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Communications

Hyperbranched Polymers Containing Cyclopentadienyliron Complexes

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A number of hyperbranched polymers containing cyclopentadienyliron moieties were prepared using the $A_2 + B_3$ method. The A_2 compounds used were common diols, dithiols or dichloroarenecomplexes. B_3 compounds included either prepared star-shaped molecules or a purchased triol. The effect of the reaction conditions on the properties of the products was probed. Analysis of the prepared polymers was conducted using ^1H and ^{13}C NMR, viscometry, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Viscometry values were generally found to be low, in the range of 0.175–0.300 dl/g. TGA showed losses starting at approximately 230°C and ending at 280°C, corresponding to the decomposition of the cyclopentadienyliron moiety. Degradation of the polyether backbone was found to occur starting at 390–567°C. Glass transition temperatures were found to be between 60 and 134°C, whereas melting temperatures ranged from 155 to 190°C.

KEY WORDS: Cyclopentadienyliron; hyperbranched polymers; nucleophilic aromatic substitution; star-shaped molecules; thermal properties.

1. INTRODUCTION

The theoretical foundations of hyperbranched polymers were laid out by Flory in a series of articles published in the 1940s and early 1950s [1–6]. Synthetic preparation of these polymers was not thoroughly investigated until the late 1990s [7,8]. Industrially these polymers are preferred over dendrimers due to the ease of synthesis [7]. Most hyperbranched polymers are organic in nature and prepared from an AB_x monomer.

A common method to prepare hyperbranched polymers is to use a self-polymerizable monomer with two different functional groups such as an AB_2 monomer [6–23]. This method is preferred even though most AB_x monomers are not commercially available [7]. This synthesis requires that (a) no side reactions occur, (b) no intramolecular cyclizations occur and (c) that the B groups are of equal reactivity [7,9,24].

Another method for hyperbranched polymer synthesis is to polymerize two monomers of different functionalities, namely an $A_2 + B_x$ polymerization [1–5,7,24–34]. This has the advantage of readily available starting materials, although gelation or a 3-D network occurs when high conversion has been reached [1–7,9,24–27].

Other methods of forming hyperbranched polymers have also been investigated such as: $AB_2 + AC_2$ [35], $AB_2 + AB$ [36], $A_2 + BB_2$ [25], polycyclotrimerization [37], self-assembly [23,38], self-condensing vinyl polymerization (SCVP) [8,9,39], and ring opening multi-branched polymerization (ROMBP)

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[7,8,40]. The amount of intramolecular cyclization has been shown to decrease via the usage of 4,4-bis-(4-hydroxyphenyl)valeric acid [7]. As a result, statistical hyperbranched growth is more likely to occur [7].

Characteristics commonly associated with hyperbranched polymers prepared by the AB_2 method are: high solubility, thermal stability, irregular structure, low viscosity, lack of chain entanglements, globular shape, and a lack of crystallization [8,9]. Hyperbranched polymers from the $A_2 + B_3$ method share the same characteristics with the omission of low viscosity [24]. High viscosities have been found in some cases for unknown reasons. The viscosity of hyperbranched polymers has been shown to increase with increasing molecular weight [1,24]. Multiplication of NMR peaks is also common due to the presence of terminal, linear and branching units.

The degree of branching (DB) is a parameter that may be calculated for hyperbranched polymers according to the following [7–10,14,17,24,26, 31, 35]:

$$\mathrm{DB} = \frac{D+T}{D+T+L} = \frac{2T}{D+T} \qquad (1)$$

where D, T and L refer to the amount of the polymer in the dendritic, terminal and linear form respectively. The DB is used as an indicator of the amount of branching [7,9], where dendrimers have $\mathrm{DB} = 1$ and linear polymers have a $\mathrm{DB} = 0$.

In examples of hyperbranched polymers prepared by the SCVP and the AB_2 method, the glass transition temperature (T_g) has been shown to increase with lower molecular weight and decrease with branching and conversion [41]. This is due to the globular, entanglement free nature of the hyperbranched polymer [41]. The opposite trend has been noticed for liquid crystal hyperbranched polymers [36]. The T_g has also been related to molar mass, where oligomers have shown a large increase in T_g as their molecular weight increased [15,31]. At a certain molecular weight, however, there was little change in the glass transition temperature [15,31]. In some cases, lack of glass transition and melting temperatures has been noted [18,31].

Applications of hyperbranched polymers include: coatings, crosslinking and melt additives, nanoporous materials, catalysis, and soluble functional supports [7,9]. The incorporation of metals into hyperbranched polymers has not been widely accomplished [23,27,28,34,38].

Cyclopentadienyliron complexes have been used to activate aromatic compounds towards nucleophilic substitution reactions [42,43]. As a result, common etherification reactions using cyclopentadienyliron complexes have been conducted at room temperature or at 60°C. Decomplexation of the metal occurs at higher temperatures [43–45]. Removal of the metal has also been achieved via photolysis [46–49]. Thermal stability of the cyclopentadienyliron complex in linear polymers has been reported in the range of 210–250°C, whereas for star-shaped molecules it was in the range of 205–285°C [44,47–51]. Linear polymers had T_g's between 140 and 180°C and star-shaped molecules were between 120 and 200°C [44, 47,48,51]. Melting points for cyclopentadienyliron based compounds have not been observed.

Within this paper the influence of the mode of synthesis and the variation of starting materials will be investigated for organoiron hyperbranched polymers prepared by the $A_2 + B_3$ method. Differences, or lack thereof, imparted by experimental changes were explored using ^1H and ^{13}C NMR, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) as well as viscometry.

