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# Synthesis and Characterization of Linear−Dendritic Aromatic Etherimide Copolymers: Tuning Molecular Architecture To Optimize Properties and Processability

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Reports on the synthesis of discrete dendrimers and their unique physical properties (end group dominated physical properties) have permeated the literature in the past 10 years.[1] Recently, much attention has been directed toward hyperbranched polymers (HBP's) as alternatives for obtaining dendrimer-like properties without the extreme cost and difficulty of dendrimer synthesis.[2] Significant efforts have focused on maximizing the branching content through techniques such as slow addition[3,4] and postsynthetic modification[5] in order to ensure an architecture resembling dendrimers. It has been suggested that a high degree of branching (DB) and numerous end groups per molecule will make HBP's economical polymer additives that behave as rheological modifiers[6] as well as surface modifying agents where high levels of branching and end group composition are important variables.[7,8] However, if branched molecules are to be used as stand-alone materials where good mechanical performance is required, then it may not be beneficial to maximize the branching content. Alternatively, lowering the branching content by systematically increasing AB content may identify an optimal material that affords structural integrity along with ease of processing (low viscosity, high solubility). This may be most important for amorphous polymers including advanced thermoplastics such as Ultem, where small amounts of branching will not have deleterious physical property effects due to the absence of crystalline domains in the parent materials. Hawker[9] has compared dendrimers and hyperbranched polymers to their exact linear analogues, but surprisingly, little effort has been dedicated to systematic studies of high molecular weight materials with architectures that vary from hyperbranched to linear.[10,11]

The idea of adding short chain and long chain branching to modify properties and processablility is not new.[12] One way in which small amounts of branching can be added to linear polymers is through the addition of $B_n$ ($n \geq 3$) monomers to either AB or AA/BB type polymerizations.[11,12] The downside to this approach is that, in order to preclude gel formation, the $B_n$ content and/or conversion must be kept low. To circumvent this problem, $A_1$ end-capping groups have been employed that allow the incorporation of more branching and higher conversions without cross-linking.[11] However, stoichiometery must be rigorously controlled and gel formation can occur, especially if the reactive groups are not all of equal reactivity. These problems make a systematic branching study between fully linear and hyperbranched polymers impossible for AA/BB/$B_n$/$A_1$ systems. However, if an AB/$AB_2$ method is employed, a systematic study can easily be executed since cross-linking is not possible even if reactivity is unequal and if stoichiometry is imperfect.

The theoretical framework for molecular weight distributions of AB/$AB_2$ copolymers was described by Flory[13] in 1940, and theoretical DB calculations have been put forth more recently by Frey.[10] Kricheldorf[14] has described the synthesis and characterization of AB/$AB_2$ polyester copolymers, and a recent article published by Guan[15] described a catalyst that controlled the DB of polyethylene between that of a linear and hyperbranched polymer by variation in reaction pressure. Here we report a rapid change in solution viscosities and film-forming ability as a function of copolymer composition for aromatic etherimide polymers.

We recently described a new method for the rapid synthesis of hyperbranched aromatic polyetherimides.[16] The method utilizes $AB_2$ monomers that contain a pair of *tert*-butyldimethylsilyl (TBDMS) protected phenols and an activated aryl fluoride group in combination with a catalytic amount of CsF. It was discovered that the polymerization of $AB_2$ monomer **1** (Scheme 1) at 240 °C proceeded very rapidly and yielded high molecular weight hyperbranched polymer **2** with a DB of 0.66 and fully intact TBDMS end groups. Upon further investigation, it was discovered that the polymerization of linear AB monomer **3** at 240 °C proceeded rapidly as well yielding high molecular weight linear polyetherimide **4**. Given these results, we targeted a series of polymers with DB 0.00−0.66 to observe the effects that DB and the number of end groups per molecule have on physical properties. This effort was motivated by the search for an optimum composition to impart high solubility, low viscosity, and mechanical performance in a high-temperature polymer.

