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## Supporting Information for "Synthesis and Characterization of Linear-Dendritic Aromatic Etherimide Copolymers: Tuning Molecular Architecture to Optimize Properties and Processibility"

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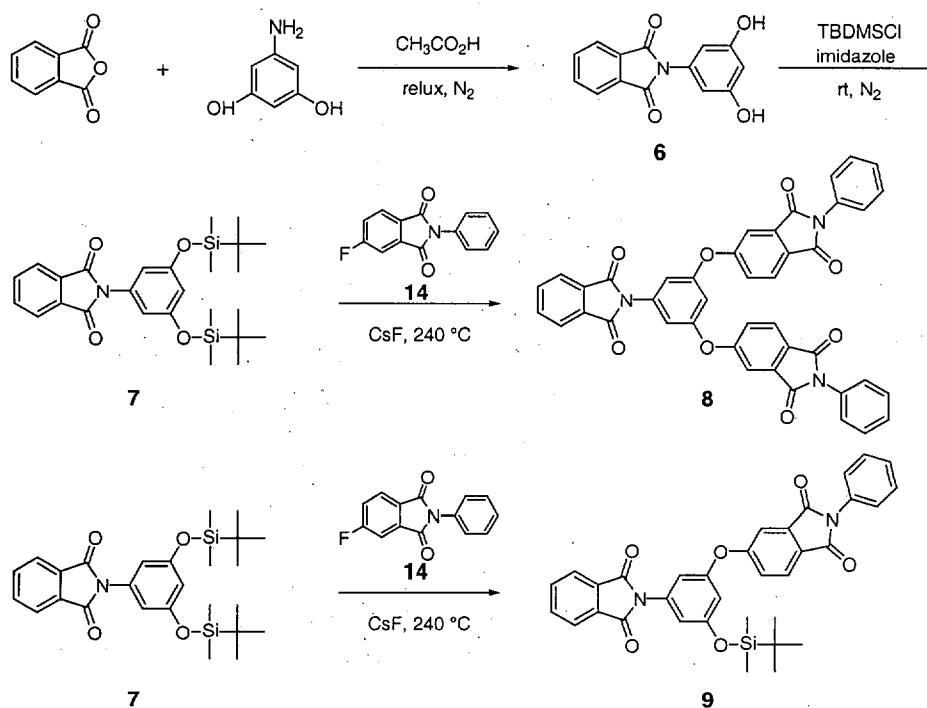
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### I. Experimental

All materials and solvents used were reagent grade and used without further purification unless noted otherwise. <sup>1</sup>H NMR spectra were taken on a Varian Unity 500 MHz spectrometer using residual solvent peak as a reference. Gel Permeation Chromatography (GPC) measurements were performed in NMP with 0.05 M LiBr at 65 °C with a Waters 515 HPLC pump, Viscotek model 300 TDA refractive index detector, NMP with 0.05 M LiBr at 65 °C and a series of three Polymer Laboratories PLgel 10um Mixed B LS (7.8 x 300 mm) columns that were calibrated with narrow molecular weight polystyrene standards over the range 1100 Da to 4.5 x 10<sup>6</sup> Da with a column exclusion limit of 1.0x10<sup>7</sup> Da. Thermal analysis measurements were conducted on the copolymers with a Mettler/Toledo DSC in aluminum pans in air and a Mettler/Toledo TGA—in alumina crucibles in either air or nitrogen (the composition of the purge gas was shown to have little to no effect on the 10% wt loss). Inherent viscosity measurements were made with an Ubbelohde capillary viscometer for etherimide copolymer solutions at concentrations of 0.5g/dL in DMAc. Temperature was maintained at 25 ± 0.1 °C with a Neslab RTE 111 circulating system. Films were prepared by making 10 weight % copolymer solutions in DMAc and casting them drop-wise with a glass pipette onto a glass slide and drying them in an oven at 150 °C for 1 h.

#### A. Model Compounds and Monomers

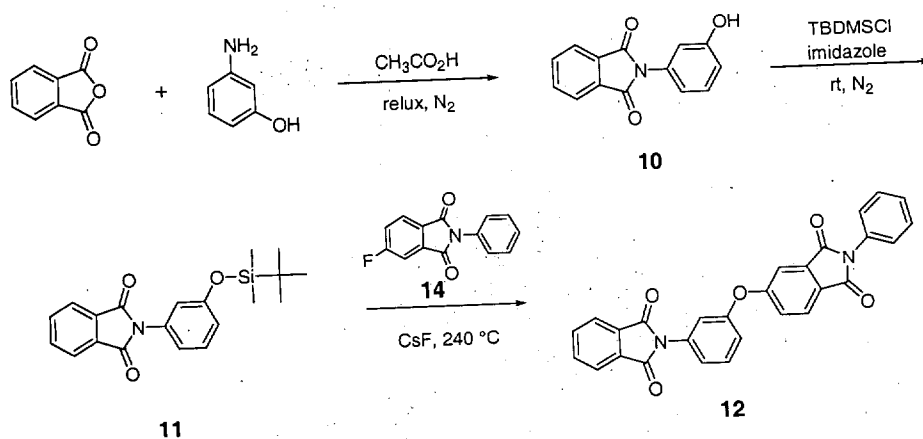
**N-(3,5-Hydroxyphenyl) phthalimide (6).** To a 500 mL round bottom flask fitted with a reflux



condenser and stir bar was charged phthalic anhydride (18 g, 70.53 mmol), 3,5-dihydroxyaniline (20 g, 159.85 mmol), and 200 mL glacial acetic acid. The mixture was stirred at room temperature for 10-15 minutes then placed into a 115 °C oil bath and brought to reflux. The reaction became homogeneous and was stirred under a nitrogen atmosphere for 3 hours. The flask was then cooled to room temperature, resulting in formation of a precipitate. This solid was collected by vacuum filtration, washed with cold glacial acetic acid followed by distilled H<sub>2</sub>O and dried overnight to afford white solid **6** in 90 % yield. <sup>1</sup>HNMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 8.52 (br s, 2 H), 7.91 (m, 4 H), 6.49 (d, 2 H, *J* = 2.03), 6.41 (t, 1 H, *J* = 2.14).

