1890 *Macromolecules* **1997,** *30,* 1890−1896

Synthesis and Characterization of Hyperbranched Polycarbonates

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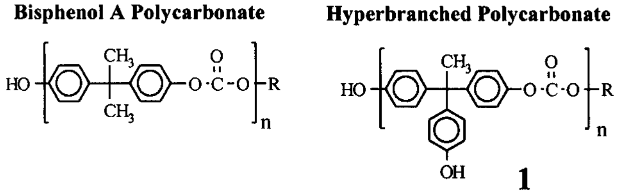
Received November 30, 1996; Revised Manuscript Received January 21, 1997⊗

ABSTRACT: Hyperbranched aromatic polycarbonates were prepared by the polymerization of an A_2B monomer derived from 1,1,1-tris(4′-hydroxyphenyl)ethane. Protection of one of the three phenols of the triphenol by a *tert*-butyldimethylsilyl group was followed by conversion of the remaining two phenolic groups to carbonylimidazolide functionalities to give the A_2B monomer. Polymerization was accomplished *via* the anhydrous removal of the silicon protecting group and subsequent reaction of the phenoxide with a carbonylimidazolide moiety to yield the hyperbranched aryl polycarbonate bearing carbonylimidazolide chain ends. Subsequent cleavage of these end groups by reaction with methanol upon precipitation, yielded the phenol-terminated hyperbranched polycarbonate. Silylation of the phenol-terminated material with *tert*-butyldimethylsilyl chloride, followed by degradation of the carbonate linkages by reaction with lithium aluminum hydride and analysis of the products by HPLC allowed for the degree of branching to be determined as 53%. The molecular weights (M_w) of the carbonylimidazolide-, phenol-, and *tert*-butyldimethylsilyl ether-terminated hyperbranched polycarbonates were 16 000, 77 000, and 82 000 amu from GPC based on polystyrene standards, 23 000, 180 000, and 83 000 from GPC with LALLS, and 24 000, 160 000, and 88 000 from GPC with SEC,[3] respectively.

Introduction

Bisphenol A polycarbonate resin has found extensive use as an engineering thermoplastic material due to a combination of excellent physical and mechanical properties.[1,2] Aircraft and automobile parts, optical disk substrates, appliances, medical devices, and safety glass are some of the areas of application which resulted in a 148% increase in the production of polycarbonate from 1981 to 1991.[3] The introduction of a multifunctional co-monomer[4] has been used to incorporate branching segments within the polycarbonate structure which leads to properties that make the material more suitable for blow molding applications,[5] such as the fabrication of hollow items or panels. Branched polycarbonate has also been obtained by reaction of a linear polycarbonate with a multifunctional coupling agent, in the presence of a carbonate equilibration catalyst and a chain terminating agent.[6] Both of these processes have the possibility for cross-linking reactions, making a more controlled method for the production of branched polycarbonate desirable.

Hyperbranched polymers, possessing greater than *ca.* 50% branching and no crosslinks, are synthesized through the polymerization of A_xB monomer units. These structures have shown promise as highly functionalized, globular macromolecules possessing low viscosity and high solubility and are receiving considerable attention.[7] None of the hyperbranched polymers studied to date have demonstrated good mechanical properties. A hyperbranched polycarbonate is, therefore, also expected to be a brittle material, but such a structure may prove interesting as a highly-functionalized prepolymer for composites, coatings, and other applications.


Bisphenol A Polycarbonate
Hyperbranched Polycarbonate

1

Figure 1. Repeat units of linear bisphenol A polycarbonate and the phenol-terminated hyperbranched polycarbonate, **1**.

The synthesis of a hyperbranched polycarbonate is not trivial, since most of the synthetic routes for the formation of polycarbonates involve the condensation of AA/BB monomer mixtures or ring-opening polymerization techniques, which are not readily applicable to the generation of a hyperbranched analog. We have recently developed an AB polymerization method for the production of linear aliphatic polycarbonates[8] involving the condensation reaction between alkoxide and carbonylimidazolide functionalities. The extension of this chemistry to the polymerization of an A_2B monomer for the preparation of a hyperbranched aryl polycarbonate is now described.

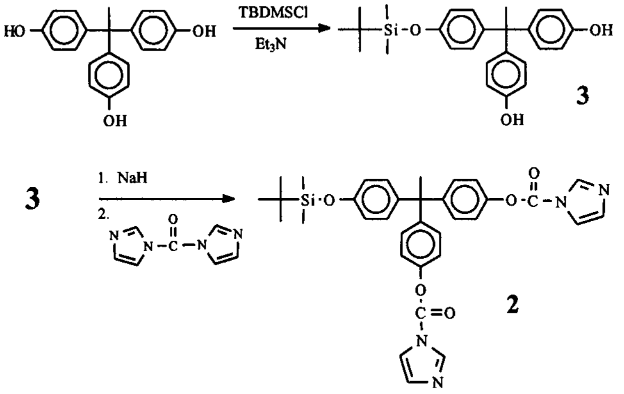
Results and Discussion

Synthesis. The repeat unit **1**, shown in Figure 1, was selected as the first system for the study of a hyperbranched polycarbonate. As can be seen, this structure simply possesses a reactive phenolic group as a replacement for one of the methyl groups of bisphenol A polycarbonate.[9]

The precursor to this hyperbranched polycarbonate is the A_2B monomer, **2**, bearing two carbonylimidazolide groups and one *tert*-butyldimethylsilyl-protected phenol. As shown in Scheme 1, the A_2B monomer is prepared in two steps. Silylation of 1,1,1-tris(4′-hydroxyphenyl)ethane with *tert*-butyldimethylsilyl chloride in the presence of triethylamine gives the monoprotected product, **3**, in 43% yield, after purification by column chromatography and recrystallization. The silyl aryl ether of **3** is readily hydrolyzed, requiring storage under inert atmosphere. Reaction of **3** with sodium hydride, followed by 1,1′-carbonyldiimidazole (>2× excess per phenol) yields the A_2B monomer, **2**. Crystallization of **2** was unsuccessful, and due to its hydrolytic and thermal instability, **2** was purified by filtration and precipitation into hexane to give a spectroscopically and elementally pure product in 82% yield.