Monomer **1** was synthesized as previously described[16] and was 99+% pure as determined by analytical HPLC. Monomer **3**[17] was synthesized by similar methods and purified to 99+% as well. Nine copolymers were prepared under identical reaction conditions with varying AB/$AB_2$ (mol/mol) compositions as seen in Scheme 1.[17] To determine the architecture of the copolymers, we used an NMR solvent that provided sufficient dispersion such that the three protons needed to calculate degree of branching (DB) by Frey's definition[10] (eq 1) were sufficiently resolved.

$$\mathrm{DB}_{\mathrm{Frey}} = \frac{2[D_{\mathrm{AB}_2}]}{2[D_{\mathrm{AB}_2}] + [L_{\mathrm{AB}_2}] + [L_{\mathrm{AB}}]} \qquad (1)$$

The terms $[D_{\mathrm{AB}_2}]$, $[L_{\mathrm{AB}_2}]$, and $[L_{\mathrm{AB}}]$ represent mole fractions of dendritic and linear segments, respectively. By using model compounds[17] that represent the linear, dendritic, and terminal portions of the copolymers, it was determined that $CD_2Cl_2$ gave the necessary proton dispersion to determine DB. Branched polymers **5a**−**d** were soluble in $CD_2Cl_2$, though **5c,d** showed evidence of aggregation (extreme broadening in the $^1$H NMR) and gave spectra unsuitable for analysis. The integration of the dendritic and linear protons allowed for the determination of DB for polymers **5a,b** (Table 1). The theoretical DB (Table 1) was derived by Frey's analysis which assumes equally reactive B groups. An elevated DB for polymers **5a,b** above that predicted theoretically

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**Scheme 1. Synthesis of Linear (2), Hyperbranched (3), and Branched (5a–i) Polyetherimides**

