Indirect Method for Determining Degree of Branching in Hyperbranched Polymers

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Received June 6, 2001

ABSTRACT: In an attempt to relate architecture to physical properties through a systematic study of degree of branching (DB), we recently reported the copolymerization of a series of AB/AB$_2$ monomers ranging from 0 to 1 mole fraction AB monomer content (x_{AB}). However, the DB of copolymers with $0.25 < x_{AB} < 1.0$ were not measurable by standard ^{1}H NMR due to severe aggregation and lack of dispersion. To indirectly measure the DB of the whole series, a reaction scheme involving nonpolymerizable small molecules that contain the A, B, and B$_2$ functionalities ((A + B)/(A + B$_2$) model reaction), whose products represent the linear and dendritic connectivities in the AB/AB$_2$ copolymer products, was devised. By control of the stoichiometry and utiliziation of reaction conditions identical to those of the polymerizations, the products representing hyperbranched polymer units were produced and their ratios were monitored by ^{1}H NMR and/or HPLC to indirectly determine the DB. In all reactions the A functionality was consumed in 2.5 min or less ($p_A = 1$ at 2.5 min) and no detectable side products were observed in either analytical technique. Excellent agreement in DB was observed for copolymer compositions that could be measured and the corresponding model reactions, validating our indirect method for measuring DB in our AB/AB$_2$ ether−imide copolymers.

Introduction

The architectural parameter of branching introduces new physical properties and levels of control not possible in strictly linear polymers.[1] Recently, much interest has been given to highly branched polymers such as perfectly branched dendrimers[2] and randomly branched hyperbranched polymers[3] (HBP's). High levels of branching have introduced the added variable of end group dominated physical properties. Typically, this higher concentration of end groups leads to increased solubility and blend compatibility and also leads to reduced viscosity and crystallinity relative to linear analogues.[4]

Dendrimers are synthesized discretely by convergent or divergent methods using AB$_m$-type monomers in a repetitive protection-deprotection manner. Production of high molecular weight monodisperse, perfectly branched dendrimers typically requires multiple reactions and purifications. The tedious and labor intensive nature of the synthesis limits their use in large-scale applications. To circumvent this problem, many researchers have focused on the one-pot polymerization of AB$_m$ ($m \geq 2$) monomers to produce highly branched, polydisperse, high molecular weight polymers in quantities suitable for bulk applications. The theoretical framework for predicting molecular weight distributions via random condensation polymerizations of AB$_m$ type monomers was originally put forth by Flory.[5,6] Due to the random, unpredictable nature of the branching reactions and the polydispersity inherent in all polymerizations, a complex mixture of molecular weight and architectural variants results.

Historically, these mixtures have been characterized by measuring molecular weight via size exclusion chromatography and by extracting architectural information by determining the average degree of branching (DB) within the mixture. This architectural parameter was originally defined by Frechet[7] as in eq 1, where D, T,

$$\mathrm{DB(AB_2)} = \frac{T_{\mathrm{AB_2}} + D_{\mathrm{AB_2}}}{T_{\mathrm{AB_2}} + D_{\mathrm{AB2}} + L_{\mathrm{AB_2}}} \tag{1}$$

and L represent the three possible connectivities (dendritic, terminal, and linear) from an AB$_2$ random polymerization. If conversion of A is high, $D \approx T$, the formula is reduced to the more widely used equation put forth by Frey:[8]

$$\mathrm{DB(AB_2)} = \frac{2D_{\mathrm{AB_2}}}{2D_{\mathrm{AB_2}} + L_{\mathrm{AB_2}}} \tag{2}$$

By definition, a linear polymer has no dendritic segments and DB equals zero. In contrast, dendrimers exhibiting perfect branching have no linear segments and therefore DB equals unity. Because HBP's have both linear and dendritic units, a reliable analytical method must be sought to measure the relative concentrations of these units to calculate their DB's which fall in the architectural continuum between linear polymers and dendrimers.