**N-(3,5-*t*-butyldimethylsiloxyphenyl) phthalimide (7).** To a 500 mL flask with a stir bar was charged bisphenol **6** (12.9 g, 50.7 mmol), *t*-butyldimethylsilylchloride (16.8 g, 111.5 mmol), imidazole (7.6 g, 111.5 mmol), and 200 mL CH<sub>2</sub>Cl<sub>2</sub>. This heterogeneous solution was stirred under a nitrogen atmosphere overnight. The imidazolium salts were removed by filtration and the product was run through a plug of silica gel, eluting with CH<sub>2</sub>Cl<sub>2</sub>, and concentrated *in vacuo*. The resulting yellow solid was slurried in EtOH and filtered to provide a white solid in 89% yield. <sup>1</sup>HNMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.92 (m, 2 H), 7.81 (m, 2 H), 6.57 (d, 2 H, *J* = 2.1), 6.39 (t, 1 H, *J* = 2.1), 0.99 (s, 18 H), 0.24 (s, 12 H). Anal. Calcd for C<sub>26</sub>H<sub>37</sub>NO<sub>4</sub>Si<sub>2</sub>: C, 64.55; H, 7.71; N, 2.90. Found: C, 64.55; H, 7.78; N, 3.00.

**N-3,5-bis-(4-phenoxy-N-phenyl phthalimide) phenyl phthalimide (8).** To a 200 mL flask with a stir bar was charged bis-TBDMS **7** (1.0 g, 2.06 mmol), fluorophthalimide **14** (1.0 g, 4.13 mmol), and diphenyl sulfone (DPS) as solvent (2.0g). This mixture was placed into a 230 °C silicone oil bath. The solids quickly melted and a small amount of CsF (spatula tip) was added; vigorous evolution of TBDMS fluoride could be visually detected. The reaction was stirred for 5 minutes, then removed from the oil bath and allowed to cool slightly. EtOH (caution: Flashpoint exceeded!) was added to quench the reaction and, upon cooling, precipitation occurred. The solid was boiled in EtOH, filtered, and dried. This process was repeated with EtOAc and dried to yield 56% of an off-white solid. <sup>1</sup>HNMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.95 (m, 4 H), 7.83 (m, 2 H), 7.61 (dd, 2 H, *J* = 2.2, 0.5), 7.51 (m, 6 H), 7.42 (m, 6 H), 7.24 (d, 2 H, *J* = 2.3), 6.93 (t, 1 H, *J* = 2.3). HRMS (FAB, *m/z*) for C<sub>42</sub>H<sub>23</sub>N<sub>3</sub>O<sub>8</sub>, calcd 697.148, found 698.156 (*M* + 1).

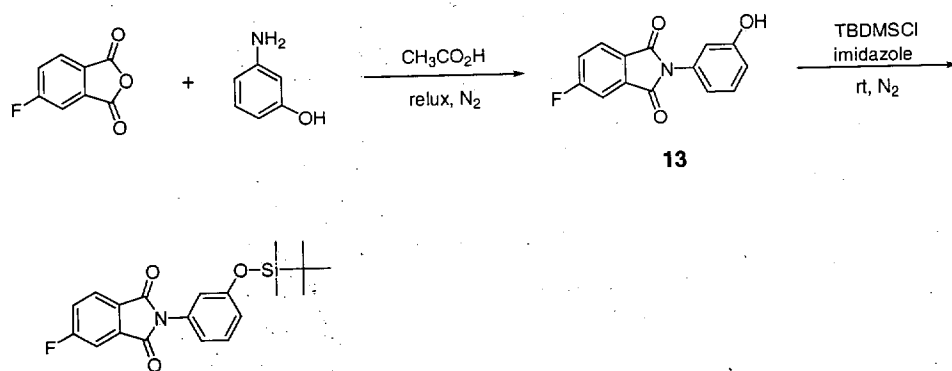


**N-3-(4-phenoxy-N-phenyl phthalimide)-5- *t*-butyldimethylsiloxy phenyl phthalimide (9).** To a 100 mL flask with a stir bar was charged bis-TBDMS **7** (1.0 g, 2.06 mmol), fluorophthalimide **14**

(0.5 g, 2.06 mmol), and diphenyl sulfone as solvent (1.5g). This mixture was placed into a 240 °C silicone oil bath. The solids quickly melted and a small amount of CsF (spatula tip) was added; vigorous evolution of TBDSMF could be visually detected. The reaction was stirred for 2.5 minutes, then removed from the oil bath and allowed to cool slightly. The reaction was quenched with EtOAc and some solid precipitated upon cooling. This precipitate was collected by filtration and was identified as **8**. The resulting mother liquor grew crystals, which were separated and identified as DPS. Flash column chromatography (40% EtOAc/hexanes) provided the desired product in 50 % yield. <sup>1</sup>HNMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.94 (m, 2 H), 7.91 (d, 1 H, *J* = 8.2), 7.82 (m, 2 H), 7.52 (m, 3 H), 7.42 (m, 4 H), 6.92 (ddd, 2 H, *J* = 4.1, 3.8, 1.9), 6.66 (t, 1 H, *J* = 2.2), 1.00 (s, 9H), 0.27 (s, 6 H). HRMS (EI, *m/z*) for C<sub>34</sub>H<sub>30</sub>N<sub>2</sub>O<sub>6</sub>Si, calcd 590.187, found 590.188.

**N-3-Hydroxyphenyl phthalimide (10).** To a 300 mL round bottom flask fitted with a reflux condenser and stir bar was charged phthalic anhydride (10 g, 67.5 mmol), 3-aminophenol (7.4 g, 67.5 mmol), and 150 mL glacial acetic acid. The mixture was stirred at room temperature for 10-15 minutes, then placed into a 115 °C oil bath and brought to reflux. The reaction became homogeneous and was stirred under a nitrogen atmosphere for 3 hours. The flask was then cooled to room temperature, resulting in formation of a precipitate. Water (60mL) was added and the solid was collected by vacuum filtration, washed with H<sub>2</sub>O, and dried overnight to afford a white fluffy solid in 93% yield. <sup>1</sup>HNMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 9.75 (s, 1 H), 7.92 (m, 2 H), 7.86 (m, 1 H), 7.19 (t, 1 H, *J* = 8.24), 6.84 (m, 2 H), 6.82 (dd, 1 H, *J* = 2.3, 0.89).