2. EXPERIMENTAL

2.1. Characterization

Solution-phase ^1H and ^{13}C NMR spectra were collected using a Gemini 200 NMR spectrometer (200 and 50 MHz, respectively) and a Bruker Avance DXP300 (300 and 75 MHz, respectively). Solvent residues were used for reference and reported values were collected on a Gemini 200 NMR unless otherwise stated. Solid-state ^{13}C NMR was done on a Varian Inova 600, with magic-angle spinning (MAS) at 20 kHz in a 3.2 mm rotor. C-13 chemical shifts are reported relative to TMS, using external adamantane as a secondary reference. Chemical shifts were calculated in ppm and J couplings were calculated in hertz (Hz). Thermogravimetric analysis was performed with a Mettler TGA/SDTA851^e using a heating rate of 20°C/min under a flow of nitrogen. Differential scanning calorimetry was executed using a Mettler 821^e at a heating rate of 20°C/min under a flow of nitrogen. Viscometry was measured using a Brookfield Model DV II + Viscometer at 100 rpm with a UL adapter set to 25°C in dimethylsulphoxide (DMSO). Molecular weights of the hyperbranched polymers were calculated from the viscosity data and are relative to star-shaped cyclopentadienyliron containing macromolecules [51] of known molecular weights.

2.2. Materials

Complexes **2**, **3**, **8**, **18** were synthesized according to our previously established methods [42,50,51]. Hydroquinone (**9**), 4,4-bis-(4-hydroxyphenyl)valeric acid (**10**), bisphenol A (**11**) and 4,4′-thiobisbenzenethiol (**12**) were purchased from Aldrich. Phloroglucinol (**1**) was purchased from Fluka. Solvents were HPLC grade. All purchased chemicals and solvents were used without purification.

2.3. Synthesis and Characterization

*2.3.1 Synthesis of Polymers **4a**, **5a**, **13a**, and **19a***

In a 25 ml round bottom flask, 0.5 mmol A_2 to 0.5 mmol B_3 in 5 ml of room temperature dimethylformamide (DMF) and 2 mmol of potassium carbonate (K_2CO_3) were stirred under inert atmosphere for 16 h, shielded from light. After the addition of the reaction mixture to an HCl solution (10% aqueous), ammonium hexafluorophoshate (NH_4PF_6) was added. The precipitate was collected in a sintered glass crucible, washed with water and allowed to dry under reduced pressure, covered from light.

4a: Yield: 80% ^{1}H NMR (DMSO-d_6, δ): 5.19, 5.21, 5.26 (s, Cp), 6.07–6.84 (br. m, complexed Ar, Ar), 9.81 (s, OH). ^{13}C NMR (300 MHz, DMSO-d_6, δ): 74.86 (complexed Ar–CH), 77.93 (Cp), 79.08 (complexed Ar–CH), 103.42 (complexed Ar–C), 106.18 (Ar–CH), 130.31 (complexed Ar–C), 155.41, 159.89, 161.10 (Ar–C).

5a: Yield: 72% ^{1}H NMR (DMSO-d_6, δ): 1.65 (br. s, CH_3), 2.07 (br. s, CH_2), 2.38 (br. s, CH_2), 5.19, 5.20, 5.21, 5.26 (s, Cp), 6.07 (s, Ar), 6.25 (s, complexed Ar), 6.41 (d, J = 5.08 Hz, complexed Ar), 6.80 (d, J = 4.69 Hz, complexed Ar), 7.15 (s, Ar), 7.26 (br. s, Ar), 7.34 (br. s, Ar), 9.29, 9.80 (br. s, OH). ^{13}C NMR (300 MHz, DMSO-d_6, δ): 26.92 (CH_3), 29.65, 45.00 (CH_2), 74.48, 74.87, 75.18, 75.57 (complexed Ar–CH), 77.28, 77.72, 78.15, 78.83, 79.19 (Cp), 86.71 (complexed Ar–CH), 103.50 (complexed Ar–C), 114.85, 119.85, 121.15 (Ar–CH), 127.83 (complexed Ar–C), 129.79, 130.16, 131.91 (Ar–CH), 137.91 (complexed Ar–C), 145.99, 146.44, 150.97, 151.59, 154.61, 155.25, 159.84 (Ar–C), 174.17 (carbonyl).

13a: Yield: 64% ^{1}H NMR (DMSO-d_6, δ): 5.27, 5.29 (s, Cp), 6.60 (d, J = 8.0 Hz, complexed Ar), 6.72 (s, complexed Ar), 6.88 (d, J = 6.25 Hz, complexed Ar), 7.41 (d, J = 4.30 Hz, Ar). ^{13}C NMR (300 MHz, DMSO-d_6, δ):76.91 (complexed Ar–CH), 79.21 (Cp), 86.58 (complexed Ar–CH), 103.97 (complexed Ar–C), 110.67 (Ar–CH), 130.91 (Ar–CH), 155.74 (Ar–C).

19a: Yield: 89% ^{1}H NMR (DMSO-d_6, δ): 5.15, 5.18, 5.20, 5.24, 5.25, 5.29, 5.30 (s, Cp), 6.17–6.48 (m, complexed Ar), 6.89 (d, J = 8.59 Hz, Ar), 7.11 (d, J = 8.59 Hz, Ar), 7.27 (d, J = 3.52 Hz, Ar), 7.33, 7.47, 7.59 (s, Ar), 9.75 (s, OH). ^{13}C NMR (DMSO-d_6, δ): 73.23, 73.79, 74.45, 74.95, 76.00 (complexed Ar–CH), 77.58, 77.80, 77.92, 78.21 (Cp), 112.54, 116.80, 121.98, 122.76, 124.83 (Ar–CH), 127.65, 128.60, 130.84 (complexed Ar–C), 131.93, 132.07, 132.35, 144.62, 150.81, 151.56, 155.76, 156.48 (Ar–C).

*2.3.2 Synthesis of Polymers **4b**, **5b**, **13b**, **14**, **15**, **16**, and **19b***

0.3 mmol of A_2, 0.2 mmol of B_3, 1 mmol K_2CO_3 and 2 ml of DMF were placed in a 25 ml round bottom flask. This mixture was stirred in the dark, under nitrogen at room temperature until the solution became viscous or 16 h had elapsed. The product was precipitated by pouring into 10% HCl and the addition of NH_4PF_6. The solid was then filtered in a sintered glass crucible, washed with water and allowed to dry in the dark under reduced pressure.

