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Synthesis and Characterization of Hyperbranched Aromatic Poly(ether imide)s with Varying Degrees of Branching

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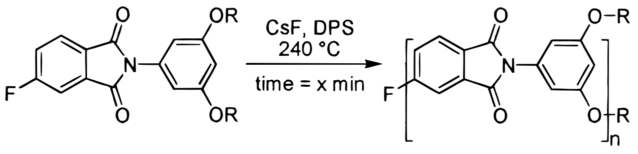
ABSTRACT: A series of high molecular weight hyperbranched poly(ether imide)s (HBPEI), derived from the AB_2 monomer *N*-[3,5-di(*tert*-butyldimethylsilyloxy)phenyl]-4-fluorophthalimide (**1**), were synthesized in a single-step process involving a rapid fluoride-catalyzed arylation reaction. NMR analysis of the degree of branching shows that changes in the polymerization reaction time, from 2.5 to 20.0 min, result in hyperbranched polymers with degrees of branching ranging from 66% to 42%, respectively. Reactions of selected model compounds show that changes in the degree of branching are a result of molecular rearrangements occurring via a transetherification mechanism. Such rearrangements lead to an increase in M_w while M_n remains relatively constant. Correlations between rheological data and the degree of branching of the hyperbranched poly(ether imide)s were observed. For solutions of the hyperbranched poly(ether imide)s, rheological measurements showed that shear thinning and normal stress effects increased as the degree of branching decreased and that birefringence as a function of shear rate increased with decreasing degree of branching. While strong correlations between the degree of branching and rheological properties exist, light scattering GPC measurements show that M_w increases significantly with reaction time. This variation in M_w suggests that the differences in rheological properties may be largely due to changes in molecular weight and makes it difficult to determine the role that changes in the degree of branching, which are manifested in altered molecular architecture, have on macroscopic physical properties.

Introduction

We have previously reported on a new method for the rapid synthesis of hyperbranched aromatic poly(ether imide)s (HBPEIs).[1] The method involves the fluoride-catalyzed reaction of AB_2 monomers containing a pair of *tert*-butyldimethylsilyl (TBDMS) protected aromatic hydroxyl groups and a single activated aryl fluoride. Specifically, the polymerization of *N*-[3,5-di(*tert*-butyldimethylsilyloxy)phenyl]-4-fluorophthalimide (**1**) at 240 °C proceeded very rapidly (2.5 min), yielding high molecular weight hyperbranched poly(ether imide) **2a** with a degree of branching (DB) of 66% (Scheme 1).[2] Upon further investigation, we discovered that the degree of branching of the hyperbranched poly(ether imide) is sensitive to the polymerization time where DB decreases with increasing reaction time. To our knowledge, there are no other reported condensation methods for the synthesis of hyperbranched polymers that can yield a series of polymers with varying degrees of branching from a single monomer. This polymerization method can thus be used to gain access to a variety of materials of the same constitution but with differing structures due to changes in branching and molecular weight. It also provides a unique opportunity to investigate whether macroscopic phenomena, such as rheological properties, are affected by molecular architecture differences brought on by changes in the degree of branching. This paper describes the synthesis, characterization, and selected rheological properties of a series of five hyperbranched poly(ether imide)s with differing degrees of branching.