**N-3-*t*-butyldimethylsiloxyphenyl phthalimide (11).** To a 500 mL flask with a stir bar was charged phenol **10** (15.1 g, 63 mmol), *t*-butyldimethylsilylchloride (20.9 g, 138.6 mmol), imidazole (9.43 g, 138.6 mmol), and 250 mL CH<sub>2</sub>Cl<sub>2</sub>. This heterogeneous solution was stirred under a nitrogen atmosphere overnight. The imidazolium salts were removed by filtration and the product was run through a plug of silica gel, eluting with CH<sub>2</sub>Cl<sub>2</sub>, and concentrated *in vacuo* to provide a white crystalline solid in 86 % yield. <sup>1</sup>HNMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.94 (m, 2H), 7.81 (m, 2 H), 7.37 (t, 1 H, *J* = 8.2), 7.04 (ddd, 1 H, *J* = 7.9, 2.0, 1.8), 6.94 (t, 1 H, *J* = 2.1), 6.91 (ddd, 1 H, *J* = 8.1, 2.5, 0.9), 1.01 (s, 9H), 0.25 (s, 6H). HRMS (EI, *m/z*) for C<sub>20</sub>H<sub>23</sub>NO<sub>3</sub>Si, calcd 353.144, found 353.144.

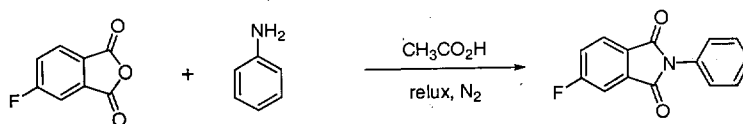


**N-3-(4-phenoxy-N-phenyl phthalimide) phenyl phthalimide (12).** To a 100 mL flask with a stir bar was charged TBDMS-protected phenol **11** (1.0 g, 2.82 mmol), fluorophthalimide **14** (0.68 g, 2.82 mmol), and diphenyl sulfone as solvent (2.0g). This mixture was placed into a 240 °C silicone oil bath. The solids quickly melted and a small amount of CsF (spatula tip) was added; vigorous evolution of TBDSMF could be visually detected. The reaction was stirred for 5 minutes, then

removed from the oil bath and allowed to cooled resulting in solidification. The solid was slurried in EtOH and filtered; the cake was washed with hot EtOAc and dried to yield 66% of an off-white solid.  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.95 (m, 2 H), 7.91 (d, 1 H,  $J = 8.3$ ), 7.83 (m, 2 H), 7.60 (t, 1 H,  $J = 8.1$ ), 7.52 (m, 3 H), 7.42 (m, 5 H), 7.30 (t, 1 H,  $J = 2.2$ ), 7.19 (ddd, 1 H,  $J = 8.3, 2.3, 1.0$ ). HRMS (FAB,  $m/z$ ) for  $\text{C}_{28}\text{H}_{16}\text{N}_2\text{O}_5$ , calcd 460.105, found 461.113 ( $M + 1$ ).

**4-Fluoro-N-3-Hydroxyphenyl phthalimide (13).** To a 500 mL round bottom flask fitted with a reflux condenser and stir bar was charged 4-fluorophthalic anhydride (30.4 g, 183.3 mmol), 3-aminophenol (20 g, 183.3 mmol), and 250 mL glacial acetic acid. The mixture was stirred at room temperature for 10-15 minutes, then placed into a 130 °C oil bath and brought to reflux. The reaction was stirred under a nitrogen atmosphere for 4 hours. The flask was then cooled to room temperature, resulting in formation of a precipitate. Water (250mL) was added and the solid was collected by vacuum filtration, washed with  $\text{H}_2\text{O}$ , and dried overnight to afford a white solid in 95% yield.  $^1\text{H NMR}$  ( $d_6$ -DMSO):  $\delta$  9.77 (s, 1 H), 8.02 (dd, 1 H,  $J = 8.3, 4.6$ ), 7.86 (ddd, 1 H,  $J = 7.6, 2.3, 0.5$ ), 7.72 (ddd, 1 H,  $J = 9.5, 8.3, 2.4$ ), 7.30 (m, 1 H), 6.85 (m, 3 H). Anal. Calcd for  $\text{C}_{14}\text{H}_8\text{NO}_3\text{F}$ : C, 65.37; H, 3.13; N, 5.45. Found: C, 65.43; H, 2.95; N, 5.23.

**4-Fluoro-N-3-*t*-butyldimethylsiloxyphenyl phthalimide (3).** To a 500 mL flask with a stir bar was charged phenol **13** (44 g, 171 mmol), *t*-butyldimethylsilylchloride (27.1 g, 180 mmol), imidazole (12.3 g, 180 mmol), and 250 mL  $\text{CH}_2\text{Cl}_2$ . This heterogeneous solution was stirred under a nitrogen atmosphere overnight. The imidazole salts were removed by filtration and the mother liquor was concentrated *in vacuo* and crystallized from hexane to give a white powder (94%).  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.95 (ddd, 1 H,  $J = 8.2, 4.6, 0.5$ ), 7.61 (ddd, 1 H,  $J = 7.2, 2.4, 0.5$ ), 7.48 (ddd, 1 H,  $J = 9.3, 8.3, 2.3$ ), 7.37 (m, 1 H), 7.02 (ddd, 1 H,  $J = 8.1, 1.9, 1.1$ ), 6.92 (m, 2 H), 1.00 (s, 9 H), 0.24 (s, 6 H)