Theoretical degrees of branching for AB$_m$-type homopolymers and AB$_m$/AB copolymers have recently been discussed by Frey.[9] Equal reactivity of B functional groups, the absence of intramolecular cyclization, and the absence of secondary reactions must be assumed in his treatment. The calculations give a DB = 0.5 for condensation polymerizations of AB$_2$ monomers at complete conversion ($p_A = 1$) if all of these prerequisites are satisfied. The theoretical DB for AB/AB$_2$ copolymers as a function of the starting mole fraction AB monomer (x_{AB}) and varies between 0.50 and 0.00 for fully hyperbranched and fully linear polymers, respectively.

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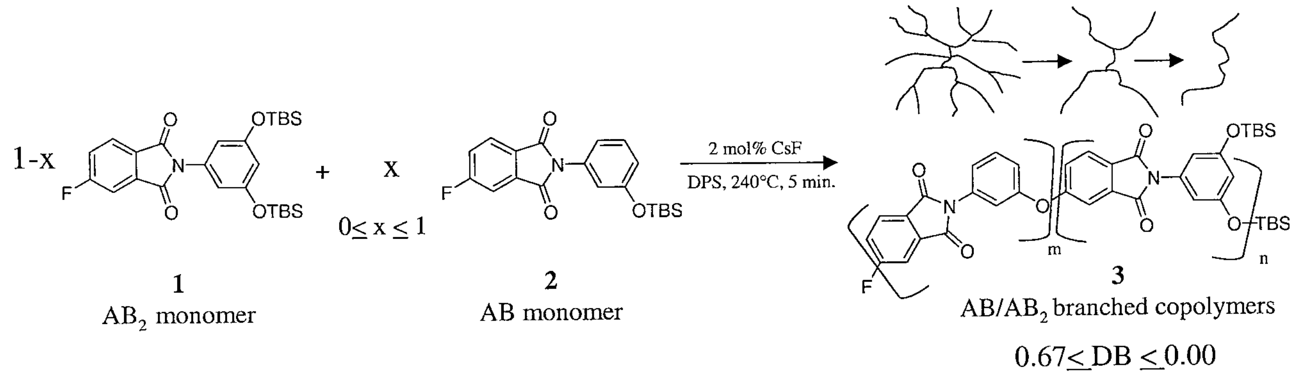
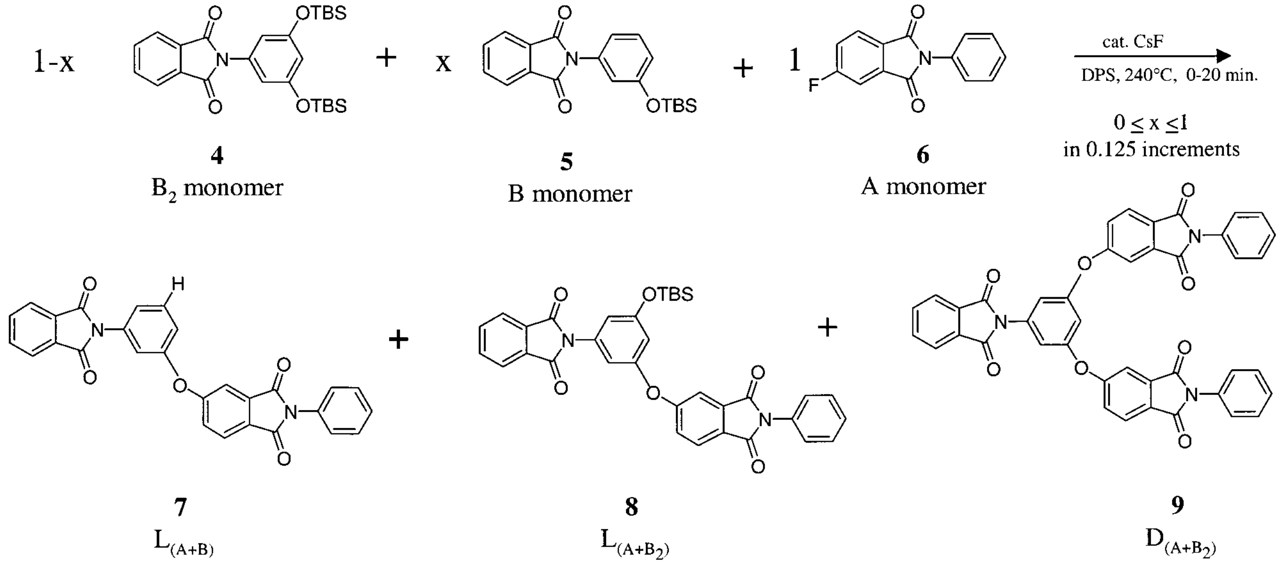
10.1021/ma010980n CCC: $22.00