⊗ Abstract published in *Advance ACS Abstracts,* March 15, 1997.

Scheme 1. Synthesis of the A_2B Monomer Unit, Bearing Two Carbonylimidazolide Functionalities and One *tert*-Butyldimethylsilyl-Protected Phenol



Polymerization of **2** was then attempted under several reaction conditions, including the use of potassium fluoride or cesium fluoride as the fluoride ion source,[10] the addition of crown ethers, the use of different solvents such as THF, acetonitrile, CH_2Cl_2, tetramethylene sulfone, and combinations of these solvents, as well as variation of the temperature. However no polymer was formed. Because of the failure of the A_2B polymerization and the previous report[11] that the condensation of a phenolate with a carbonylimidazolide group does not proceed to the formation of an aryl carbonate, small molecule model reactions were investigated.

(Phenylcarboxylato)imidazolide, **4**, and the *tert*-butyldimethylsilyl ether of *m*-cresol, **5**, were prepared by the same chemistry used in the synthesis of **2**, from phenol and *m*-cresol, respectively. Reaction of **5** with **4** in the presence of cesium fluoride in acetonitrile gives no carbonate products, but does result in exchange of the carbonylimidazolide group of **4** to generate *m*-cresolcarbonylimidazolide, as observed by GC−MS. Presumably, this result is due to the relative basicities of the aryloxide and imidazolide anions. It seems that only aryloxide exchange reactions occur from the tetrahedral intermediate involved in this addition−elimination reaction mechanism, due to the better leaving ability of the aryloxide ion in comparison to the imidazolide anion. This reaction is expected to be an equilibrium, and to aid in the elimination of the imidazolide salt as well as to prevent its reaction with the product carbonate **6**, $AgNO_3$ was added to the reaction mixture. A combination of CsF and $AgNO_3$ removes the silicon protecting group from **5**, allows for reaction of the aryloxide with the carbonylimidazolide of **4**, and forms the insoluble silver imidazolide salt[12] to drive the reaction toward carbonate formation. Each of the three possible products **6**, **7**, and **8** were formed and their relative amounts were determined by GC−MS (Scheme 2). Silver fluoride also successfully promoted the reaction and was more convenient than a mixture of CsF and $AgNO_3$. The ratios of the products formed by reaction with AgF did not differ from those obtained with the mixture of CsF and $AgNO_3$. However, the relative amounts of the three products (**6**, **7**, and **8**) were affected by the ratios of starting materials and the temperature of the reaction mixture, with the desired asymmetric diaryl carbonate, **6**, being the major product under all conditions. An optimized yield of **6** was obtained by the reaction of **5** with excess amounts of **4** and AgF in acetonitrile heated at 45 °C.

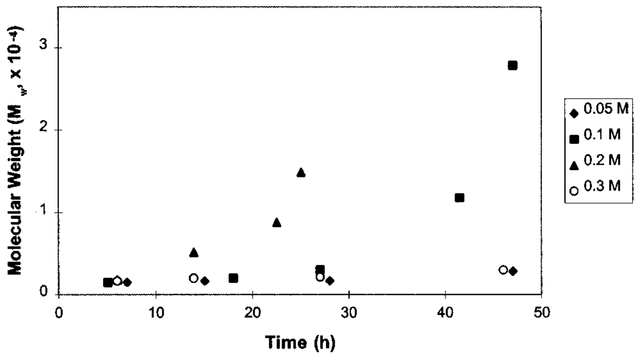
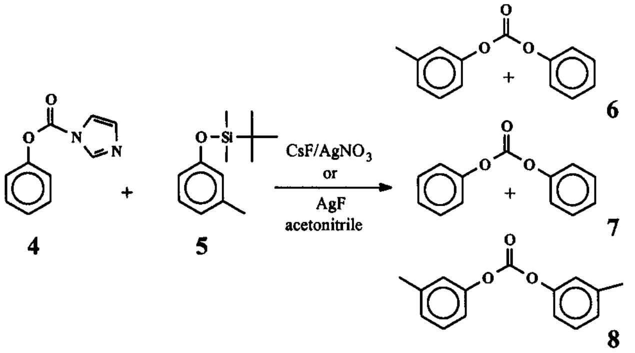


Figure 2. Weight-average molecular weight (M_w) *vs* time for the polymerization of **2**, with variation in concentration at constant temperature (45 °C).

Scheme 2. Small Molecule Model Reactions Used To Investigate the Condensation of Carbonylimidazolide and Phenolate Functional Groups To Yield Diaryl Carbonates



The polymerization of **2** was then reinvestigated. In contrast to the model study, differences in solubility between the small molecules and polymer required the use of a solvent system which included tetrahydrofuran (THF). A mixture of **2** and excess AgF was allowed to react in 20% acetonitrile/THF and heated at 70 °C under a nitrogen atmosphere, while polymer growth was monitored by GPC. The molecular weight of the polymer steadily increased for the first 2 days of reaction, followed by more rapid growth and increasing amounts of insoluble products. Therefore, after 2 days, the salts and insoluble products were removed by filtration, the reaction mixture was concentrated, and the carbonylimidazolide-terminated hyperbranched polymer **9** was isolated by precipitation from THF into diethyl ether. Cleavage of the carbonylimidazolide groups was accomplished simply by precipitation of **9** from THF into wet methanol to give the phenol-terminated product, **1**.