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**4-Fluoro-N-phenyl phthalimide (14).** To a 250 mL round bottom flask fitted with a reflux condenser and stir bar was charged 4-fluorophthalic anhydride (10.7 g, 64.4 mmol), aniline (6 g, 64.4 mmol) and 80 mL glacial acetic acid. The mixture was stirred at room temperature for 10-15 minutes, then placed into a 120 °C oil bath and brought to reflux. The reaction quickly became homogeneous and was stirred under a nitrogen atmosphere for 2.5 hours. The flask was then cooled to room temperature, resulting in formation of a precipitate. Water (200mL) was added and the solid was collected by vacuum filtration, washed with  $\text{H}_2\text{O}$ , and dried. The product was recrystallized from  $\text{CH}_2\text{Cl}_2/\text{EtOH}$  and afforded white crystals in 79% yield.  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.96 (ddd, 1 H,  $J = 8.1, 4.3, 0.5$ ), 7.62 (ddd, 1 H,  $J = 7.1, 2.3, 0.5$ ), 7.49 (m, 6 H). Anal. Calcd for  $\text{C}_{14}\text{H}_8\text{NO}_2\text{F}$ : C, 69.71; H, 3.34; N, 5.81. Found: C, 69.44; H, 3.08; N, 5.52. HRMS (EI,  $m/z$ ) for  $\text{C}_{14}\text{H}_8\text{NO}_2\text{F}$ , calcd 241.054, found 241.053.

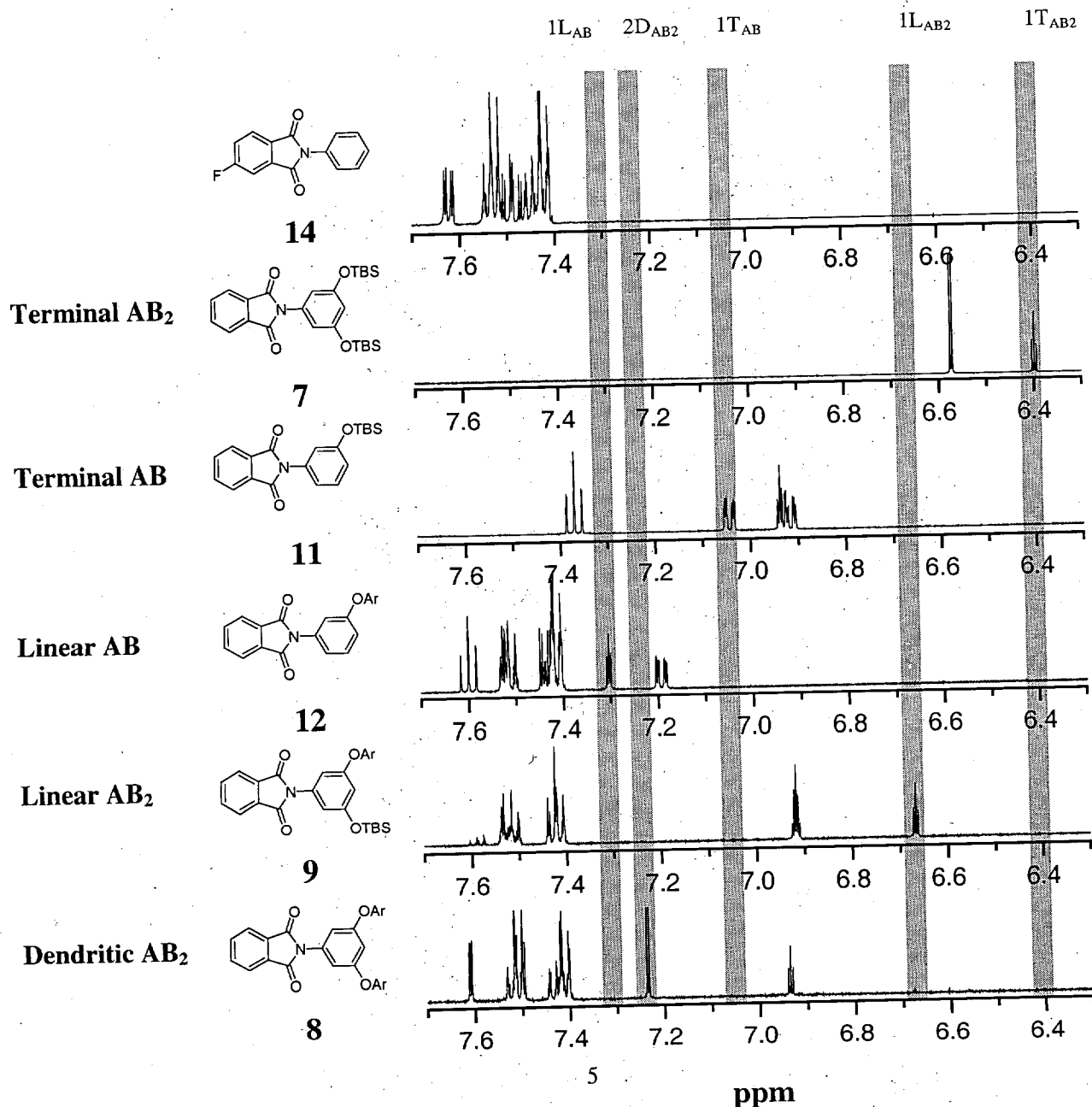
## B. Polymers and Copolymers

The polycondensations were performed by quickly immersing a polymerization vessel containing monomers **1** and **3** (10 mmol), 5 g diphenyl sulphone (DPS), and a catalytic amount of cesium fluoride (30 mg, 2 wt %) into a preheated 240 °C silicon oil bath stirred under a nitrogen atmosphere. The solid reagents melted immediately and formed a slightly yellow molten solution.