Scheme 1. Reaction Scheme for AB/AB$_2$ for Branched Polyetherimides



Scheme 2. Reaction Scheme for (A+B)/(A+B$_2$) Model Compound Reactions



Given the assumptions present in the theoretical treatment, experimental observations often do not adhere to theory, necessitating experimental approaches to determine DB. Some of these approaches include analysis by NMR spectroscopy (^{1}H or ^{13}C) of the resultant polymer or degradation of the polymer followed by analysis of the resulting dendritic, terminal, and linear fragments.[10] Typically, ^{1}H NMR is used to measure the dendritic and linear values of the polymer after synthesizing suitable model compounds representing dendritic and linear units in order to determine the chemical shifts of key protons for each unit.[11] A basic requirement is that the model compounds and the branched polymer to be measured must be soluble in the same deuterated solvent for comparison. In addition, there must be adequate ^{1}H dispersion and resolution of peaks of the polymer for accurate integration of the dendritic and linear contributions. However, in the case where solubility, dispersion, and resolution are problematic, another method for DB determination must be sought. Herein, we describe a specific case in which the traditional ^{1}H NMR determination of DB for a series of AB/AB$_2$ copolymers (Scheme 1) was inadequate for many of the aforementioned reasons. Therefore, model reactions of nonpolymerizable small molecules with independent A, B, and B$_2$ functionalities were reacted together and their dendritic and linear product ratios were used to indirectly monitor DB as a function of reaction time for AB/AB$_2$ poly(ether−imide) (PEI) copolymers (Scheme 2).

Experimental Section

All materials and solvents used were reagent grade and used without further purification unless noted otherwise. ^{1}H NMR spectra were taken on a Varian Unity 500 MHz spectrometer using residual solvent peak as a reference. HPLC analyses were performed with a Waters 600 pump and a Waters 2487 dual wavelength detector. The isocratic mobile phase composition consisted of 18% HPLC grade ethyl acetate and 82% HPLC grade hexane. The column was a normal phase (4.6 × 25 mm) silica column produced by Rainin (80−125-C5). The wavelength used to correlate absorbance to concentration was 275 nm. Differences in molar absorptivity were corrected by running known concentrations of mixtures of **7**−**9** and determining appropriate scale factors. To normalize concentration the absorbance areas of **8** were divided by 0.95 and those of **9** were divided by 1.59 to normalize for differences in molar absorptivity between products **7**−**9**.

General Synthetic Procedure ($x_{(A+B)} = 0$). To a 25 × 200 mm Pyrex glass tube equipped with N$_2$ purge and a magnetic stir bar was charged **4** (0.484 g, 1.00 mmol), **5** (0.241 g, 1.00 mmol), and diphenyl sulfone (0.500 g), this was quickly submerged into a silicon oil bath that was preheated to 240 °C. All solids melted quickly and after 1 min when all solids had disappeared a spatula tip of CsF was added. The reaction began to bubble immediately and aliquots were removed with disposable glass pipets (30 s intervals until 5 min, then 1 min intervals until 10 min, and then 2.5 min intervals until 20 min) and quickly dissolved in CD$_2$Cl$_2$ or CH$_2$Cl$_2$ depending on the analyticial technique (NMR or HPLC). Represenative chromatograms and the resulting DB caclulations for the preceding reaction can be seen in Figure 1 for a reaction time of 5 min.