The polymerization conditions were further examined for optimization of monomer concentration and polymerization temperature. As shown in Figure 2, the polymer molecular weight increased with increasing monomer concentration, up to 0.2 M. At higher concentrations, solubility problems lead to substantial precipitation of even low molecular weight polymer. The reaction temperature was also found to have an effect upon the polymer growth (Figure 3), in which higher molecular weight products were obtained in shorter reaction times with increasing temperatures, up to 60 °C. Due to the thermal instability of the carbonylimidazolide functionality, the polymerization temperature was maintained at or below 70 °C.

Degree of Branching. The degree of branching could not be determined by NMR experiments, due to the lack of unique proton or carbon resonances. Therefore, a functionalization-degradation procedure[13] was used to evaluate the relative amounts of branching and linear repeat units within the polymer, thus allowing for calculation of the degree of branching. Analysis of

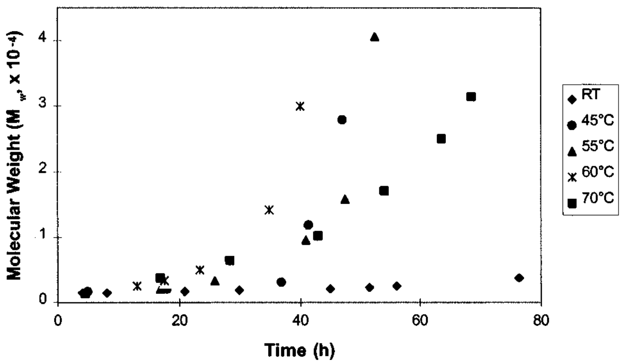


Figure 3. Weight-average molecular weight (M_w) *vs* time for the polymerization of **2**, with variation in temperature at constant concentration (0.1 M).

the hyperbranched structure **1** reveals three different repeat units—bearing zero, one, or two phenolic groups. Degradation of **1** would give only 1,1,1-tris(4′-hydroxyphenyl)ethane and would not allow for the differentiation of the unique repeat units. However, modification of the phenolic groups of **1**, with a stable functionality allows for degradation of the carbonate linkages and the production of three compounds—bearing three, two, or one phenolic groups from the branching, linear, or chain end repeat units, respectively. The branching and chain end repeat units contribute to a branched structure, and the degree of branching is calculated as

$$\text{DB} = (\text{no. of branched units} + \text{no. of chain ends})/(\text{no. of branched units} + \text{no. of chain ends} + \text{no. of linear units})$$

Attempts at methylation of the phenolic groups of **1**, using diazomethane or methyl iodide in the presence of various bases or silver oxide, resulted in degradation of the polymer. However, silylation gave complete functionalization of the phenolic groups (determined by ^{1}H NMR) with no degradation observed by GPC. To aid in the solubility of **1** during silylation, pyridine was used as the solvent, and reaction with *tert*-butyldimethylsilyl chloride in the presence of triethylamine gave the *tert*-butyldimethylsilyl-terminated hyperbranched polymer, **10** in 75% yield (Scheme 3). As shown in Scheme 4, reaction of **10** with lithium aluminum hydride gives selective reduction of the carbonates with no cleavage of the *tert*-butyldimethylsilyl ether end groups,[14] to yield three different compounds, **11** (branched), **3** (linear), and **12** (chain end). Compounds **3** and **12** were synthesized independently and used as standards for the HPLC studies. Degradation of the carbonate linkages was accomplished by reduction with lithium aluminum hydride (Scheme 4). The relative amounts of compounds **11**, **3**, and **12** were then determined by HPLC (silica gel column, 20% diethyl ether/CH_2Cl_2 as eluent), as 30%, 47%, and 23%, respectively. The degree of branching was then calculated to be 53%.

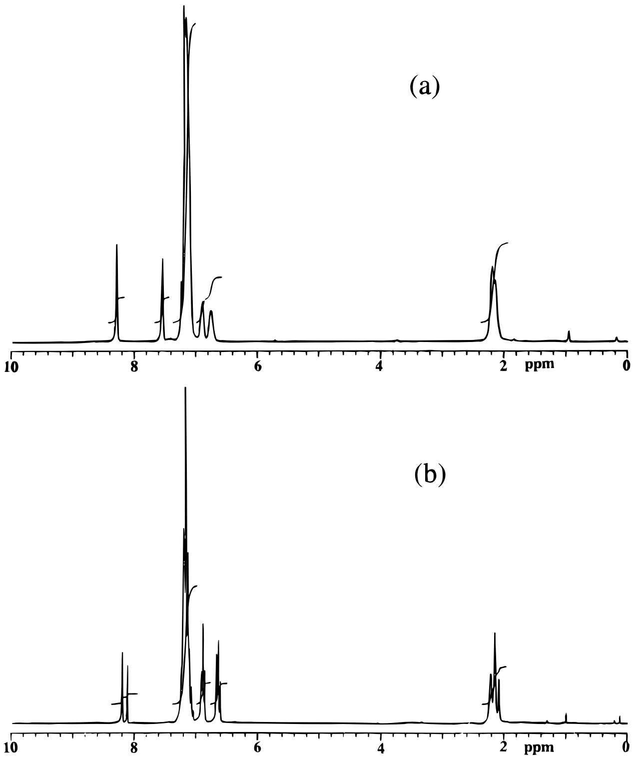


Figure 4. ^{1}H NMR (300 MHz) spectra of (a) **9** as a solution in $CDCl_3$ and (b) **1** as a solution in acetone-d_6.