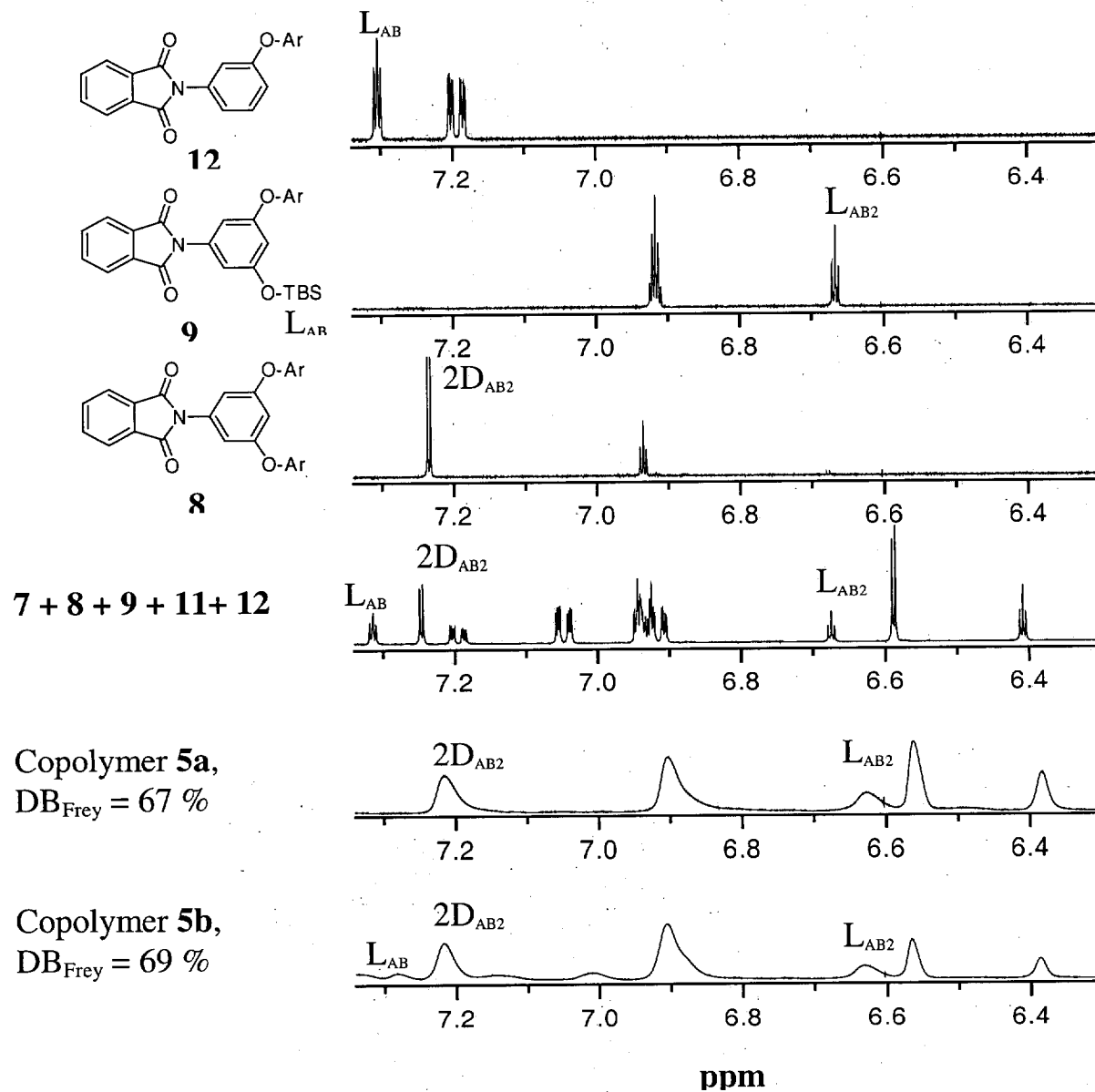
Within seconds of melting, the reaction mixture began bubbling vigorously and TBDMS fluoride evolution was observed. After the mixture was mechanically stirred for the designated time (5 min. after all solids had melted) the reaction vessel was removed from heat and allowed to cool slightly. Before solidification, the contents were diluted with 30 mL DMAc and filtered to remove the insoluble catalyst. The DMAc solution was then precipitated by dropwise addition to rapidly stirred hot ethanol and the polymer was separated from the solution by filtration and isolated as a white amorphous powder. The resulting polymer was dried under vacuum at 140 °C for 24 h. After drying,  $^1\text{H}$  NMR analysis in  $d_6$ -DMF was used to confirm the absence of residual DPS. If DPS was detected, the polymers were re-dissolved in 30 mL of DMAc and reprecipitated into hot ethanol, filtered, and dried again at 140 °C for 24 h.

## II. Stacked $^1\text{H}$ NMR Plots of Model Compounds and Polymers in $\text{CD}_2\text{Cl}_2$

A. **Model compounds in  $\text{CD}_2\text{Cl}_2$ .** Excellent dispersion exists between model compounds 7,8,9,11, and 12 that represent the five possible structural units in an AB/AB<sub>2</sub> copolymer.



**B) Determining DB in  $\text{CD}_2\text{Cl}_2$ .** The linear and dendritic peaks needed for DB calculation are clearly isolated in both the model compound and in copolymers **5a,b**. Integration experiments carried out on a mixture of model compounds revealed the method to be very accurate in determining DB. Subsequent integrations of the appropriate proton signals in the copolymer solutions gave an accurate DB of the copolymers.