4b: 16 h. Yield: 62% ^{1}H NMR (DMSO-d_6, δ): 5.16, 5.22, 5.26 (s, Cp), 6.20–6.81 (br. m, complexed Ar, Ar), 10.68 (br. s, OH). ^{13}C NMR (DMSO-d_6, δ): 75.35, 76.40 (complexed Ar–CH), 77.85, 79.21 (Cp), 86.58 (complexed Ar–CH), 103.01 (Ar–CH), 103.56 (complexed Ar–C), 105.05, 105.45 (Ar–CH), 129.52 (complexed Ar–C), 131.46, 154.70, 155.36, 160.72 (Ar–C).

5b: 16 h. Yield: 80% ^{1}H NMR (DMSO-d_6, δ): 1.65 (br. s, CH_3), 2.03 (br. s, CH_2), 2.39 (br. s, CH_2), 5.20, 5.23, 5.27 (s, Cp), 6.12 (s, Ar), 6.26, 6.41 (s, complexed Ar), 6.76 (d, J = 14.45 Hz, complexed Ar), 6.99, 7.26, 7.33 (s, Ar), 9.38, 9.92, 10.83, 12.18 (s, OH, COOH). ^{13}C NMR (DMSO-d_6, δ): 26.90 (CH_3), 29.74, 36.02, 44.85 (CH_2), 74.42, 74.96, 75.41, 76.18 (complexed Ar–CH), 77.84, 79.25 (Cp), 86.72 (complexed Ar–CH), 98.42, 100.53 (Ar–CH), 103.39 (complexed Ar–C), 105.21, 114.84, 119.84, 120.08, 129.50 (Ar–CH), 129.73, 129.95, 130.14 (complexed Ar–C), 131.87, 145.90, 146.37, 150.80, 151.42, 154.31, 155.33 (Ar–C), 159.81, 160.78, 174.18 (carbonyl).

13b: 3 h. Yield: 68% ^{1}H NMR (DMSO-d_6, δ): 5.22, 5.27 (s, Cp), 6.18 (d, J = 5.86 Hz, complexed Ar), 6.37 (br. s, complexed Ar), 6.59 (br. s, complexed Ar), 6.89 (d, J = 8.99 Hz, Ar), 7.11 (d, J = 8.40 Hz, Ar), 7.32 (s, Ar), 7.43 (d, J = 11.33 Hz, Ar), 9.77 (br. s, OH). ^{13}C NMR (DMSO-d_6, δ): 73.57, 74.88, 75.92 (complexed Ar–CH), 77.78, 78.05 (Cp), 109.90, 116.81, 121.97, 122.81 (Ar–CH), 128.83 (complexed

Ar–C), 129.25, 130.45, 131.92 (Ar–C), 144.63 (complexed Ar–C), 150.88, 155.76, 156.47 (Ar–C).

14: 3 h. Yield: 71% ^{1}H NMR (300 MHz, DMSO-d$_6$, δ): 1.44 (s, CH$_3$), 1.92, 2.20 (br. s, CH$_2$), 5.26, 5.33 (br. s, Cp), 6.65 (br. s, complexed Ar), 6.91, 7.52 (br. s, Ar). ^{13}C NMR (300 MHz, DMSO-d$_6$, δ): 27.14 (CH$_3$), 29.90, 43.86 (CH$_2$), 76.89 (complexed Ar–CH), 79.42 (Cp), 86.70 (complexed Ar–CH), 103.94 (complexed Ar–C), 111.96, 114.58, 127.66 (Ar–CH), 131.79 (complexed Ar–C), 139.25, 154.91, 155.69 (Ar–C), 174.61 (carbonyl).

15: 3 h. Yield: 97% ^{1}H NMR (DMSO-d$_6$, δ): 1.61, 1.68 (br. s, CH$_3$), 5.22 (s, Cp), 6.28, 6.52 (br. s, complexed Ar), 7.19, 7.37 (br. s, Ar), 9.25 (s, OH). ^{13}C NMR (DMSO-d$_6$, δ): 30.56, 30.65 (CH$_3$), 74.77, 75.91 (complexed Ar–CH), 77.92 (Cp), 79.37 (complexed Ar–CH), 99.32, 100.53, 101.77, 103.20, 110.24, 114.71, 119.89, 120.00, 127.30, 128.72 (Ar–CH), 130.58 (complexed Ar–C), 147.75, 148.85, 151.17, 156.27 (Ar–C).

16: 0.5 h. Yield: 74% ^{1}H NMR (DMSO-d$_6$, δ): 5.16 (s, Cp), 6.32, 6.68 (br. s, complexed Ar), 7.45, 7.61 (br. s, Ar). ^{13}C NMR (DMSO-d$_6$, δ): 76.88 (complexed Ar–CH), 78.66 (Cp), 84.94 (complexed Ar–CH), 128.24 (Ar–CH), 131.29 (complexed Ar–C), 132.02, 135.01 (Ar–CH), 136.29 (Ar–C), 148.14 (complexed Ar–C), 155.63 (Ar–C).

19b: 16 h. Yield: 98% ^{1}H NMR (DMSO-d$_6$, δ): 5.18, 5.21, 5.26, 5.30 (s, Cp), 6.20, 6.34, 6.53 (br. s, complexed Ar), 6.89 (d, $J = 10.00$ Hz, Ar), 7.11 (d, $J = 9.77$ Hz, Ar), 7.33, 7.47, 7.59 (br. s, Ar), 9.74 (s, OH). ^{13}C NMR (DMSO-d$_6$, δ): 73.79, 74.82, 76.00, 76.90 (complexed Ar–CH), 77.59, 77.81, 78.02 (Cp), 109.44, 112.54, 116.79, 121.96, 122.79, 124.66 (Ar–CH), 128.66, 129.06 (complexed Ar–C), 130.19, 130.75, 131.95, 132.37, 144.64, 150.82, 150.96, 151.62, 155.19, 155.68, 156.40 (Ar–C).