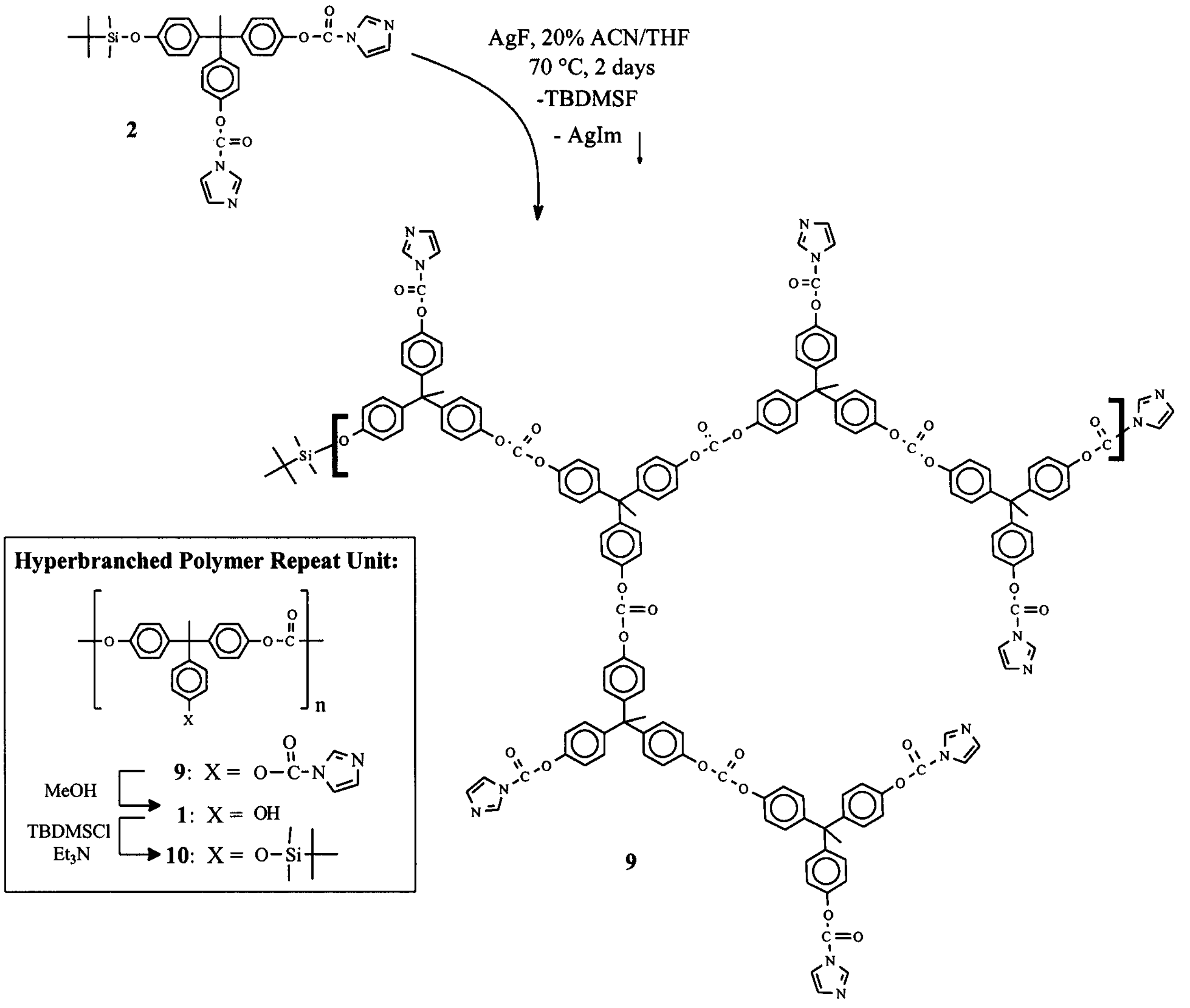
Table 1. Molecular Weight Data for Hyperbranched Polycarbonates, 9, 1, and 10, Calculated from GPC Based upon Conventional Calibration with Polystyrene Standards Using Refractive Index (RI) Detection, Low-Angle Laser Light Scattering (LALLS) Detection, and a Combination of RI, LALLS, and Viscometry (SEC^3)

	conventional		Wyatt LALLS		Viscotek SEC^3	
sample	M_w	M_n	M_w	M_n	M_w	M_n
9	16 000	5 400	23 000	5 200	24 000	5 900
1	77 000	11 000	180 000	17 000	160 000	16 000
10	82 000	11 000	83 000	17 000	88 000	14 000

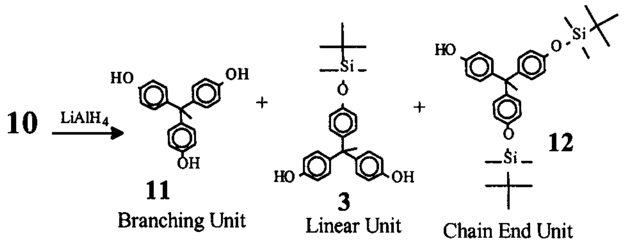
Characterization. All of the compounds were characterized by standard techniques including ^{1}H and ^{13}C NMR, FT-IR, and elemental analysis. Figure 4 shows the ^{1}H NMR spectra for **9** and **1**. The imidazole protons of the carbonylimidazolide chain ends of **9** are observed as resonances at 7.2, 7.57, and 8.25 (overlapping with aromatic phenyl protons) ppm. The protons of the phenyl carbonate and (phenylcarboxylato)imidazolide rings appear as a broad signal at 7.0–7.3 ppm. The aryl protons of the *tert*-butyldimethylsilyl aryl ether end groups and phenolic groups resulting from a small amount of loss of the carbonylimidazolide functionality give the broad quartet (ABq) at 6.7 and 6.9 ppm. Integration of each of the phenyl proton resonances and comparison with the methyl protons at 2.2 ppm allows for the amount of carbonylimidazolide loss to be determined as *ca.* 10%. Upon precipitation of **9** into methanol, complete cleavage of the carbonylimidazolide chain ends occurs to give the phenol-terminated material, **1**. The ^{1}H NMR spectrum of **1** displays the loss of the imidazole and phenyl protons of the (phenylcarboylato)-imidazolide groups and the appearance of the phenolic aryl (6.65 and 6.9 ppm) and hydroxyl protons (8.15 and 8.2 ppm, exchangeable with D_2O). Similar structural information was obtained from the ^{13}C NMR spectra.