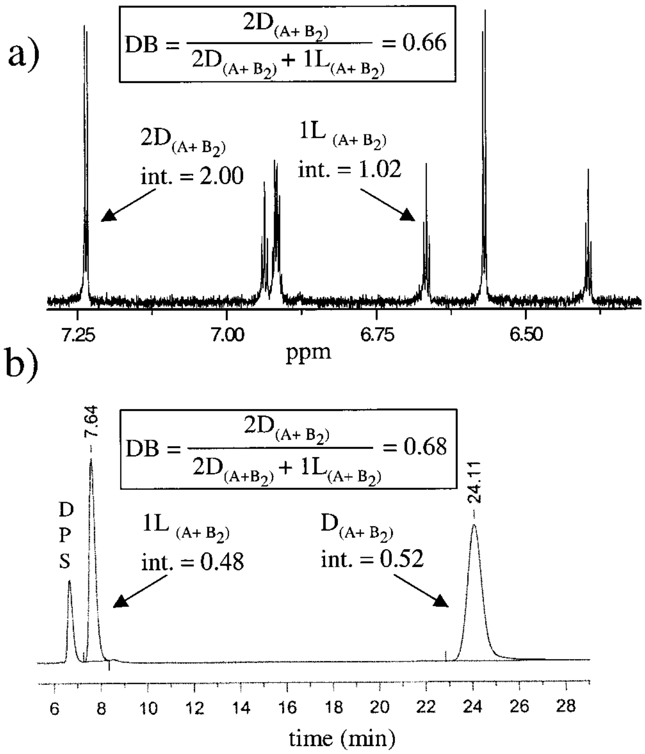


Figure 1. (a) ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum and (b) HPLC spectrum of model compound reaction with $x_{A+B} = 0.0$ (5 min reaction time) and subsequent DB calculation from area integration of the appropriate dendritic and terminal segments.

Results and Discussion

In an attempt to relate architecture to physical properties through a systematic study of DB, we recently reported the copolymerization of a series of AB/AB_2 monomers ranging from 0 to 1 x_{AB} (Scheme 1).[12] From previous work, we found that our AB_2 monomer (**1**) had unequal reactivity rates for the B groups and during polymerization aryl ether exchange reactions occurred. The reasons for this unequal reactivity and the rearrangement reaction are not yet fully understood; however, both phenomena contributed to nonideal DB behavior (DB ranged from 0.66 to 0.44 with reaction time) in the AB_2 homopolymers.[11,13] The extent to which these nonidealities occurred for the AB/AB_2 copolymer series needed to be determined experimentally, preferably using measurable ^{1}H NMR signals. Due to the additional linear unit found in AB/AB_2 copolymers, the equation for calculating DB (at $p_A = 1$)[7] expands to

$$\mathrm{DB(AB/AB_2)} = \frac{2D_{AB_2}}{2D_{AB_2} + L_{AB_2} + L_{AB}} \tag{3}$$

As described previously,[11] model compounds **4**, **5**, and **7**–**9** representing the five possible units in an AB/AB_2 copolymer were synthesized. ^{1}H NMR experiments in CD_2Cl_2 gave the dispersion and resolution of the linear and dendritic segments necessary for DB calculations in the corresponding copolymers (Figure 2). When the AB/AB_2 copolymers were synthesized, the DB was measurable by this traditional method for copolymers having $x_{AB} \leq 0.25$. Deviations from ideal predictions were expected due to unequal reactivity of the B groups. However, the DB of copolymers with $x_{AB} > 0.25$ were not measurable by ^{1}H NMR due to severe aggregation, lack of dispersion, and/or lack of solubility (Figure 3). Attempts to identify a solvent that dissolved the model compounds and polymers and dispersed all signals to determine the DB of the whole AB/AB_2 series were unsuccessful. To determine the DB for copolymers with $0.25 < x_{AB} < 1.0$, an indirect method of determining DB was needed.