Scheme 1. Synthesis of HBPEIs



1
R = TBDMS

2a x = 2.5 min
2b x = 5.0 min
2c x = 7.5 min
2d x = 10.0 min
2e x = 20.0 min

Experimental Section

Measurements. ^{1}H NMR spectra of hyperbranched poly(ether imide)s in CD_2Cl_2 were obtained on a Varian Unity 500 MHz spectrometer using the residual ^{1}H solvent peak as a reference. Gel permeation chromatography (GPC) measurements were performed in *N*-methylpyrollidinone (NMP) with 0.05 M LiBr at 65 °C with a Waters 515 HPLC pump, a Viscotek model 300 triple detector array, and a series of three Polymer Laboratories Plgel 10 μm mixed bed light scattering (7.8 × 300 mm) columns. Molecular weight data were determined using Viscotek's TriSEC software. The light scatttering constant, mass constant, and viscosity constant were determined from a single 90 kDa narrow polystyrene standard and checked against other known polystyrene standards for accuracy. High-performance liquid chromatography (HPLC) separations were performed on a silica 80-125-C5 analytical column (4.6 × 25 mm) using a Waters 600 HPLC pump and a Waters 2487 dual wavelength absorbance detector monitoring a single wavelength at 290 nm.

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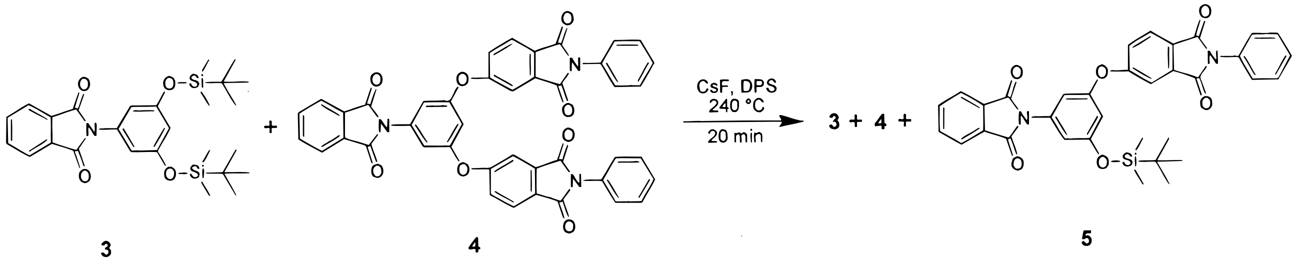
Scheme 2. Model Reaction To Show that Observed Changes in Degree of Branching Are a Result of Transetherification



Simple shear and creep measurements were made on a TA Instruments AR 1000 N constant stress rheometer using a cone and plate geometry. All experiments were conducted with a 2 cm 2° cone that is accurate to ±3%. The hyperbranched poly(ether imide)s were dissolved in 1,2-dichlorobenzene to prepare solutions ranging from 20 to 45 wt % polymer. In addition to shear viscosity, the normal stress response in simple shear flow was also measured. A solvent trap was used to prevent evaporation, and experiments were performed in the temperature range from 5 to 25 °C. Temperature control was achieved with a Peltier plate (0−100 °C) to a precision of 0.1 °C.

Steady-state flow birefringence measurements were made for 0.5 g/dL solutions of the poly(ether imide)s in 1,2-dichlorobenzene. Stock solutions were made by slow stirring with a magnetic stirrer 1 day prior to the experiment. A couette flow cell was used to measure linear birefringence over a range of shear rates from 1 to 600 s^{-1}. The rotor diameter was 3.7 cm, and the gap size was 0.7 mm. All measurements were performed in the flow-shear plane, i.e., the beam propagated vertically (down the vorticity direction) through the gap. Details on the apparatus, optical configurations, and methods of analysis can be found in several papers and an associated thesis study.[3−5] Temperature was maintained at 25 ± 0.1 °C with a Neslab RTE 111 circulating system.