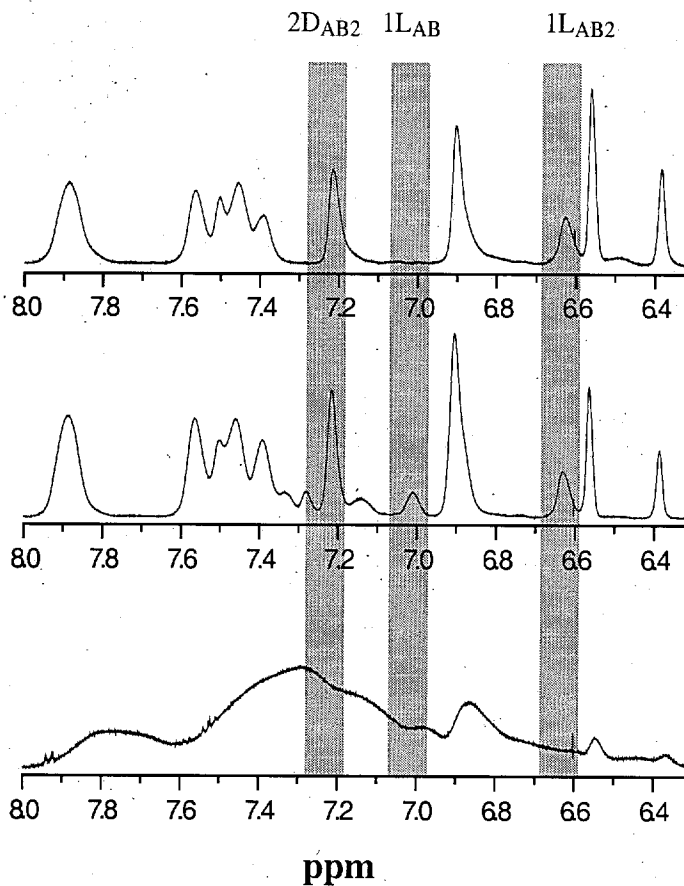


**B. Polymers in  $\text{CD}_2\text{Cl}_2$ .** The linear and dendritic peaks needed for DB calculation are clearly isolated, but the analysis cannot be done in this solvent below 75%  $\text{AB}_2$ .