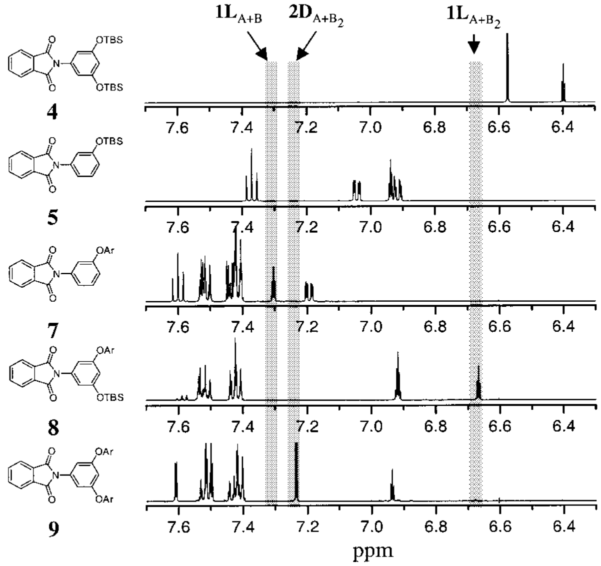


Figure 2. ^{1}H NMR (500 MHz, CD_2Cl_2) of model compounds representing the five type of units found in PEI AB/AB_2 and showing adequate dispersion for DB calculations.

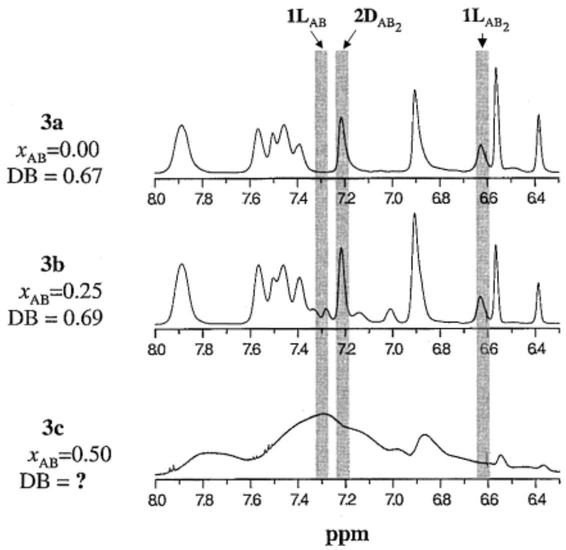


Figure 3. ^{1}H NMR (500 MHz, CD_2Cl_2) of 0.00, 0.25, and 0.50 x_{AB} copolymers. The DB is measurable for 0.00 and 0.25 x_{AB}, but the DB of copolymers with x_{AB} >0.25 could not be measured due to aggregation, lack of dispersion, and/or insolubility in CD_2Cl_2.

Because the model compounds **4**, **5**, and **7**–**9** originally synthesized to identify key ^{1}H NMR signals gave necessary dispersion and resolution in ^{1}H NMR and HPLC, it was hypothesized that the reaction of **4** + **5** with **6** (B_2 + B with A, respectively) would provide small molecule products **7**–**9** whose relative concentrations could be quantified as a function of reaction time. The DB could then be calculated by substituting the resulting concentrations of the dendritic (**9**) and linear (**7**–**8**) model compounds into the DB equation (equation 3). To precisely mimic the polymerization conditions the concentration of **6** was kept constant and the total concen-

Table 1. Initial Reaction Condtions for (A + B)/(A + B_2) Model Compound Reactions

$x_{(A+B)}$	compound **4** (mmol/g)	compound **5** (mmol/g)	compound **6** (mmol/g)	DPS (g)	CsF	reacn temp (°C)	reacn time (min)
0.000	(1.00/0.484)	–	(1.00/0.241)	0.5	spatula tip	240	20
0.125	(0.875/0.429)	(0.125/0.044)	(1.00/0.241)	0.5	spatula tip	240	20
0.250	(0.750/0.363)	(0.250/0.088)	(1.00/0.241)	0.5	spatula tip	240	20
0.375	(0.625/0.303)	(0.375/0.132)	(1.00/0.241)	0.5	spatula tip	240	20
0.500	(0.500/0.242)	(0.500/0.177)	(1.00/0.241)	0.5	spatula tip	240	20
0.625	(0.375/0.182)	(0.625/0.221)	(1.00/0.241)	0.5	spatula tip	240	20
0.750	(0.250/0.121)	(0.750/0.246)	(1.00/0.241)	0.5	spatula tip	240	20
0.875	(0.125/0.061)	(0.875/0.309)	(1.00/0.241)	0.5	spatula tip	240	20
1.000		(1.00/0.484)	(1.00/0.241)	0.5	spatula tip	240	20