The molecular weights of the polymers were determined by gel permeation chromatography (GPC). Detection of the samples was by a combination of refractive index, viscometry, and low angle laser light scattering, thus allowing for molecular weight characterization by several methods. The molecular weights were calculated by (1) conventional calibration with polystyrene standards, (2) Wyatt Astra software using both RI and LALLS data, and (3) Viscotek's SEC^3 method using all three detectors (Table 1). For each of the samples, the three detection/calculation methods agree fairly well. The carbonylimidazolide-terminated polycarbonate **9** had substantially lower molecular weight values than **1** or **10**, due to the presence of a large amount of low molecular weight oligomers that were not removed by

Scheme 3. Polymerization of the A_2B Monomer, 2, To Produce the Hyperbranched Polycarbonate, 9, and Reaction of the Chain End Groups of 9 To Give 1 and Then 10



Scheme 4. Degradation of 10, by Reduction with $LiAlH_4$ To Give the Three Different Repeat Units for Determination of the Degree of Branching of the Hyperbranched Polymers



precipitation into ether. Cleavage of the carbonylimidazolide groups gave the phenol-terminated material, in which the oligomers were soluble in methanol and were separated by precipitation, resulting in recovery of higher molecular weight material and a decreased yield for **1**. The GPC chromatogram of **1** showed a high molecular weight shoulder, which was not observed for **10**. Therefore, the M_w values for **1**, determined using LALLS and SEC,[3] were much larger than those measured for **10** even though the overall GPC chromatograms of **1** and **10** were nearly identical.

Comparable retention volumes were observed for each of the products, demonstrating that there was no attraction of the phenol-terminated sample to the GPC column packing material.[15] The samples behaved as highly-branched macromolecules, giving a large signal by light scattering at the high molecular weight prepeak where the RI detector shows very low concentration, and weaker signals in both the LALLS and in the viscometry chromatograms at longer retention times (lower molecular weights).[16]

^{1}H NMR end group analysis was also used for the calculation of the number average molecular weights for **1** and **9**, which were found to be in agreement with the GPC results. Integration of the resonances due to the methyl and *tert*-butyl groups of the single *tert*-butyldimethylsilyl chain end that is present on each of the polymer molecules, and comparison with the remainder of the protons in the structure gave calculated M_n's of 14 300 and 6700 for **1** and **9**, respectively.

Each of the polymers were soluble in common organic solvents. However, expected differences were observed corresponding to the differences in chain end functionalities. THF and acetone were solvents for **9**, **1**, and **10**; **9** and **10** were additionally soluble in chloroform while **1** required more polar solvents such as pyridine and *N*-methylpyrrolidinone.

The thermal stability of the polymers was determined by thermogravimetric analysis in air. The phenol-terminated polycarbonate, **1**, is thermally stable in air up to 350 °C. After loss of the thermally labile carbonylimidazolide functionality of **9** at 150−200 °C, **9** and **1** show similar thermal behavior. Differential scanning calorimetry (DSC) demonstrated slight differences between the hyperbranched materials with different chain end groups. A glass transition was not observed for **9**, prior to decomposition of the carbonylimidazolide functionalities. The T_g of **1** was observed at 205 °C, while silicon protection of the phenolic chain ends and elimination of hydrogen-bonding resulted in a decrease in T_g to 200 °C. In contrast, several families of dendritic and hyperbranched polymers have exhibited dramatic differences in T_g with variation of chain end polarities.[17] While we do not currently understand this difference in behavior, the dynamics of the hyperbranched polycarbonate materials are being studied by solid-state NMR.

Molecular motions in a number of linear polycarbonates have been characterized using dipolar rotational spin-echo (DRSE) solid-state ^{13}C NMR.[18] For linear bisphenol A polycarbonate, undulations of the polymer backbone gate aromatic 180° ring flips. Preliminary DRSE experiments, which measure motionally-averaged ^{1}H−^{13}C dipolar interactions, show that substantially fewer large-amplitude ring motions are present in hyperbranched polycarbonate. The cooperative motions which gate aromatic ring flips in linear polycarbonate are apparently not present in the hyperbranched materials. Further characterization of aromatic ring and main chain motions are presently under investigation.

Experimental Section

Measurements. ^{1}H NMR spectra were recorded as solutions on either a Varian Unity 300 MHz spectrometer or on a Varian Gemini 300 MHz spectrometer with the solvent proton signal as standard. ^{13}C NMR spectra were recorded at 75.4 MHz as solutions on either a Varian Unity 300 spectrometer or on a Varian Gemini 300 spectrometer with the solvent carbon signal as standard. IR spectra were obtained on a Mattson polaris spectrometer as thin films on NaCl plates. Size exclusion chromatography was conducted on a Hewlett-Packard series 1050 HPLC with a Hewlett-Packard 1047A refractive index detector, Wyatt MiniDawn low angle laser light scattering (LALLS) detector, and a Viscotek Model 110 differential viscometer: data analysis was done by Viscotek (Houston, TX) Trisec GPC Software, version 2.70, Wyatt Technology Corp. (Santa Barbara, CA) Astra Software, version 4.20, and Trisec GPC-LS-Viscometry (SEC^3) software version 3.0. Two 5-μm Polymer Laboratories PL gel columns (300 × 7.7 mm) connected in series, in order of increasing pore size (500 Å mixed bed E), were used with THF distilled from CaH_2 as solvent. Glass transition temperatures were measured by differential scanning calorimetry on a Perkin-Elmer DSC 4 differential scanning calorimeter. Heating rates were 10 K/min and T_g was taken as the midpoint of the inflection tangent, upon the third or subsequent heating scan. Thermogravimetric analyses were done on a Perkin-Elmer TGS-2 Thermogravimetric Analyzer. For both DSC and TGA, the Perkin-Elmer instruments were upgraded with Instrument Specialists, Inc. (Antioch, IL) temperature program interface-PE, and data were acquired and analyzed using TA-PC software version 1.0a (Instrument Specialists Inc.). GC−MS experiments were performed on a Hewlett-Packard 5890 Series II gas chromatograph equipped with a Hewlett-Packard 5971 Series mass selective detector with the temperature held at 100 °C for 2 min and then ramped at 10 °C/min to a maximum of 250 °C.