Synthesis. Monomer **1** was synthesized as previously described and was 99.7% pure as determined by analytical HPLC.[1] A series of five hyperbranched poly(ether imide)s **2a**−**e** (Scheme 1) were prepared with reaction times of 2.5, 5.0, 7.5, 10.0, and 20.0 min. For all reaction times, the polycondensation of **1** was performed by quickly immersing a polymerization vessel containing monomer, diphenyl sulfone (DPS) (Aldrich 97%), and a catalytic amount of cesium fluoride (Aldrich 99.9%), under a nitrogen atmosphere, into a preheated 240 °C silicon oil bath. The solid reagents melted immediately forming a slightly yellow molten solution. Within seconds of melting, the reaction mixture began bubbling vigorously, and TBDMS fluoride evolution was observed. After the mixture was mechanically stirred for the designated time (time zero being the complete melting of the solid reagents), the reaction vessel was removed from heat and cooled in air for aproximately 30 s. Toluene was added to the reaction mixture before solidification and was followed by acetone. The solution was filtered to remove insoluble catalyst, and the solvent was removed in vacuo yielding a white powder. This powder was slurried in hot ethanol, and the insoluble polymer was separated from the DPS by filtration and isolated as a white amorphous powder. The absence of DPS was verified by NMR. The resulting polymer was dried under vacuum at 140 °C for 24 h. The synthesis and characterization of model compounds **3**−**5** (Scheme 2) have been previously reported.[1,6,7]

Results and Discussion

Polymer Characterization. All of the hyperbranched polymers **2a**−**e** exhibit high solubility in common organic solvents. Gel permeation chromatography data for hyperbranched poly(ether imide)s **2a**−**e** are given in Table 1. The number-average molecular weight (M_n) increased modestly with increasing reaction time through the series of polymers from 52 to 85 kDa. The weight-average molecular weight (M_w) increased significantly from 82 to 322 kDa on going from a reaction time of 2.5 to 10.0 min and then decreased to 295 kDa at 20.0 min. The polydispersity index (PDI) of the polymers **2a**−**2d** increased from 1.6 to 4.1 as the degree of branching decreased and then decreased to 3.5 for polymer **2e**.

Table 1. Yield, Degree of Branching[a] (DB), and GPC Molecular Weights[b] for Hyperbranched Poly(ether imide)s as a Function of Reaction Time

reaction time (min)	M_n (kDa)	GPC (NMP) M_w (kDa)	PDI	yield (%)	DB[a]
2.5	51.6	82.2	1.6	90	0.66
5.0	70.8	141.8	2.0	94	0.59
7.5	75.8	176.0	2.3	96	0.52
10.0	77.5	322.6	4.1	98	0.44
20.0	85.0	295.4	3.5	99	0.42

[a] Determined by ^1H NMR. [b] GPC data were obtained in NMP with 0.05 M LiBr with light scattering calibration.

The degree of branching for the poly(ether imide)s **2a**−**e** was determined by ^1H NMR analysis[1] utilizing Frey's definition for the calculation of degree of branching[8]

$$DB_{\mathrm{Frey}} = \frac{2[D]}{2[D] + [L]} \tag{1}$$

where [D] and [L] represent the fractions of dendritic and linear segments, respectively. The spectra used for the determination of DB for each of the poly(ether imide)s are shown in Figure 1. The integration of the dendritic protons H_b and the linear proton H_a, normalized to a value of 1.00, gives the DB values shown in Table 1.

The change in degree of branching as a function of reaction time is not accompanied by the appearance of any new resonances in the ^1H NMR, suggesting that a secondary reaction occurs which scrambles the original polymer structure formed in the early stages of polymerization. The vigorous bubbling observed during the polycondensation of **1**, which is associated with TBDMS−fluoride evolution, ceases after approximately 2.5 min, indicating that the polymerization is near completion. From the observed changes in the degree of branching, it is apparent that the reaction responsible for the reduction in branching occurs after the consumption of monomer. The reaction that alters the degree of branching likely proceeds via a transetherification mechanism which is catalytic in phenoxide anion. Reactions of this type involving aryloxyphthalimides are known.[9,10] Evidence supporting such a transetherification mechanism for the hyperbranched poly(ether imide)