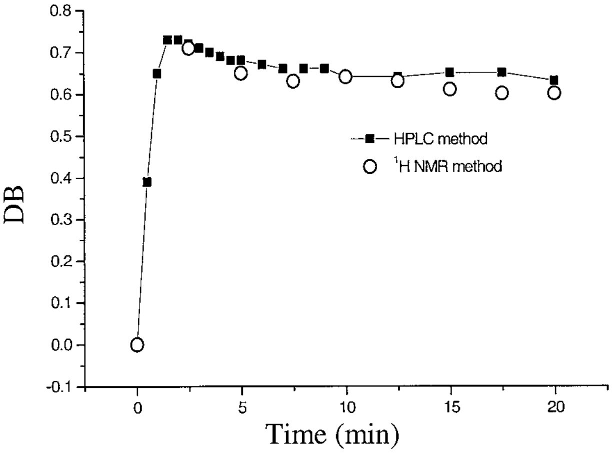


Figure 4. Comparison of HPLC and ^{1}H NMR technique for the determination of DB of model reactions with $x_{(A+B)} = 0.00$. Line added for clarity and does not represent a fitted function.

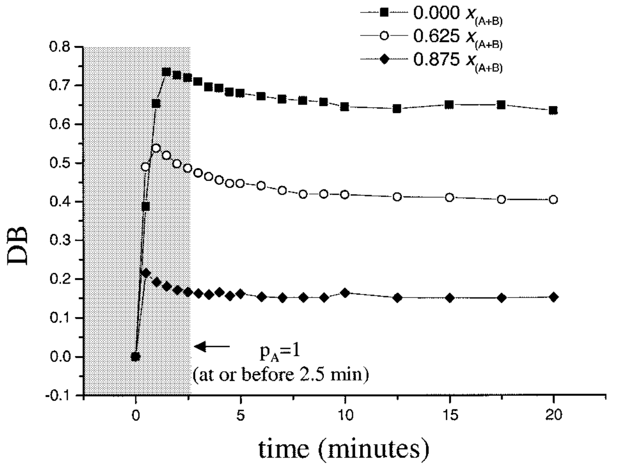


Figure 5. Representative plots of DB vs reaction time for model compound reactions with 0.00, 0.625, and 0.875 $x_{(A+B)}$ as determined by HPLC. Lines were added for clarity and do not represent a fitted function

tration of **4** + **5** was kept constant and equal to that **6** to give the (A + B)/(A + B_2) model reaction correlating to the AB/AB_2 polymerization reactions (Scheme 2). To describe the initial monomer concentrations, we chose to use the molar fraction of [**5**]/([**4**] + [**5**]) denoted $x_{(A+B)}$, the corollary to x_{AB} in the AB/AB_2 polymerization scheme.

To verify that both ^{1}H NMR and HPLC gave the same results in the DB calculation the reaction in Scheme 2 was performed with $x_{(A+B)} = 0.0$. The relative intensities of the linear (**8**) and dendritic (**9**) products were measured as a function of time using ^{1}H NMR and HPLC. The DB at each time interval was then calculated using eq 3 and plotted as a function of time. Both measurement techniques gave the same trend (Figure 4). The degree of branching rises steadily and peaks at about 2.5 min, then slightly decreases over time and stabilizes by 10 min. HPLC became the preferred technique to monitor DB for the rest of the series because it was more amenable to high through-put data collection, has higher resolution capabilities at low concentration, and was very consistent with the ^{1}H NMR data (see Figures 1 and 4).

The reactions depicted in Scheme 2 were run under the same conditions as the polymerizations and $x_{(A+B)}$ was varied in the range from 0 to 1 in 0.125 increments. All reactions showed the same general DB trend, with DB reaching a maximum before 2.5 min, at a time that roughly coincides with the complete consumption of the A functionality (**6**), which could no longer be detected by HPLC in any of the reactions after 2.5 min. As expected, DB decreased with increasing concentration of **5 (**B monomer) as can be seen in Figure 5. The slow decrease in DB after 2.5 min may be explained by a secondary transetherification reaction.[13] In AB_2 homopolymers, this side-reaction was responsible for larger DB decreases with longer reaction time (reaction times > 5 min). To alleviate this potential problem, the AB/AB_2 copolymerizations previously reported[12] were run for only 5 min, which was adequate to produce high molecular weight polymers without significant side reactions.