((Phenyloxy)carboxylato)imidazole (4). To a solution of freshly distilled phenol (3.07 g, 0.0326 mol) in dry THF (30 mL) under N_2 was added NaH (1.95 g, 0.0488 mol, 60% in mineral oil, rinsed with hexane), and the reaction mixture was then transferred to an addition funnel above a suspension of 1,1′-carbonyldiimidazole (15.13 g, 0.0933 mol) in dry THF (60 mL). The phenoxide solution was added dropwise to the suspension of 1,1′-carbonyldiimidazole over 26 min and was allowed to react for 2 h at room temperature. The mixture was then passed through a medium pore size sintered glass funnel, the solids were washed with THF, and the solvent was removed under reduced pressure. The resulting solids were dissolved in CH_2Cl_2 (150 mL) and washed with 10% Na_2CO_3 (50 mL), followed by washing with water (2 × 50 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated. The product was purified by recrystallization from hexane (125 mL) to yield 4.85 g (79%) of needle-like crystals; mp 60.1−62.9 °C. IR: 3250−3100, 1774, 1596, 1490, 1476, 1382, 1318, 1288, 1252, 1212, 1092, 995, 748 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.13 (1H, Im***H***), 7.24 (dd, 2H, J_{AB} = 8 Hz, J_{AC} = 2 Hz, *ortho* Ph$\boldsymbol{H_A}$), 7.32 (tt, 1H, J_{CB} = 8 Hz, J_{CA} = 2 Hz, *para* Ph$\boldsymbol{H_C}$), 7.44 (overlapping dd, 2H, J_{BA} = 8 Hz, J_{BC} = 8 Hz, *meta* Ph$\boldsymbol{H_B}$), 7.54 (1H, Im***H***), 8.27 (1H, Im***H***) ppm; ^{13}C NMR ($CDCl_3$) δ 117.09 (Im***C***), 120.69 (*ortho* Ar***C***OCOIm), 126.66 (*para* Ar***C***OCOIm), 129.50 (*meta* Ar***C***OCOIm), 130.74 (Im***C***), 137.10 (Im***C***), 146.90 (ipso Ar***C***OCOIm), 149.44 (carbonyl ***C***) ppm. GC−MS: retention time 8.63; *m/z* 188.

tert*-Butyldimethylsilylated *m*-Cresol (5).** *m*-Cresol (3.05 g, 0.0282 mol) and triethylamine (6.14 g, 0.0607 mol) were dissolved in dry THF (25 mL) under N_2. A solution of *tert*-butyldimethylsilyl chloride (8.34 g, 0.0553 mol) in dry THF (20 mL) was added, and the mixture was then heated at reflux under N_2 overnight. The progress of the reaction was monitored by TLC (CH_2Cl_2). The THF was removed under reduced pressure and the residual yellow oil was dissolved in CH_2Cl_2 (175 mL). The CH_2Cl_2 solution was washed with 10% Na_2CO_3 (50 mL) followed by washing with water (2 × 50 mL). The organic layer was collected, dried over $MgSO_4$, and filtered, and the solvent was removed under reduced pressure. The remaining yellow oil was vacuum distilled (60 °C, 0.1 mmHg) to yield 4.39 g (70%) of **5** as a colorless oil. IR: 3033−2860, 1604, 1586, 1488, 1360, 1278, 1257, 1160, 1006, 955, 842, 780, 692, 665 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.36 (s, 6H, SiC$\boldsymbol{H}_3$), 1.16 (s, 9H, SiC(C$\boldsymbol{H}_3$)$_3$), 2.44 (s, 3H, ArC$\boldsymbol{H}_3$), 6.80 (d, 1H, J = 8 Hz, ArH***), 6.83 (s, 1H, Ar***H***), 6.90 (d, 1H, J = 8 Hz, Ar***H***), 7.24 (overlapping dd, 1H, J = 8 Hz, Ar***H***) ppm. ^{13}C NMR ($CDCl_3$): δ −4.42 (Si***C***H$_3$), 18.18 (Si***C***(CH$_3$)$_3$), 21.35 (Ar***C***H$_3$), 25.72 (SiC(***C***H$_3$)$_3$), 116.97, 120.85, 122.11, 129.05, 139.23, 155.56 (Ar***C***) ppm. GC−MS: retention time, 5.81; *m/z* 222.

Synthesis of 3-Methylphenyl Phenyl Carbonate (6) Using CsF and $AgNO_3$. To a solution of **4** (0.0766 g, 0.461 mmol) and **5** (0.1050 g, 0.4721 mmol) in dry acetonitrile (1.5 mL) under N_2 was added CsF (0.3308 g, 2.178 mmol), followed by $AgNO_3$ (0.3161 g, 1.861 mmol). The solids immediately turned black. The reaction was allowed to stir at 45 °C overnight and was monitored by GC−MS, giving products **6** (retention time 11.22 min; *m/z* 228), **7** (retention time 9.99; *m/z* 214), **8** (retention time 12.40; *m/z* 242).

Synthesis of 3-Methylphenyl Phenyl Carbonate (6) Using AgF. To a solution of **4** (0.1139 g 0.6053 mmol) and **5** (0.0904 g, 0.407 mmol) in dry acetonitrile (1.5 mL) under N_2 was added AgF (0.1162 g, 0.9159 mmol). The entire flask was covered with aluminum foil, and the reaction was allowed to stir at 45 °C overnight. Product ratio was determined by GC−MS: **6** (retention time 11.22 min; *m/z* 228); **7**, (retention time

9.99 min; *m/z* 214); **8**, (retention time 12.40 min; *m/z* 242). EI-MS of **6** gave fragments at *m/z* 51, 65, 77, 91, 141, 155, 169, 184, and 228. EI-MS of **7** gave fragments at *m/z* 51, 65, 77, 141, 169, and 214. EI-MS of **8** gave fragments at *m/z* 51, 65, 91, 155, 198, and 242.