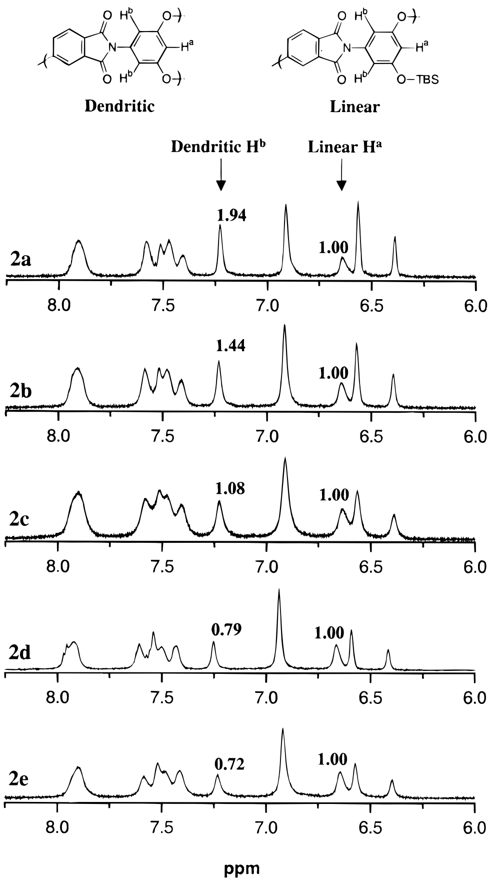


Figure 1. ^{1}H NMR plots (CD_2Cl_2, 22 °C, 500 MHz) of the aromatic region for HBPEIs **2a**–**e** showing integrations used to determine the DB (H^a normalized to 1.0).

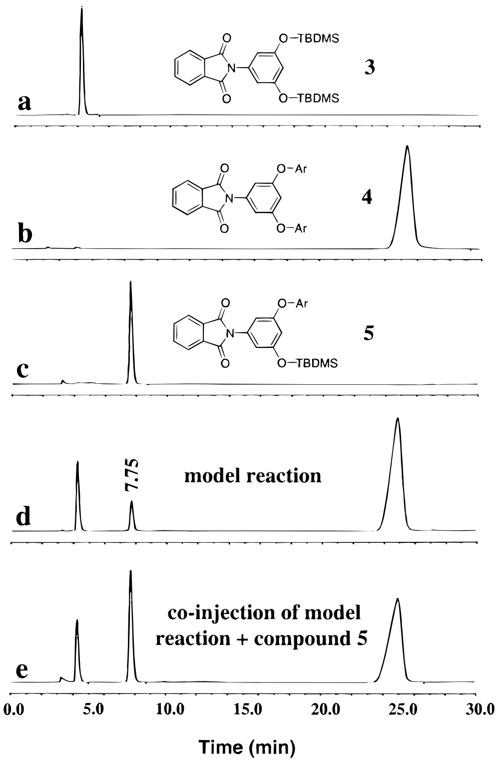


Figure 2. HPLC chromatograms for model transetherification reaction (Scheme 2): (a) *N*-[3,5-di-*tert*-butyldimethylsilyloxy)-phenyl]phthalimide (**3**); (b) *N*-[3,5-bis(4-phenoxy-*N*-phenyl phthalimide)phenyl]phthalimide (**4**); (c) *N*-[3-(4-phenoxy-*N*-phenylphthalimide)-5-(*tert*-butyldimethylsiloxy)phenyl]-phthalimide (**5**). (d) Reaction mixture obtained upon heating model compounds **3** and **4** for 20.0 min at 240 °C in the presence of a catalytic amount of CsF. (e) Co-injection of the crude reaction of model compounds **3** and **4** after 20.0 min and an authentic sample of compound **5**.