2.3.3 Synthesis of Polymer ***13c***

Using the amounts set out for the synthesis of **13b**, the solution was allowed to react until a solid gelatinous mass was obtained (approximately 4 h). This solid was broken up with a spatula and washed with diethyl ether to remove the solvent and to facilitate filtration into a sintered glass crucible. The product was dried under reduced pressure in the dark. Yield: 92% ^{1}H NMR (DMSO-d$_6$, δ): 4.67, 5.22 (Cp), 6.50 (d, $J = 16.41$ Hz, complexed Ar), 7.01 (br. s, Ar). ^{13}C MAS NMR (600 MHz, δ): 80 (Cp, complexed Ar–CH), 132 (Ar–CH), 153 (complexed Ar–C), 158 (Ar–C), 168 (Ar–C). Despite some peak overlap, the integrated intensity ratio is consistent with the polymeric formula proposed.

2.3.4. Synthesis of Polymers ***6****,* ***7****,* ***17****, and* ***20***

The procedure for the room temperature polymers (**4b**, **5b**, **13b**, **14**, **15**, **16**, **19b**) was followed with the following modification, the reaction was conducted at 60°C. Work up and isolation of the resultant polymers also followed the procedure for the room temperature polymers (**4b**, **5b**, **13b**, **14**, **15**, **16**, **19b**).

6: Yield: 93% ^{1}H NMR (DMSO-d$_6$, δ): 5.05, 5.22 (s, Cp), 6.02–6.65 (br. m, complexed Ar, Ar), 10.71 (s, OH). ^{13}C NMR (DMSO-d$_6$, δ): 72.83, 75.49 (complexed Ar–CH), 77.06, 77.96 (Cp), 86.70 (complexed Ar–CH), 103.03, 105.06, 110.51 (Ar–CH), 127.59, 129.61 (complexed Ar–C), 155.52, 156.33, 160.72 (Ar–C).

7: Yield: 98% ^{1}H NMR (DMSO-d$_6$, δ): 1.65 (br. s, CH$_3$), 2.06 (br. s, CH$_2$), 2.41 (br. s, CH$_2$), 5.04, 5.20, 5.22, 5.27 (s, Cp), 6.10 (s, Ar), 6.19, 6.41 (s, complexed Ar), 6.74 (d, $J = 17.58$ Hz, complexed Ar), 7.00, 7.25, 7.33 (s, Ar), 9.85 (br. s, OH), 12.14 (br. s, COOH). ^{13}C NMR (DMSO-d$_6$, δ): 26.93 (CH$_3$), 29.82, 44.95 (CH$_2$), 74.45, 75.02, 75.55, 76.23 (complexed Ar–CH), 77.89, 79.30 (Cp), 86.76 (complexed Ar–CH), 98.50, 100.64 (Ar–CH), 103.48 (complexed Ar–C), 105.24, 119.91, 120.13, 129.25 (Ar–CH), 130.23 (complexed Ar–C), 131.96, 146.07, 146.35, 150.98, 151.52, 154.42, 155.44 (Ar–C), 159.89, 160.87, 174.30 (carbonyl).

17: Yield: 64% ^{1}H NMR (DMSO-d$_6$, δ): 4.08, 4.55, 5.03, 5.08, 5.17 (Cp), 6.28 (br. s, complexed Ar), 6.33 (br. s, complexed Ar), 6.66 (br. s, Ar), 6.96 (br. s, Ar), 7.12 (br. s, Ar), 9.38, 9.78, 10.23, 10.68, 11.40 (br. s, OH). ^{13}C NMR (DMSO-d$_6$, δ): 69.25, 72.32, 73.06, 74.03 (complexed Ar–CH), 76.45, 77.32 (Cp), 81.31 (complexed Ar–CH), 99.92, 101.90, 103.40, 115.71, 116.24, 119.51, 120.04, 120.97, 121.46 (Ar–CH), 128.82, 128.89 (complexed Ar–C), 130.11, 131.11 (Ar–C), 144.11 (complexed Ar–C), 147.83, 149.90, 150.44, 151.83, 152.91, 154.28, 155.19, 159.64 (Ar–C).

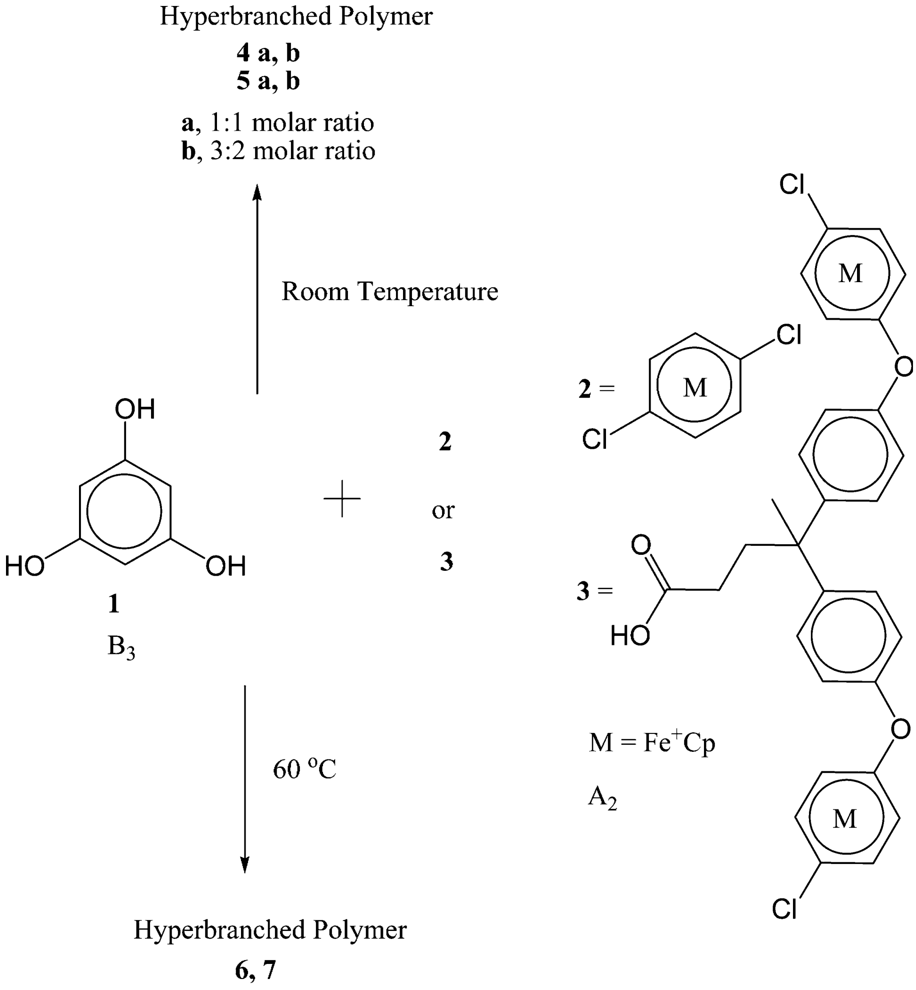
20: Yield: 98% ^{1}H NMR (DMSO-d$_6$, δ): 5.07, 5.18, 5.19 (s, Cp), 5.21, 5.28 (br. s, Cp), 6.06–6.64 (br. m, complexed Ar), 6.91, 7.13, 7.38, 7.45, 7.62 (br. s, Ar), 9.76 (s, OH). ^{13}C NMR (DMSO-d$_6$, δ): 72.80, 73.59, 74.85, 75.42, 75.83 (complexed Ar–CH), 77.05, 77.67, 77.92 (Cp), 102.67, 104.93, 108.01, 109.77, 116.81, 121.99, 122.79, 124.87 (Ar–CH), 127.73, 128.54, 128.88, 129.09, 129.56 (complexed Ar–C), 130.37, 131.18, 131.31, 131.66, 131.90, 132.24, 144.68, 150.66, 150.84, 151.25, 154.88, 155.72, 160.67 (Ar–C).