1,1-Bis(4′-hydroxyphenyl)-1-(((4′-*tert*-butyldimethylsilyl)oxy)phenyl)ethane (3) and 1-(4′-hydroxyphenyl)-1,1-bis(((4′-*tert*-butyldimethylsilyl)oxy)phenyl)ethane (12). To a solution of 1,1,1-tris(4′-hydroxyphenyl)ethane (10.10 g, 0.0330 mol) (Aldrich Chemical Co., 99%) and triethylamine (6.84 g, 0.0676 mol) in dry THF (200 mL) under N_2 was added a solution of *tert*-butyldimethylsilyl chloride (5.09 g, 0.0338 mol) in dry THF (70 mL) dropwise. The reaction was heated to reflux and was followed by TLC (15% diethyl ether/CH_2Cl_2), showing the tri- ($R_f = 1.0$), di- ($R_f = 0.81$), mono- ($R_f = 0.72$), and nonsilylated ($R_f = 0.17$) compounds. The solids were filtered off, the solvent was removed *in vacuo*, and the products were separated by silica gel flash chromatography eluting with 100% CH_2Cl_2 to give the disilylated product **12** as a yellow solid which was then crystallized from hexane to yield white crystals (yield 3.54 g, 20%); mp 122.9−124.1. IR: 3650−3150, 3050−2850, 1607, 1504, 1472, 1464, 1263, 1177, 1113, 1013, 918, 838, 800, 781, 734 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.23 (s, 12H, $SiC\boldsymbol{H}_3$), 1.02 (s, 18H, $SiC(C\boldsymbol{H}_3)_3$), 2.12 (s, 3H, $Ar_3CC\boldsymbol{H}_3$), 6.70 (d, $J = 8.7$ Hz, 2H, Ar***H***OH), 6.76 (d, $J = 8.7$ Hz, 4H, Ar***H***OSi), 6.95 (d, $J = 8.7$ Hz, 6H, Ar***H***OH and Ar***H***OSi) ppm. ^{13}C NMR ($CDCl_3$): δ −4.39 ($Si\boldsymbol{C}H_3$), 18.16 ($Si\boldsymbol{C}(CH_3)_3$), 25.67 ($SiC(\boldsymbol{C}H_3)_3$), 30.74 ($Ar_3C\boldsymbol{C}H_3$), 50.61 ($Ar_3\boldsymbol{C}CH_3$), 114.48 (Ar***C***OH), 119.09 (Ar***C***OSi), 129.57 (Ar***C***OSi), 129.79 (Ar***C***OH), 142.01 (Ar***C***OH), 142.37 (Ar***C***OSi), 153.33 (Ar***C***OH), 153.39 (Ar***C***OSi); HR-FAB MS: calcd for $C_{23}H_{46}O_3Si_2$, $[M]^+$ 534.2985; found, 534.2985. Anal. Calcd for $C_{32}H_{46}O_3Si_2$ (534.89): C, 71.86; H, 8.67. Found: C, 72.03; H, 8.70.

Continued elution with 10% diethyl ether/CH_2Cl_2 gave the monosilylated product **3** as a yellow solid which was crystallized in a minimal amount of CH_2Cl_2 to yield **3** as white crystals (6.02 g, 43%); mp 183−186 °C. IR: 3600−3200, 3100−2900, 1607, 1510, 1261, 1177, 918, 835 cm^{-1}. ^1H NMR (CD_3OD): δ 0.16 (s, 6H, $SiC\boldsymbol{H}_3$), 0.96 (s, 9H, $SiC(C\boldsymbol{H}_3)_3$), 2.01 (s, 3H, $Ar_3CC\boldsymbol{H}_3$), 6.64 and 6.85 (ABq, 8H, $J = 9$ Hz, Ar***H***OH), 6.68 and 6.90 (ABq, 4H, $J = 9$ Hz, Ar***H***OSi) ppm. ^{13}C NMR (CD_3OD): δ −4.2 ($Si\boldsymbol{C}H_3$), 19.04 ($Si\boldsymbol{C}(CH_3)_3$), 26.20 ($SiC(\boldsymbol{C}H_3)_3$), 31.39 ($Ar_3C\boldsymbol{C}H_3$), 51.62 ($Ar_3\boldsymbol{C}CH_3$), 115.32 (Ar***C***OH), 120.05 (Ar***C***OSi), 130.68 (Ar***C***OH), 130.73 (Ar***C***OSi), 142.08 (Ar***C***OH), 144.29 (Ar***C***OSi), 154.66, 156.13 (Ar***C***OH) ppm. HR-FAB MS: calcd for $C_{26}H_{32}O_3Si_2$, $[M]^+$ 420.2121; found, 420.2121.