Since the polymerizations were run for 5 min, the degrees of branching of the model reactions were measured at the same amount of reaction time. To validate the assumption that using 5 min reaction times for both polymers and small molecules would provide comparable results, we compared the DB (as measured by^{1}H NMR) for the 0.00 and 0.25 x_{AB} polymers run at 5 min with the DB (as measured by HPLC) for the 0.00 and 0.25 $x_{(A+B)}$ model reactions at 5 min, and they gave excellent agreement (Figure 6). Since we had already shown that our HPLC method of DB determination correlated well with the ^{1}H NMR method (Figure 4), we were confident that the DB of the (A + B)/(A + B_2) model reaction series calculated at 5 min was an accurate representation of the DB for the AB/AB_2 copolymer series run for 5 min. These observations indicate size-independent reactivity rates as is observed with linear polymer reaction kinetics.[6]

As seen in Figure 6, the DB for x_{AB} and $x_{(A+B)} < 0.75$ gives a larger DB than expected for an ideal hyperbranch polymerization. This is a direct result of the unequal reactivity of the B functionalities. It is interesting to note that with x_{AB} or $x_{(A+B)}$ greater than 0.75, and $p_A = 1$, despite the differences in the relative reactivities of the B groups, the measured DB values approach those predicted by theory. This is due to the fact that an increasing number of linear AB_2 (L_{AB_2}) units react further to become dendritic units (D_{AB_2}) as x_{AB} or $x_{(A+B)}$

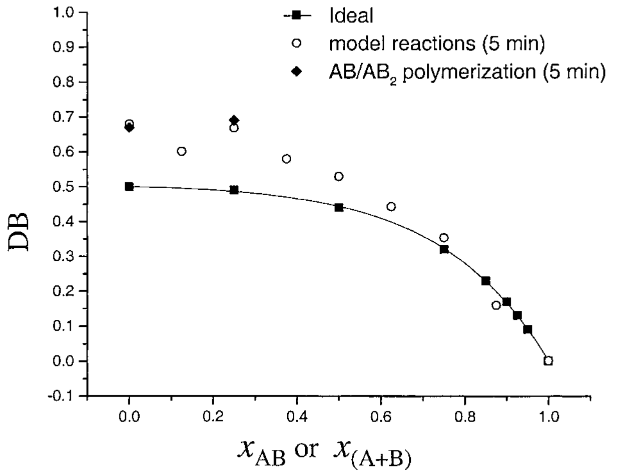


Figure 6. Plot of DB vs x_{AB} or $x_{(A+B)}$ for AB/AB$_2$ PEI polymerizations, (A + B)/(A + B$_2$) model reactions, and ideal AB/AB$_2$ polymerization with P_A=1.0.[8]

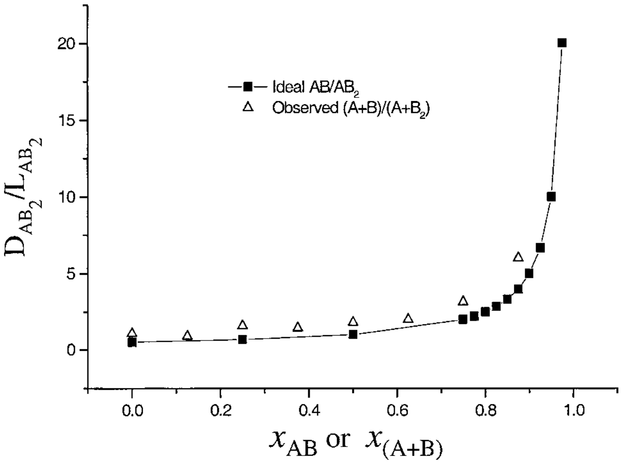


Figure 7. Plot of L_{AB_2}/D_{AB_2} vs x_{AB} or $x_{(A+B)}$ for (A + B)/(A + B$_2$) model reactions and ideal AB/AB$_2$ polymerization with P_A=1.0.

exceed 0.75. This can be illustrated by plotting the theoretical ratio of dendritic and linear units resulting from the AB$_2$ monomer (D_{AB_2}/L_{AB_2}) with respect to the x_{AB} composition at $p_A = 1$ (Figure 7).