3. RESULTS AND DISCUSSION

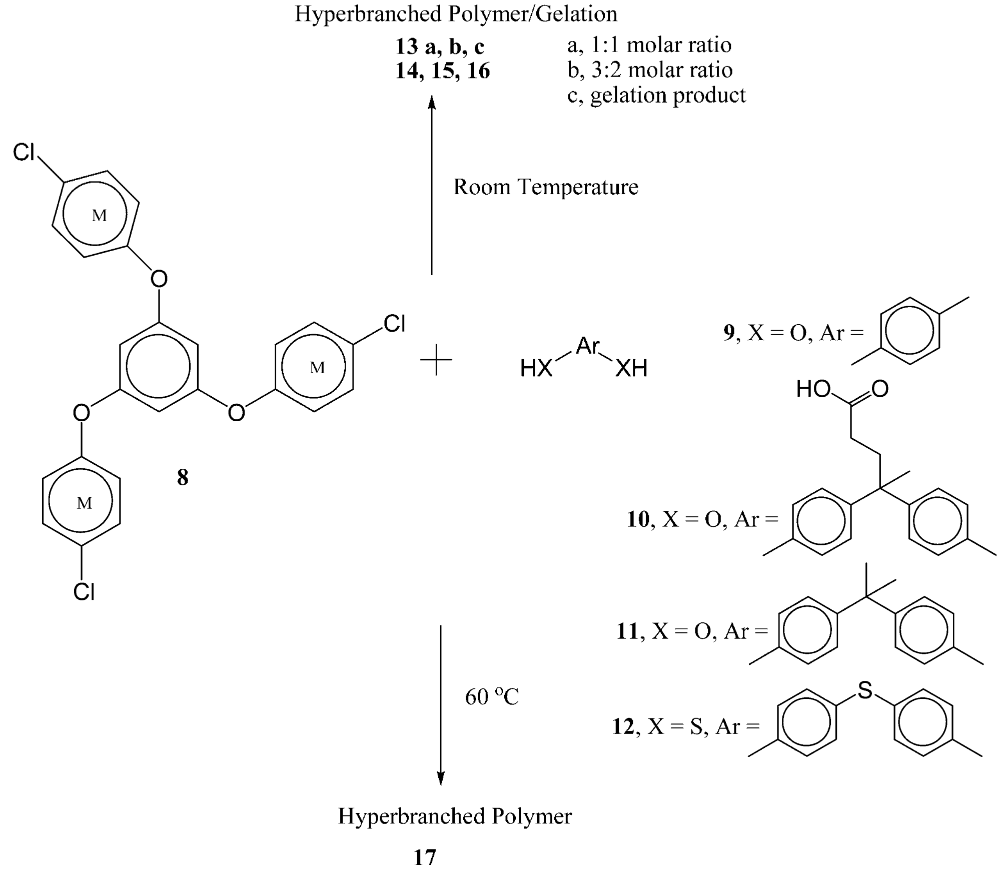
Hyperbranched polymers have been prepared in order to probe the influence of reaction conditions and the effect of the variation of the A_2 and the B_3 starting materials. Several different modes of synthesis were examined. The effect of temperature on the polymer was investigated by preparing the analogous polymers at both room temperature and at 60°C. Different molar ratios and/or different starting materials were explored to produce the same product. In conjunction with this, the effects of 4,4-bis-(4-hydroxyphenyl)valeric acid (**10**), which has been reported to decrease the amount of intramolecular cyclization [7], and its metallated derivative (**3**) were compared to other diols that have not been reported to decrease intramolecular cyclization.

Synthesis of the various hyperbranched polymers proceeded, as expected, following the A_2+B_3 method. As seen in Scheme 1, A_2 was either the *p*-dichlorobenzene–cyclopentadienyliron complex (**2**) or a bimetallic valeric acid derivative (**3**). The branching unit, B_3, was phloroglucinol (**1**). The respective A_2 was combined with **1** at room temperature in a 1:1 or a 3:2 molar ratio. A 3:2 molar ratio polymerization was also accomplished at 60°C. The 3:2 molar ratio gave a stoichiometricly equivalent number of reactive groups allowing for possible full conversion or polymerization. The 1:1 molar ratio gave an unequal number of reactive A and B groups thus decreasing the probability of full conversion and gelation. This allowed for the preparation of oligomeric hyperbranched polymers.