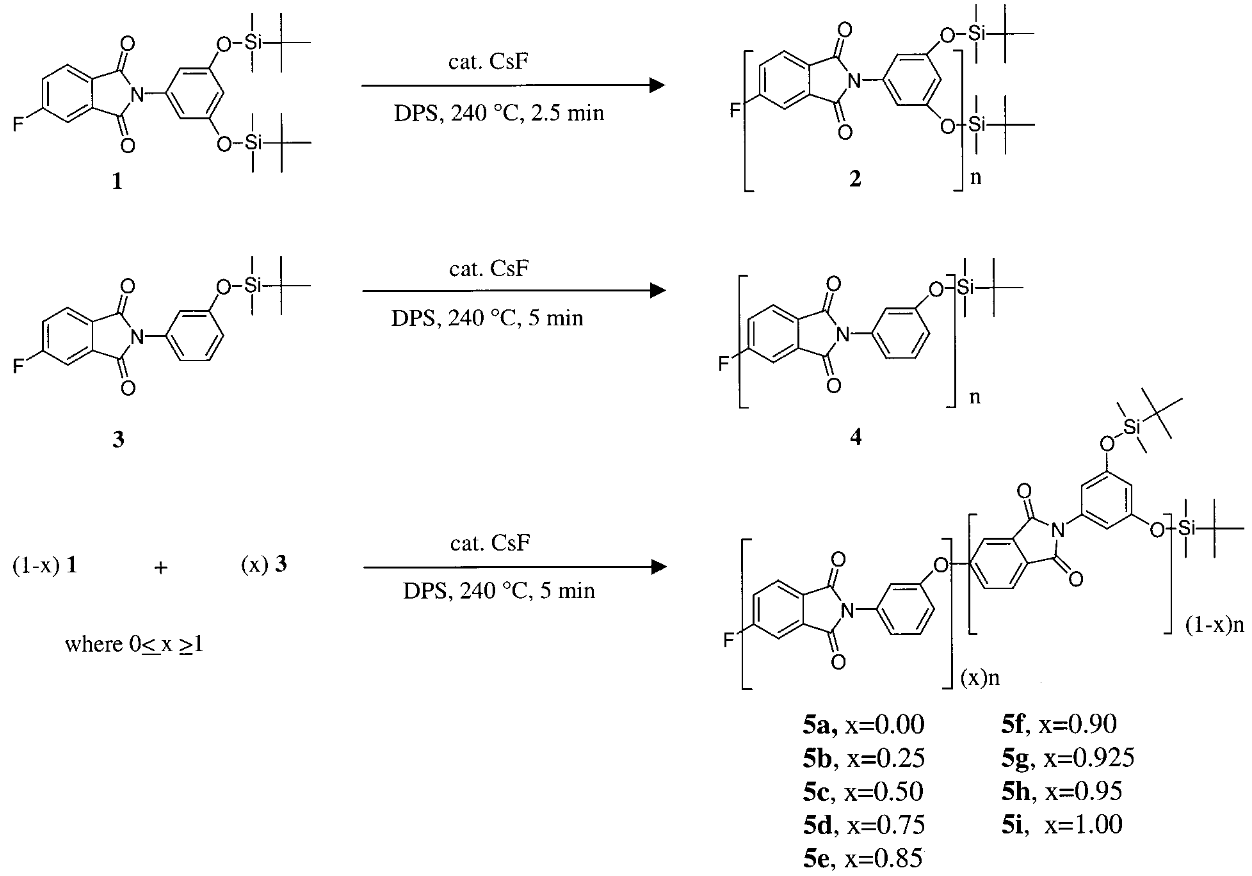

**Table 1. Results of Solubility Experiments, Thermal Analysis, Molecular Weight Determination, and Degree of Branching Analysis for Polyetherimide Copolymers**

| PEI | solubility[a] | | | | thermal analysis (°C) | | mol wt[17] | | | degree of branching | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| copolymer | EtOAc | THF | DMF | DMAc | $T_g$ | 10 wt % loss | $M_n$ | $M_w$ | PDI | theor[b] | exper |
| **5a** | + | + | + | + | 183 | 515 | 22 200 | 43 100 | 1.94 | 0.50 | 0.67 |
| **5b** | + | + | + | + | 182 | 550 | 27 200 | 61 800 | 2.27 | 0.49 | 0.69 |
| **5c** | – | + | + | + | 202 | 547 | 29 600 | 78 300 | 2.65 | 0.44 | |
| **5d** | – | + | + | + | 199 | 557 | 28 200 | 77 400 | 2.74 | 0.32 | |
| **5e** | – | – | + | + | 199 | 560 | 27 400 | 135 400 | 4.94 | 0.23 | |
| **5f** | – | – | + | + | 210 | 577 | 26 100 | 99 900 | 3.83 | 0.17 | |
| **5g** | – | – | + | + | 209 | 552 | 26 000 | 103 000 | 3.96 | 0.13 | |
| **5h** | – | – | + | + | 212 | 574 | 30 800 | 127 500 | 4.15 | 0.09 | |
| **5i** | – | – | – | + | 212 | 582 | 18 660 | 46 880 | 2.51 | 0.00 | 0 |

[a] Solubility studies were performed by adding 20 mg of polymer to 10 mL of the corresponding solvent: (+) indicates that upon stirring overnight the solution was homogeneous, giving a 2 mg/mL solution; (–) indicates that upon stirring overnight the solution was either turbid or completely insoluble. [b] The theoretical DB was determined from Frey's definition for degree of branching where $DB_{AB/AB_2} = (2Pa)(r + 1)/(r + 2)^2$ with Pa = 1 and $r = [AB]/[AB_2]$.

suggests unequal reactivity of the B groups. This observation has been previously discussed for the 100% $AB_2$ polymers.[16] Kinetic studies on model reactions are currently underway to determine the differences in monomer reactivities to infer the effect on DB since direct measurements on the entire copolymer series are currently unattainable because of solubility, aggregation, and dispersion limitations.

As the AB content of the copolymers increased, the solubility of the copolymers decreased as expected since the number of –OTBDMS end groups per molecule dropped linearly from ($n$ + 1)/molecule at 100% $AB_2$ to 1/molecule at 100% AB. It is interesting to note that only polar aprotic solvents such as DMAc and NMP could dissolve the entire series. Gel permeation chromatography data for copolymers **5a–i** taken in NMP with 0.05 M LiBr at 65 °C are given in Table 1 where it can be seen that $M_n$ ranged from18 to 30 kDa, $M_w$ ranged from 43 to 128 kDa, and PDI ranged from 1.94 to 4.94. The data indicate no consistent trends between molecular weight and copolymer composition. The absence of an increasing trend in PDI as AB content decreases (see Figure 1) goes against theoretical predictions[13] for random condensation polymers, possibly reflecting kinetic control by the fluoride catalytic species or differences in monomer reactivity.