When we assume equal reactivity we observe that below 0.75 x_{AB} the D_{AB_2}/L_{AB_2} is relatively constant then experiences a sharp rise above 0.75 x_{AB}. Above this critical value of x_{AB}, a rapid increase in the number of L_{AB_2} units that have reacted further to become D_{AB_2} can be seen. If we add to this plot our specific case where the relative rates of reactivity are unequal as indicated, we see that a very similar trend is observed, reinforcing the fact that at high x_{AB} the relative rates of reaction of the B groups become less important with regard to the polymer's architecture. Therefore, small percentages of AB$_2$ monomer can produce relatively highly branched AB/AB$_2$ copolymers regardless of reactivity rates of the B groups assuming that $p_A \sim 1.0$.

Conclusions

When describing the architecture of hyperbranched polymers and AB/AB$_2$ copolymers, the DB is typically measured by NMR or degradation methods. However, in cases where a spectroscopic handle cannot be found or chemical degradation is not feasible, another method must be sought to indirectly determine the DB of the branched polymer. By synthesizing nonpolymerizable small molecules that independently contain the A, B, and B$_2$ functionalities, a reaction scheme was devised which mimics the polymerization conditions of AB/AB$_2$ copolymers. The relative concentrations of the linear and dendritic small-molecule products can then be monitored as a function of time by an appropriate analytical method. At reaction times long enough for complete conversion of the A group ($p_A = 1.0$), the DB can then be accurately determined from the relative concentration of the linear and dendritic products. In our particular case, using the aformentioned method and utilizing HPLC as our analytical technique it was discovered that as a result of unequal reactivity of our B groups, a DB function different than that predicted by theory resulted for a series AB/AB$_2$ poly(ether−imide) copolymers. At short reaction times (5 min) for both the polymerization and model reactions, excellent agreement was obtained between direct and indirect methods. This demonstrates that small molecules that independently contain the A, B, and B$_2$ functionalities can be used to indirectly measure the DB of hyperbranched polymers or AB/AB$_2$ copolymers whose DB cannot be determined by the traditional direct methods. We believe this approach may be general for determining the degree of branching in a wide variety of hyperbranched polymers where steric effects do not inhibit chain growth.

Acknowledgment. This material is based upon work supported by, or in part by, the U.S. Army Research Laboratory and U.S. Army Research Office under grant number DAAG55-97-1-0126.

References and Notes

(1) Roovers, J. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; Wiley: New York, 1985; Vol. 2, p 478.
(2) For an up to date review of dendrimers, see: Vogtle, F.; Gestermann, S.; Hesse, R.; Schwierz, H.; Windisch, B. F. *Prog. Polym. Sci.* **2000**, *25*, 987−1041.
(3) For an up to date review of hyperbranched polymers, see: Voit, B. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2505−2525.
(4) Kim, Y. H.; Webster, O. W.; *Macromolecules* **1992**, *25*, 5561.
(5) Flory, P. J. *J. Am. Chem. Soc.* **1952**, *74*, 2718−2723.
(6) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(7) Hawker, C. J.; Lee, R.; Frechet J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583.
(8) Holter, D.; Burgath, A.; Frey, H. *Acta Polym.* **1997**, *48*, 30−35
(9) Frey, H.; Holter, D. *Acta Polym.* **1999**, *50*, 67−76.
(10) Kambouris, P.; Hawker, C. J. *J. Chem. Soc., Perkin Trans. 1* **1993**, *22*, 2717−2721.
(11) Thompson, D. S.; Markoski, L. J.; and Moore, J. S. *Macromolecules* **1999**, *32*, 4764−4768.
(12) Markoski, L. J.; Thompson, J. L.; Moore, J. S. *Macromolecules* **2000**, *33*, 5315−5317.
(13) Thompson, D. S.; Markoski, L. J.; and Moore, J. S.; Sendijarevic, I.; Lee, A.; McHugh, A. J. *Macromolecules* **2000**, *33*, 6412−6415.

MA010980N