In Scheme 2, the B_3 unit used was the chloro-capped star-shaped molecule (**8**). The A_2 unit was either 4,4-bis-(4-hydroxyphenyl)valeric acid (**10**) or hydroquinone (**9**). Bisphenol A (**11**) was also used to determine if there was size dependence based on the



Scheme 1.

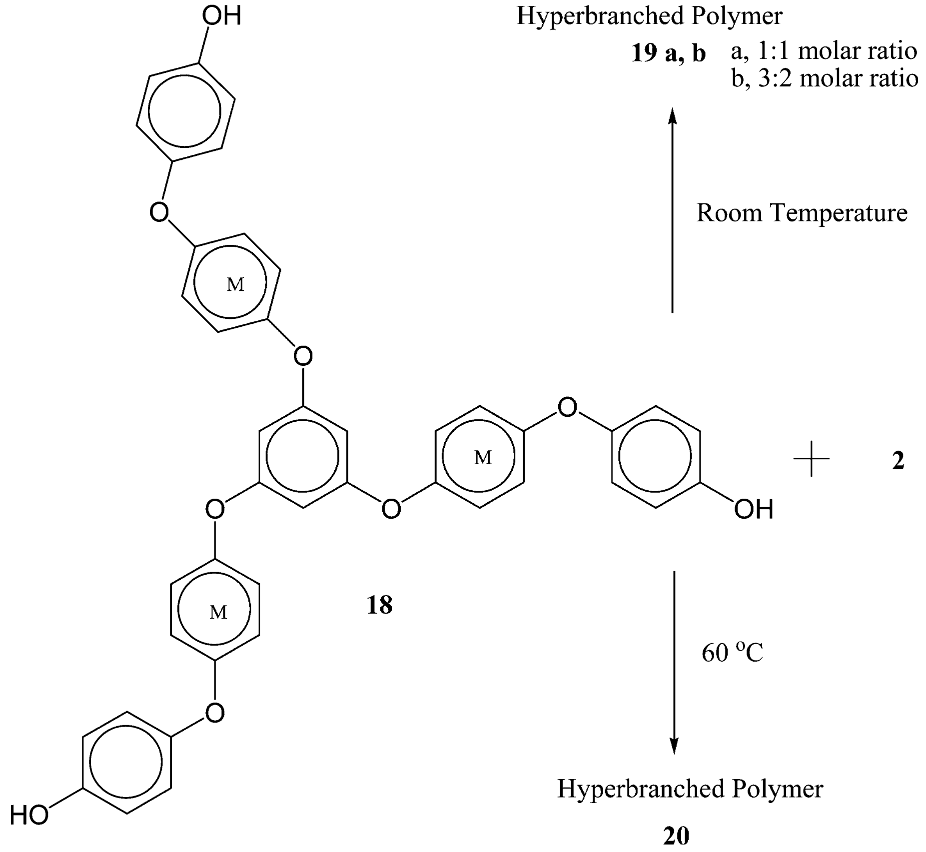


Scheme 2.

A_2 unit. There was a slight increase in the thermal stability between the A_2 spacer containing two vs. one aromatic ring. 4,4-thiobisbenzenethiol (**12**) was also polymerized to examine the effect of sulphur. Sulphur was found to influence the thermal properties of the resultant hyperbranched polymer. When the reaction was carried out at room temperature, gelation was found to occur when the A_2 unit was **9**, **11** or **12**. As a result, polymerizations were stopped just prior to the gel point. However, when **10** was used, the reaction mixture did not gelate, supporting findings by previous works that gelation is caused by intramolecular cyclization forming a 3-D network [1–7, 9, 24–27] and that 4,4-bis-(4-hydroxyphenyl)valeric acid decreases cyclization [7]. The reaction of hydroquinone (**9**) with the B_3 unit **8** at 60°C was found to result in a hyperbranched polymer as opposed to gelation.

Scheme 3 shows the reaction of the *p*-dichlorocomplex (**2**) with the alcohol-capped star-shaped molecule (**18**). This reaction was conducted at 60°C to give **20** or at room temperature to give either **19a** or **19b**. **19a** was formed in a larger volume and an equivalent molar ratio as opposed to **19b** which was prepared in a smaller volume with an equivalent stoichiometric ratio. For each hyperbranched polymer and gelation product prepared, the thermal properties, viscometry and ^{1}H and ^{13}C NMR were examined.

Analysis of the ^{1}H NMR data was simplified by the cyclopentadienyliron moiety. The cyclopentadienyl anion (Cp) appeared around 5 ppm and is sensitive to its environment. Thus its resonance functions as an excellent means of identifying the presence of terminal, linear and branched functionalities spectroscopically. Examining compounds **4a**, **4b** and **6** (Fig. 1), the relative amounts of terminal, linear and branched cyclopentadienyliron moieties changed. As the conditions were changed to favour rapid polymerization (small volume and the presence of heat), branched Cp peaks were seen to increase and linear peaks were seen to decrease in intensity. The branched Cp was clearly visible at 5.05 ppm in **6**, terminal Cp were seen at ~5.22 ppm in **4a**, **4b** and **6**. Linear Cp appeared at 5.26 ppm in **4a** and **4b**. The



Scheme 3.

oligomeric nature of **4a** and **4b** also yielded peaks at 5.19 and 5.16 ppm, these being the branched resonances of the low molecular weight hyperbranched polymers, respectively. The complexed aromatic peaks and aromatic peaks appeared overlapped in the region from 6.02 to 6.84 ppm. The phenolic protons appeared as broad singlets at 9.81, 10.68 and 10.71 ppm for compounds **4a**, **4b** and **6**, respectively.