Capillary viscosity measurements in DMAc revealed that the inherent viscosity increased gradually with increasing AB content up to 75% (Figure 2) beyond which a sharp rise was observed. This observation suggests the possible onset of an architectural change from a globular hyperbranched to an extended star-type molecule. This apparent shift to a more open structure capable of chain entanglement was also observed in the copolymer's ability to form ductile, continuous films when cast from DMAc.[17] Continuous, free-standing films

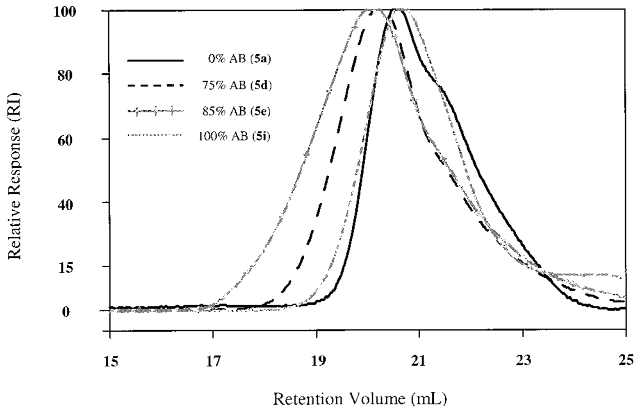

**Figure 1.** Overlay of relative RI chromatograms for copolymers **5a**−**e** and **5i** versus retention volume. It can be seen that peak broadening does not track with theoretical predictions for random condensation reaction.[13]

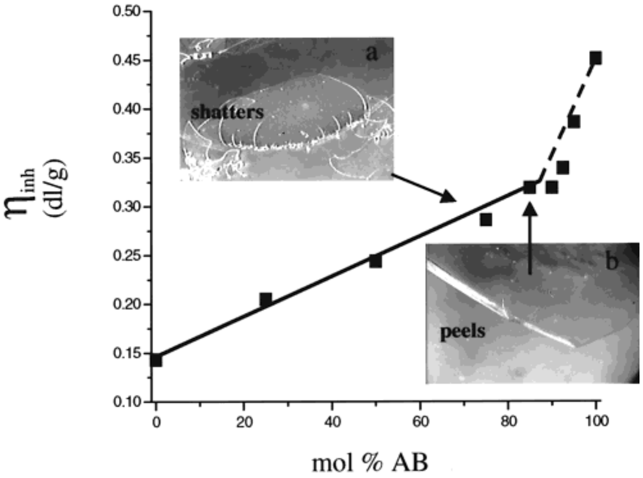

**Figure 2.** Plot of inherent viscosity vs % AB copolymer composition. Lines represent linear approximation of data. (a) Micrograph (20×) of 75% AB copolymer that shattered upon removal from glass substrate. (b) Micrograph (20×) of 85% AB copolymer that was ductile and peeled from glass substrate.

could be prepared for copolymers with AB content $\geq$75%; however, only films with 85% AB and above had the structural integrity to be peeled from a glass substrate (Figure 2, inset). Glass transition temperature measured by differential scanning calorimetry (Table 1) displayed a minimum at 0% AB and a maximum near 100%AB. The data were poorly fit using the Fox equation for copolymers.[17] This suggests that molecular composition may not be the only criterion that governs glass transition behavior; molecular architecture and the composition of the end groups may have important roles as well. Thermogravimetric analysis (Table 1) revealed a similar trend with the temperature corresponding to 10 wt % loss being greatest at 0% AB and lowest at 100% AB, which is most likely a result of the greater proportion of thermally labile TBDMS groups.[17]

In seeking amorphous thermoplastics that are easily processed but maintain good materials properties, the optimal structure will likely be found only with careful consideration to the degree of branching. By systematically reducing the DB in a series of AB/$AB_2$ polyetherimides, a narrow range of materials (85−95% AB) having good mechanical characteristics and relatively low solution viscosities was discovered. Films cast from 10 wt % solutions in DMAc showed a brittle to ductile transition between 75% and 85% AB, reflecting the possible onset of intermolecular interactions. Capillary viscometry conducted in DMAc showed a gradual increase with increasing AB content in inherent viscosity followed by a sharp change, possibly indicating a critical change in architecture from a hyperbranched to a star-type structure. Since molecular weight could not be held constant, differences in $M_w$ could account for some of the differences in the observed trends; however, we believe that the molecular weight contribution is negligible and that the observed trends mostly reflect changes in molecular architecture. Since the DB of only two copolymers could be measured directly, kinetic studies on model reactions are currently underway to determine the differences in monomer reactivities to infer the effect on DB since direct measurements on the entire copolymer series are currently unattainable.

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**Supporting Information Available:** Includes synthesis and characterization of model compounds, preparation and isolation of copolymers, stacked $^1H$ NMR plots of model compounds and polymers in $d_6$-DMF and $CD_2Cl_2$, and DSC traces and films of the copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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