**0 %  $\text{AB}$**   
DB = 0.67

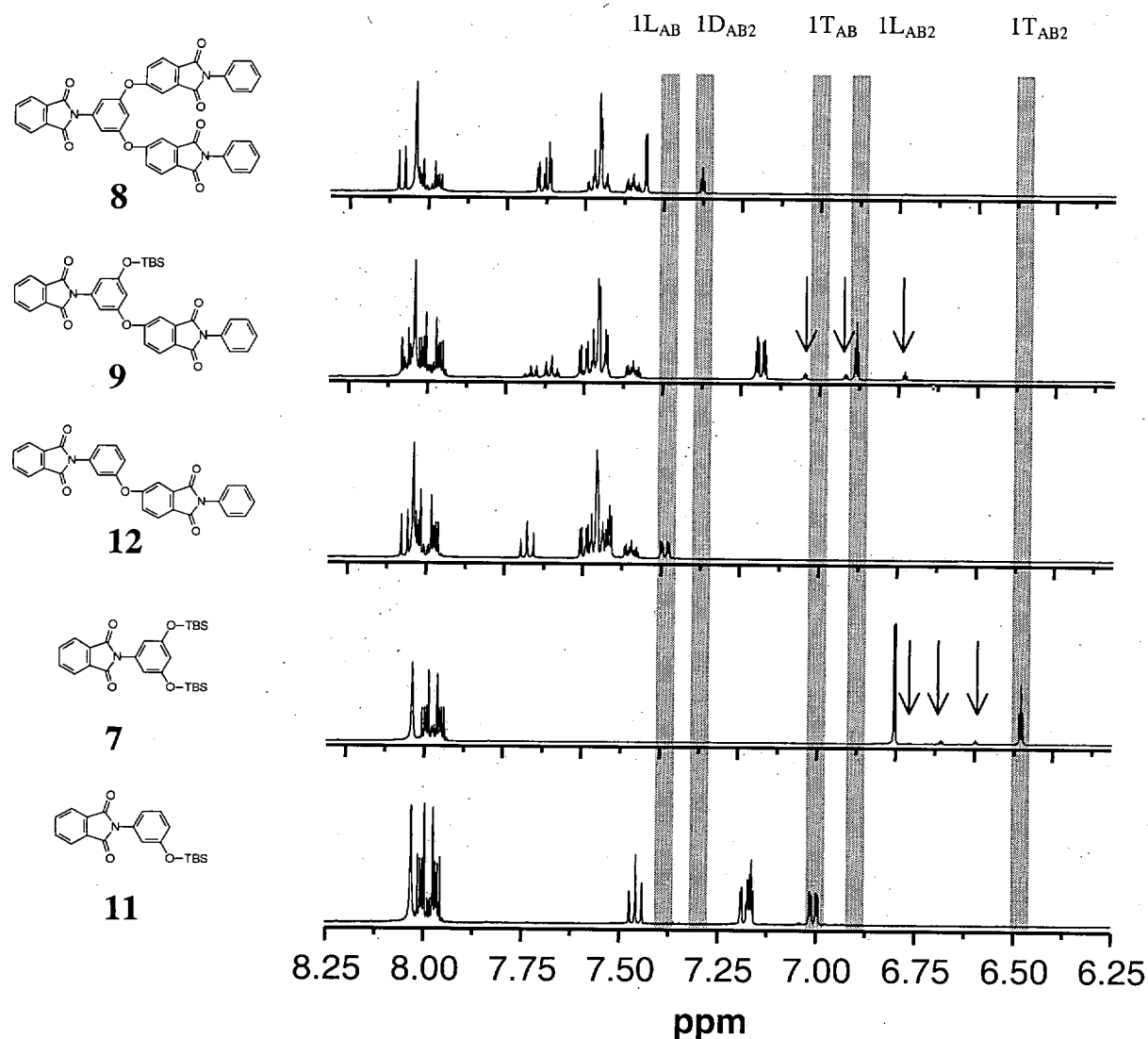
**25 %  $\text{AB}$**   
DB = 0.69

**50 %  $\text{AB}$**   
DB = unknown



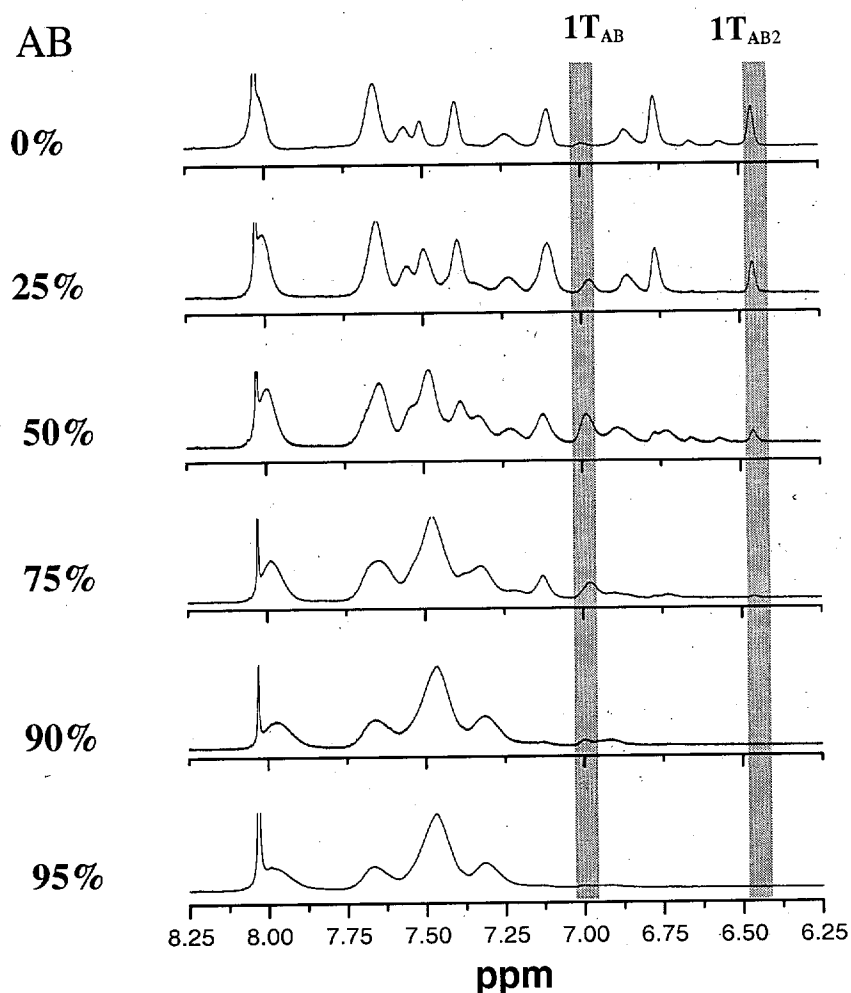
### III. Stacked $^1\text{H}$ NMR Plots of Model Compounds and Polymers in $d_6$ -DMF

**A. Model compounds in  $d_6$ -DMF.** Excellent dispersion exists for these model compounds in DMF, which would provide enough information to determine the degree of branching in the copolymer series. However, it can be seen in both the model compounds and copolymers (see **III B** below) that the TBS groups are not stable in this solvent (as shown by the arrows on the plots) and the dispersion is poor for the polymer, which leads to inaccurate integrations and a false degree of branching.



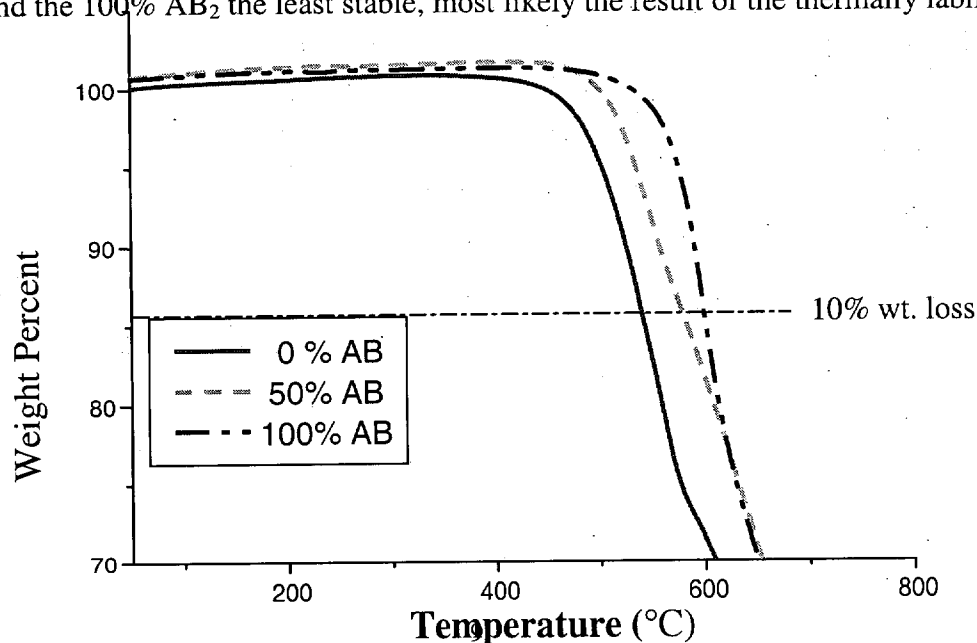
**C. Polymers in  $d_6$ -DMF.** Although the  $^1\text{H}$  dispersion is not ideal and the end-group stability is low in this solvent, it can be seen that the terminal B and B<sub>2</sub> groups appear and disappear with AB content, respectively. Also note the absence of sharp signals between 8.25 and 7.75 ppm, which confirms the absence of DPS.





### III. Thermal Analysis of Polymers

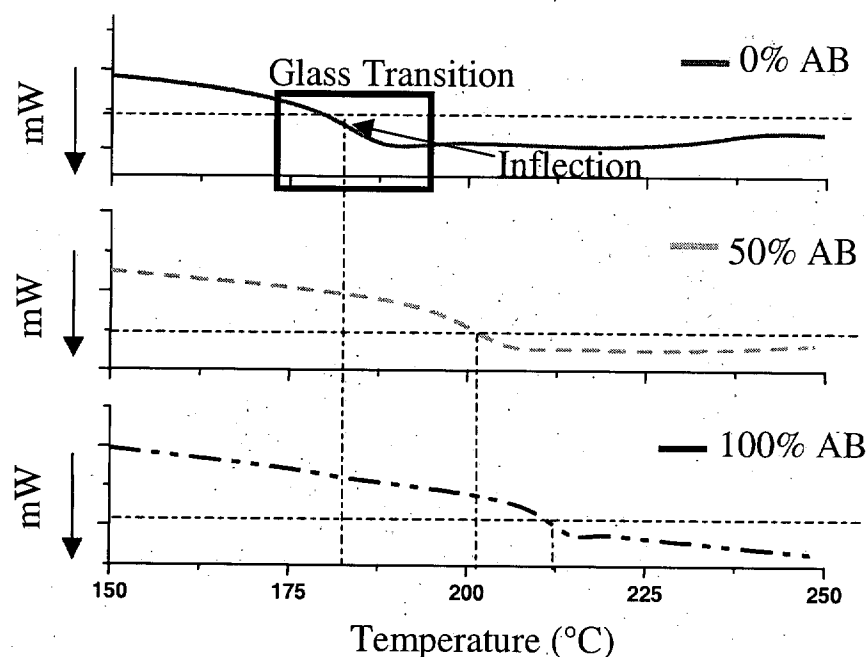
**A. Thermal Gravimetric Analysis.** Shown below are representative TGA traces. As can be clearly seen, these materials exhibit extremely high thermal stability with the 100% AB being the most stable and the 100%  $\text{AB}_2$  the least stable, most likely the result of the thermally labile TBDMS groups.