2 was obtained by us from the reaction of model compounds as shown in Scheme 2. Reaction of *N*-[3,5-di-*tert*-butyldimethylsilyloxy)phenyl]phthalimide (**3**) with *N*-[3,5-bis(4-phenoxy-*N*-phenyl phthalimide)phenyl]phthalimide (**4**) at 240 °C with 2 mol % CsF in diphenyl sulfone (DPS) mimics the reaction of terminal groups on the hyperbranched polymer with dendritic branching units in the polymer backbone. Figure 2 shows stacked HPLC chromatograms of the pure model compounds and of the reaction of model compounds **3** and **4** after 20 min. The expected transetherification product *N*-[3-(4-phenoxy-*N*-phenylphthalimide)-5-(*tert*-butyldimethylsiloxy)phenyl]phthalimide (**5**) is seen at 7.75 min in Figure 1d, and its identity was confirmed by co-injection with an independently synthesized[1,7] sample of **5** (Figure 2e). On the basis of the changes in DB and the absence of new signals in the ^{1}H NMR, combined with model compound studies (Figure 2), it is reasonable to suggest that the initial hyperbranched structure is driven to a more thermodynamically stable, less branched form by transetherification reactions catalyzed by cesium phenoxide end groups.

Rheology. Figure 3 shows the steady shear behavior of 40 wt % solutions of the hyperbranched poly(ether imide)s in 1,2-dichlorobenzene and indicates that shear thinning and the onset of normal stresses correlate with the degree of branching. As DB decreases, the magnitude of the viscosity and first normal-stress coefficient (N_1) increase. Furthermore, with a decrease in DB, the onset of shear thinning (accompanied by a rise of normal stress effects) appears at lower shear rates. The effects of DB are also observed in the shear rate dependence of the steady-state linear birefringence (Δn), shown in Figure 4. The hyperbranched poly(ether imide) **2a**, which has the highest degree of branching, shows the least birefringence, while the hyperbranched poly(ether imide) **2e**, with the lowest degree of branching, exhibits the highest birefringence. The birefringence of the other samples lie in between, with birefringence decreasing as degree of branching increases.

The birefringence observations, which are determined by the optical anisotropy of the sheared molecules and are a consequence of their deformation and orientation in the flow field, and the rise of normal stress effects, which for linear polymers is generally assumed to be proportional to the degree of chain entanglement,[11] are consistent with the global molecular shape of the hyperbranched polymers becoming more open and elongated and thus capable of higher degrees of entanglement coupling. These rheological changes are likely a convolution of both degree of branching and molecular weight effects. Even though the changes in the rheological properties correlate with the extent of branching, molecular weight data from light scattering GPC suggest that the differences in solution properties of the hyperbanched poly(ether imide)s are due largely to changes in molecular weight. To clarify the contributions of DB and molecular weight to the observed rheological properties, it would be useful to have two series of hyperbanched poly(ether imide)s: one series of varying molecular weight with constant polydisper-