The same trend of increasing branched peaks and decreasing linear peaks as conditions were varied was noted in the ^{13}C NMR using the aromatic CH's of compound **1** as an indicator (Fig. 1). Multiplication of this peak was found between 100 and 111 ppm. The branched or dendritic peak relating to the aromatic CH's of the starting material **1** appeared at 110.51 ppm for compound **6** which was expected from previous work with star-shaped molecules [50, 51]. The terminal CH's from **1** were found at ~105 ppm in both **4b** and **6**. The linear peak appeared at 103.01 ppm for **4b** and as a very minor peak at 103.03 ppm in **6**. The Cp and complexed aromatic CH peaks were in the range of 72.83–86.70 ppm. The remaining complexed aromatic carbons were found at 103.56, 127.59, 129.52 and 129.61 ppm. The aromatic C's were found between 131.46 and 160.72 ppm.

The polymers removed just prior to gelation (**13b**,**15** and **16**) showed a lack of linear structure with only the branched resonances appearing in the ^{1}H and ^{13}C NMR. Hydrogen bonding was found in the NMR data of the 4,4-bis-(4-hydroxyphenyl)valeric acid containing polymers (**5a**,**b**,**7**,**14**). This clearly appeared as a multiplication of the phenolic and carboxylic acid resonances in the ^{1}H NMR. A possible mechanism for 4,4-bis-(4-hydroxyphenyl)-valeric acid decreasing intramolecular cyclization may be based upon hydrogen bonding.

Polymers **4a, b** and **6** contained spectroscopic handles that were used to calculate the DB according to Eq. (1). For polymer **4a** the value was 0.64, **4b** was 0.67 and **6** had a DB of 0.69. Based upon these, it may be concluded that higher reaction temperature caused the hyperbranched polymer to grow in a more branched fashion. A stoichiometric molar ratio of starting materials also leads to an increased amount of branching.

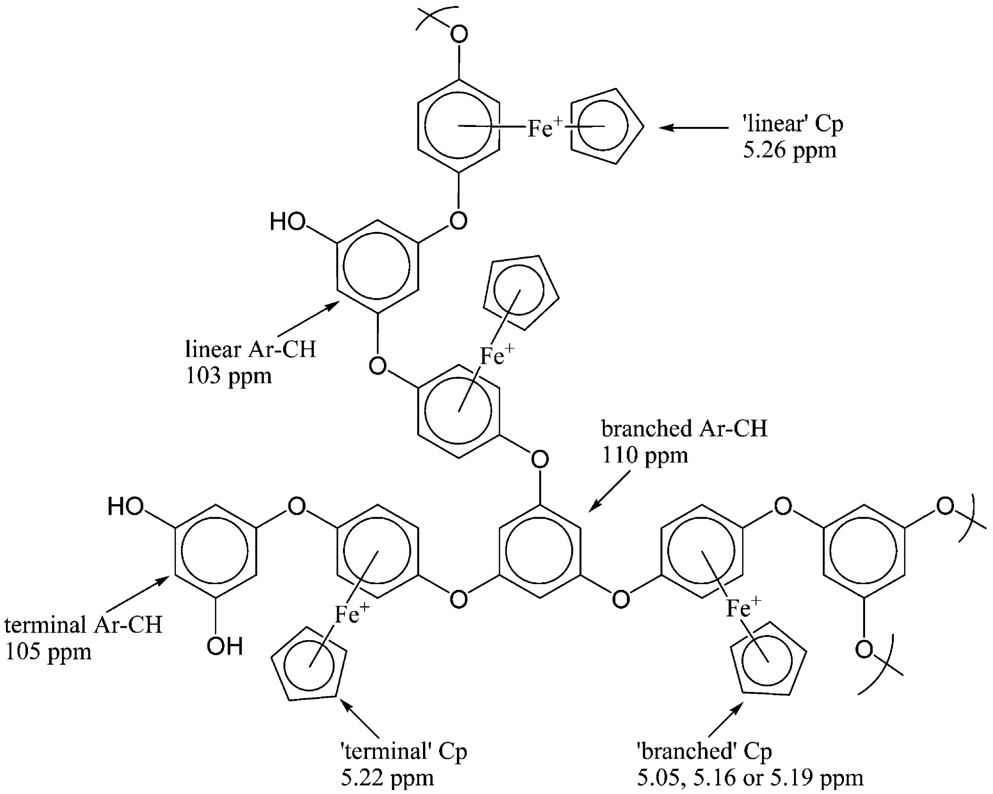


Fig. 1. Proposed partial structure of **4a**, **b** or **6** with labeled terminal, linear and branched sites along with their NMR shifts in DMSO.

Thermal data for the hyperbranched polymers is given in Tables I–IV. Pyrolysis of the cyclopentadienyliron moiety occurred at approximately the same temperature for the hyperbranched polymers as for linear polymers [45–49] and for star-shaped molecules [50, 51]. This first weight loss began above 230°C for the hyperbranched polymers with A_2 being **2** or **9** and ended around 280°C (Tables I, II). The 4,4-bis-(4-hydroxyphenyl)valeric acid based polymers (Table III) were found to have wider demetallation temperatures with pyrolysis starting at 210°C and ending at 285°C. Incorporation of an A_2 group with two aromatics was found to increase the thermal stability to 250°C with pyrolysis ending at 280°C (Table IV).

A second weight loss for these polymers and gelation products was observed and assigned to the

Table I. Thermal Analysis for Hyperbranched Polymers with $A_2 = \mathbf{2}$

	T_g	T_m	Weight Loss (%)	T_{onset} (°C)	T_{endset} (°C)
4b	107.96	190.29	25.59	238.69	269.02
			13.96	451.51	523.65
			11.07	888.95	921.40
6	114.67	180.32	26.26	236.08	268.60
			15.05	465.33	527.68
			4.78	830.03	850.70
			5.51	880.69	893.43
19b	81.41	193.03	34.00	256.96	279.03
			18.03	436.97	547.59
			5.26	851.40	866.08
20	133.90	189.43	27.59	238.33	267.78
			22.79	390.40	485.03
			13.78	850.37	874.19