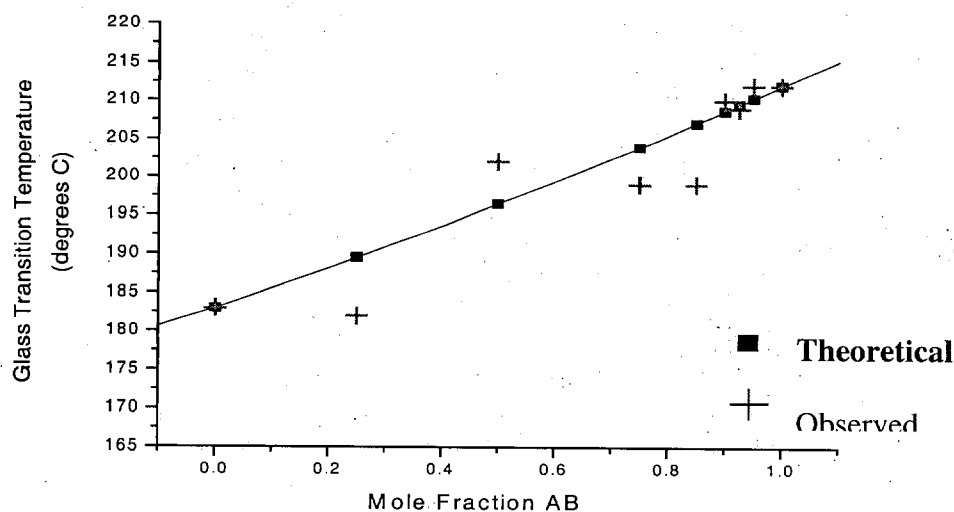
B. **Differential Scanning Calorimetry.** Representative DSC traces displayed below (i), show that 100% AB<sub>2</sub> has the lowest  $T_g$  and the 100% AB has the highest. When these two values are put into the familiar Fox equation (eq 1) for determining glass transitions of random copolymers, (where  $M_1$  and  $M_2$  represent the mole fraction of the two monomers in the copolymer and  $T_{g1}$  and  $T_{g2}$  represent the glass transition temperatures of the two homopolymers, respectively) good agreement is observed at high AB percentage and some scatter is observed at lower AB percentages (ii).

$$T_g = \frac{1}{M_1/T_{g1} + M_2/T_{g2}} \quad \text{Eq 1}$$

### i. Representative Glass Transition Temperatures

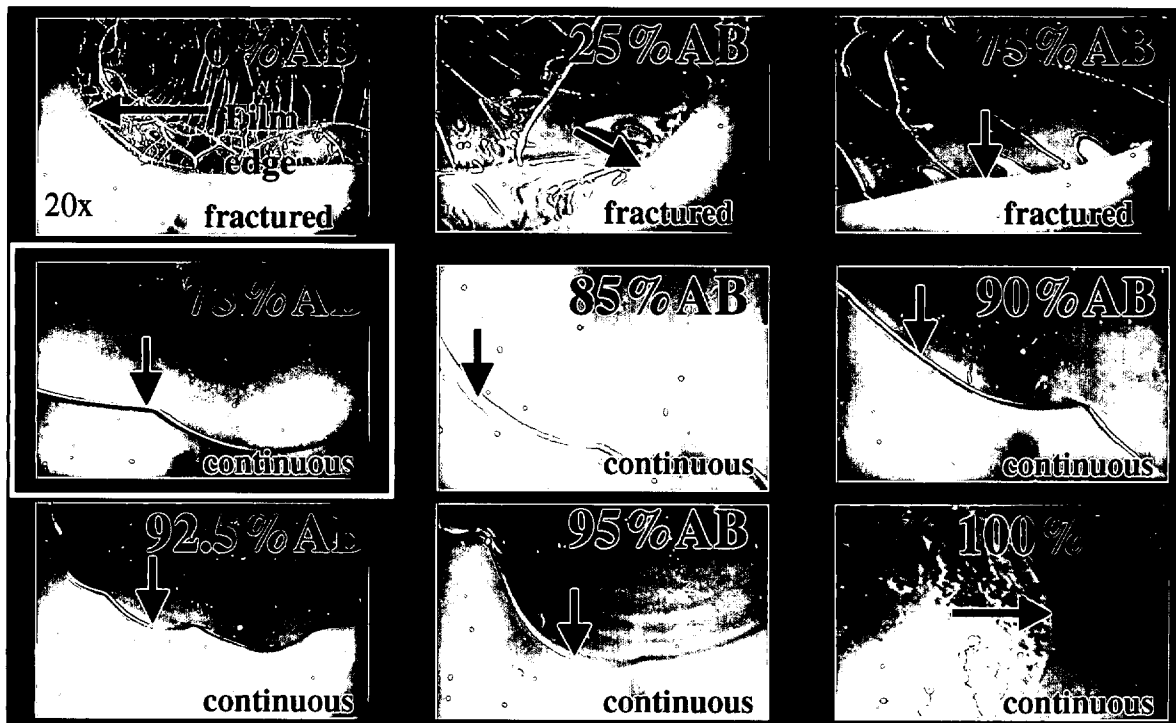


### ii. Fox Plot



#### IV. Film Forming Ability

A. Images of films cast from 10 weight percent copolymer solutions in DMAc, annealed for 1 h at 150 °C.



B. Images of annealed films after attempting to remove from glass substrate with razor blade.