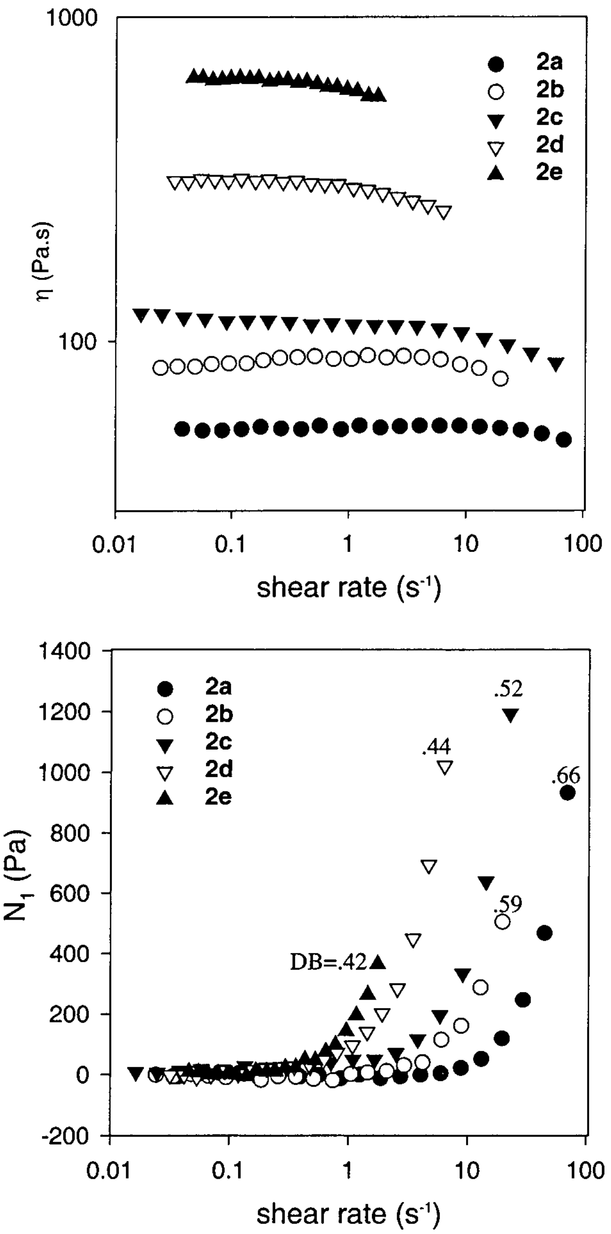


Figure 3. Simple shear flow viscosity and N_1 (first normal-stress coefficient) plotted as a function of shear rate for 40 wt % solutions of HBPEIs **2a**−**e** in 1,2-dichlorobenzene at 25 °C.

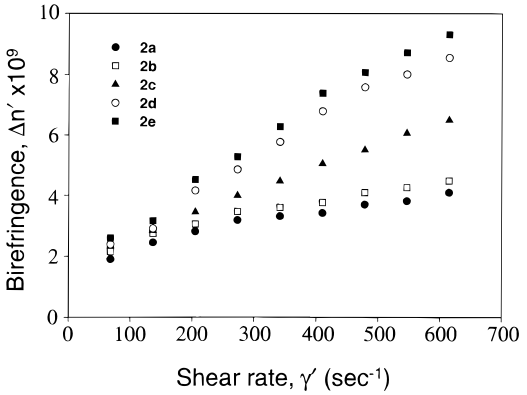


Figure 4. Birefringence as a function of shear rate for 0.5 g/dL solutions of HBPEIs **2a**, **2b**, **2d**, and **2e** in 1,2-dichlorobenzene at 25 °C.

sity and degree of branching and one series of varying degree of branching and constant molecular weight and polydispersity. The synthesis of these two series will be a substantial challenge and may not be feasible.

Conclusion

Varying the reaction time of the single-step, fluoride-catalyzed, synthesis of hyperbranched poly(ether imide)s from *N*-(3,5-di-*tert*-butyldimethylsilyloxyphenyl)-4-fluorophthalimide (**1**) resulted in a series of polymers with the same constitution but with varied extents of branching (42−66%) and molecular weight. The observed changes in the degrees of branching are a result of transetherification reactions, which occur after the initial consumption of monomer and are catalyzed by the active cesium phenoxide end groups. Further kinetic studies of the time dependence of the transetherfication rearrangement are currently underway.

Strong correlations of the degree of branching with rheological properties, where solutions of the hyperbranched poly(ether imide)s showed shear thinning and normal stress effects which increased as DB decreased and birefringence that increased with decreasing degree of branching, were observed. Nevertheless, the substantial increase in the weight-average molecular weight (M_w) with reaction time suggests that the observed differences in rheological properties may be a function of the change in molecular weight. On the basis of this work, it is not yet possible to determine whether the changes in the degree of branching, which may result in changes in molecular architecture, have a measurable effect on rheological properties. Further studies, as discussed earlier, will be necessary to answer this question.

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References and Notes

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(2) The concise visual representation of the branched nature of a hyperbranched polymer is difficult. Although the structure **2** in Scheme 1 does not represent the branched nature of the hyperbranched poly(ether imide), it does accurately represent the appropriate end group composition in the polymer.
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