most likely due to the incorporation of the long polymer fragments into propagating chains, as observed previously.<sup>11</sup> That is, the system begins to behave in a manner similar to step-growth polymerizations, where  $n$ -mers can react with  $m$ -mers to form polymers with  $(n + m)$  repeat units, resulting in higher polydispersities.

A Mark-Houwink<sup>16</sup> plot for the final product, Figure 3, shows that the branched polystyrene has a lower intrinsic viscosity than a linear polymer of similar molecular weight. This supports a branched structure, because branched polymers have lower viscosities than linear analogs of similar molecular weight.<sup>17</sup> The average number of branches per polymer chain was calculated to be 25.

In conclusion, a facile synthesis of highly branched polymers containing a number of functional groups equal to the degree of polymerization has been demonstrated by the ATRP of CMS. In addition, the copolymerization of Sty and CMS has afforded a branched polystyrene, as evidenced by light scattering and viscosity measurements.

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- (14) *Homopolymerization of CMS.* CMS was polymerized in the presence of Cu(I)Cl (1% relative to CMS) and bpy (3%), at  $110 \text{ }^\circ\text{C}$ , under oxygen free conditions, i.e., argon atmosphere. CMS was added to a flask containing Cu(I)Cl/bipyridyl. Immediately upon addition of CMS, a deep red, slightly heterogeneous mixture was obtained. Heating resulted in the color of the solution changing from red to green within 15 min of heating. After 2 h the reaction was stopped and the sample dissolved in THF. Conversion was determined by  $^1\text{H}$  NMR. The samples showed almost no observable change in viscosity at the reaction temperature, but cooling to room temperature resulted in solidification of the sample. The green copper(II) material was removed by passing through a column of alumina. Unprecipitated samples were injected into the GPC for analysis. The polymer was then purified by precipitation into methanol/brine from THF. These samples were then analyzed by  $^1\text{H}$  NMR to determine molecular weight.
- (15) *Copolymerizations of CMS and Styrene.* The monomers were degassed prior to the reaction by bubbling argon through the monomer. The reactions were carried out in 50% (w/vol) solutions using *p*-dimethoxybenzene as the solvent. The ratio of styrene:CMS:Cu(I)Cl:bpy was 50:1:1:3. The solids were placed in a flask with a rubber septum and magnetic stirrer and degassed three times by pulling a vacuum and back-filling with argon. Monomer was added via syringe. The appropriate amount of CMS was then added via syringe. The reaction was heated to  $130 \text{ }^\circ\text{C}$ , and samples were removed at various times by syringe. The samples were evaluated by GC and GPC for conversion and molecular weights, respectively. The reaction was quenched by precipitation into methanol.
- (16) Light scattering measurements, viscometry measurements, and the calculation of the average number of branches per macromolecule were performed by Viscotek Corp., using their SEC<sup>3</sup> technology.
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