Table II. Thermal Data for Hyperbranched Polymers with $A_2 = \mathbf{9}$

	T_g	T_m	Weight Loss (%)	T_{onset} °C)	T_{endset} (°C)
13b	103.37	178.61	30.78	247.44	272.23
			17.22	433.45	531.41
			8.20	827.40	869.91
13c	60.17	154.83	5.04	144.47	177.30
			10.87	231.96	261.29
			13.13	567.26	593.61
			23.72	870.58	937.97
17	77.34	168.75	20.96	237.28	261.51
			22.58	448.01	532.82
			11.30	840.68	895.33

Table III. Thermal Analysis for Hyperbranched Polymers with $A_2 = \mathbf{3}$ or **10**

	T_g	T_m	Weight Loss (%)	T_{onset} (°C)	T_{endset} (°C)
5b		165.15	18.69	229.70	262.06
			25.15	419.40	522.70
			20.00	878.18	925.44
7	85.96	177.07	18.96	234.76	266.45
			22.88	418.26	506.66
			13.62	883.29	928.71
14	99.84	170.30	38.54	211.27	284.37
			13.50	414.73	443.74

degradation of the ether bond. The starting temperature for this loss was variable with the highest temperature being the gelation product (**13c**) at 567°C. The ether bond of the 4,4-bis(4-hydroxyphenyl)valeric acid based polymers (**5b**,**7**,**14**) degraded between 415 and 523°C (Table III). The hyperbranched polymers with A_2 being **11** or **12** (Table IV) showed breakdown of the ether or thioether bond starting at 484–560°C. The remaining hyperbranched polymers based on compounds **2** or **9** (Tables I, II), showed that backbone breakdown started at 430°C and ended at 550°C.

Glass transition temperatures (T_g) were found to be highly variable and not always present (Tables I–IV). It was noted, however, that increased branching appeared to cause a decrease in the T_g. This was also reported for organic hyperbranched polymers [41]. Comparison of previous results from star-shaped [51] and linear [44,47,48] cyclopentadienyliron containing polymers, the same conclusions may be drawn. The gelation product had a lower glass transition temperature than the hyperbranched polymers. The high temperature reaction condition products also had higher glass transition temperatures than their non-gelatinous room temperature counterparts. Two phase transitions were noted for most of the hyperbranched and gelation products. The first transition was ascribed to a glass transition and the second transition observed is theoretically a melting point. Melting below the thermal degradation temperature was found for almost all of the hyperbranched polymers prepared. In most cases, increased temperature in the reaction conditions gave a lower melting point. This may have been due to increased branching. The lowest melting point was that of the gelation product, **13c**, at 155°C. The highest melting points found were those with A_2 being **2** or **12** (Table I, IV). These were between 177 and 193°C. The 4,4-bis-(4-hydroxyphenyl)valeric acid based polymers (Table III) had melting points between 165 and 177°C.

Table IV. Thermal Data for Hyperbranched Polymers with $A_2 = \mathbf{11}$ or **12**

	T_g	T_m	Weight Loss (%)	T_{onset} (°C)	T_{endset} (°C)
15		177.60	29.12	255.35	278.20
			20.95	486.35	527.35
			11.79	799.70	859.42
16	91.03	188.52	29.31	251.66	268.94
			18.55	483.87	559.77

As seen in Table V, the molecular weights of the hyperbranched polymers were often found to increase with elevated reaction temperature. The polymers taken off just prior to the gel point (**15**,**16**) had very high molecular weights. Polymers with A_2 being 4,4-bis-(4-hydroxyphenyl)valeric acid (**5b**,**7**,**14**) showed lower molecular weights than polymers with different A_2 monomers.

Viscosity was found to be low for the hyperbranched polymers. The intrinsic viscosity at a concentration of 0.5 g/dl circumventing the polyelectrolyte effect caused by the cyclopentadienyliron complex, was in the range of 0.18–0.21 dl/g for the

Table V. Molecular Weights and Inherent Viscosity in dl/g Gathered at 25°C in 18 ml DMSO

$B_3 = \mathbf{1}$		$B_3 = \mathbf{8}$		$B_3 = \mathbf{18}$	
Compound; MW	Inherent viscosity	Compound; MW	Inherent viscosity	Compound; MW	Inherent viscosity
4b; 25,500	0.209	**8**; 1255	0.089	**18**; 1476	0.120
5b; 12,200	0.175	**13b**; 56,500	0.288	**19b**; 58,500	0.293
6; 27,500	0.214	**14**; 25,100	0.213	**20**; 17,700	0.189
7; 21,600	0.199	**15**; 216,000	3.495		
		16; 390,000	5.210		
		17; 119,900	0.704		

hyperbranched polymers with B_3 being **1**. When B_3 was compound **18**, the viscosity was 0.19 dl/g for the 60°C synthesis and 0.29 dl/g for the room temperature synthesis. It should be noted that the viscosity of the B_3 star-shaped starting material (**18**) was 0.12 dl/g. When the B_3 starting material was compound **8**, a dramatic increase in viscosity was noted. The value was lower for the 4,4-bis-(4-hydroxyphenyl)valeric acid based polymer (**14**). The polymers that were stopped just prior to the gel point were found to have high relative viscosity with the hydroquinone polymer (**13b**) having 0.29 dl/g and the remaining two being upwards of 3.5 dl/g. Polymer **17**, the 60°C analogue to **13b**, also had a higher viscosity of 0.70 dl/g. The starting material **8**, had a low viscosity of 0.09 dl/g. Based upon these results, the increased viscosity of the hyperbranched polymers may be related to cyclization which leads to gelation.

4. CONCLUSIONS

A number of hyperbranched polymers containing cyclopentadienyliron moieties were prepared by the $A_2 + B_3$ method. Viscosity values were found to be lower when the B_3 starting material was phenolic in nature. When the B_3 group was chloro-capped, the viscosities were higher. Pyrolysis of the cyclopentadienyl iron moiety was found to occur between 230 and 280°C depending on the A_2 group. Degradation of the polyether backbone also showed dependence on the A_2 group and occurred above 400°C. Glass transition temperatures were found to be highly variable depending on the reaction conditions and amount of branching, whereas melting temperatures were in the range of 155–190°C.

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