1,1-Bis((imidazolyl-4′-carboxylato)phenyl)-1-(((4′-*tert*-butyldimethylsilyl)oxy)phenyl)ethane (2). To a solution of **3** (5.45 g, 0.0130 mol) in dry THF (150 mL) was slowly added NaH (1.75 g, 0.0437 mol, 60% in mineral oil, rinsed with hexane). After being stirred at room temperature under N_2 for 1.5 h, this mixture was added dropwise to a slurry of 1,1′-carbonyldiimidazole (9.49 g, 0.0585 mol) in dry THF (150 mL). This was allowed to react at room temperature for 3 h and was monitored by TLC (20% diethyl ether/CH_2Cl_2). The reaction was filtered through a sintered glass funnel and the filter cake was washed with dry THF (50 mL). The filtrate was collected, the solvent was removed under reduced pressure, and the white solid product, **2**, was washed with hexane: yield 6.49 g (82%); mp 180−183 °C. IR 3200−2800, 1774, 1605, 1505, 1473, 1313, 1290, 1240, 1209, 1175, 992, 916, 839 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.17 (s, 6H, $SiC\boldsymbol{H}_3$), 0.95 (s, 9H, $SiC(C\boldsymbol{H}_3)_3$), 2.15 (s, 3H, $Ar_3CC\boldsymbol{H}_3$), 6.74 and 6.92 (ABq, 4H, $J = 9$ Hz, Ar***H***OSi), 7.10 (m, 2H, Im***H***), 7.15 (br s, 8H, Ar***H***OCOIm), 7.51 (m, 2H, Im***H***), 8.25 (m, 2H, Im***H***) ppm. ^{13}C NMR ($CDCl_3$): δ −4.51 ($Si\boldsymbol{C}H_3$), 18.02 ($Si\boldsymbol{C}(CH_3)_3$), 25.52 ($SiC(\boldsymbol{C}H_3)_3$), 30.65 ($Ar_3C\boldsymbol{C}H_3$), 51.32 ($Ar_3\boldsymbol{C}CH_3$), 117.26 (Im***C***), 119.36 (Ar***C***OSi), 120.22 (Ar***C***OCOIm), 129.38 (Ar***C***OSi), 129.89 (Ar***C***OCOIm), 130.93 (Im***C***), 137.27 (Im***C***), 140.34 (Ar***C***OSi), 147.00 (Ar***C***OSi), 147.71 (Ar***C***OCOIm), 147.79 (Ar***C***OCOIm), 153.90 (carbonyl ***C***) ppm, assignments were verified by 2-D NMR (HMQC and HMBC). Anal. Calcd for $C_{34}H_{36}N_4O_5Si$ (608.77): C, 67.08; H, 5.96, N, 9.20. Found: C, 67.28; H, 5.78; N, 9.07.

Carbonylimidazolide-Terminated Hyperbranched Polycarbonate (9). To a solution of the monomer **2** (0.3871 g, 0.6362 mmol) in 20% acetonitrile/THF (6 mL) was added AgF (0.2629 g, 2.072 mmol), and the entire flask was covered with aluminum foil and heated to 70 °C under N_2 with stirring. The reaction was followed by GPC and stopped when the polymer reached the desired molecular weight prior to gelation. The salts were filtered off, and the polymer was precipitated into diethyl ether to obtain the carbonylimidazolide-terminated hyperbranched polycarbonate, **9**, as a white solid: yield 0.240 g (89%). $M_w = 16\,000$, $M_n = 5400$ from GPC based upon polystyrene standards; $M_w = 23\,000$, $M_n = 5200$ from GPC and LALLS; $M_w = 24\,000$ and $M_n = 5900$ from GPC and SEC^3 with $dn/dc = 0.157$; no T_g before decomposition began at 160 °C. TGA in air: 150−175 °C, 9% mass loss; 350−400 °C, 8% mass loss; 425−460 °C, 32% mass loss; 475−560 °C, 51% mass loss. IR: 3300−2800, 1775, 1600, 1503, 1386, 1291, 1240−1196, 1061, 1015, 992, 829, 756 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.17 (s, 6H, $SiC\boldsymbol{H}_3$ end group), 0.95 (s, 9H, $SiC(C\boldsymbol{H}_3)_3$ end group), 2.1−2.3 (br s, 3H, $Ar_3CC\boldsymbol{H}_3$), 6.6−6.7 and 6.85−6.95 (br ABq, 4H, Ar***H***OH from hydrolysis of ArOCOIm), 7.05 (s, 1H, Im***H***), 7.1−7.3 (br m, 8H, Ar***H***OCO), 7.6 (s, 1H, Im***H***), 8.25 (s, 1H, Im***H***) ppm. ^{13}C NMR ($CDCl_3$): δ 31.2 ($Ar_3C\boldsymbol{C}H_3$), 52.2−52.7 ($Ar_3\boldsymbol{C}CH_3$), 115.6 (Ar***C***OH from hydrolysis), 118.2 (Im***C***), 120.9−121.6 (Ar***C***OCO), 130.3−130.8 (Ar***C***OCO), 131.6 (Im***C***), 138.3 (Im***C***), 147.4−147.5, 148.0−148.2, 149.5−149.6, 150.6, 152.5, 157.2 (Ar***C***OCO and carbonyl ***C***) ppm. Anal. Calcd for $C_{25}H_{18}N_2O_5$ (426.43): C, 70.42; H, 4.25. Found: C, 70.69; H, 4.74.

Phenol-Terminated Hyperbranched Polycarbonate (1). The phenol-terminated hyperbranched polycarbonate, **1**, was prepared and isolated by addition of 90% methanol/H_2O (25 mL) to a solution of **9** (0.24 g, 0.56 mmol) in THF (5 mL). The solid phenol-terminated polymer precipitate was then collected by filtration: yield 0.13 g (68% based on **9**, 60% based on **2**). $M_w = 77\,000$, $M_n = 11\,000$ from GPC based upon polystyrene standards; $M_w = 180\,000$, $M_n = 17\,000$ from GPC and LALLS; $M_w = 160\,000$ and $M_n = 16\,000$ from GPC and SEC^3 with $dn/dc = 0.178$; T_g 205 °C. TGA in air: 50−350 °C, 5% mass loss; 350−425 °C, 39% mass loss; 475−550 °C, 56% mass loss. IR: 3600−3100, 3100−2800, 1774, 1612, 1592, 1300−1200, 1195, 1164, 1059, 1014, 891, 832 cm^{-1}. ^1H NMR (THF-d_8): δ 2.0−2.25 (3 br s, 3H, $Ar_3CC\boldsymbol{H}_3$), 6.61−6.67 and 6.86−6.92 (br ABq, 4H, Ar***H***OH), 7.07−7.21 (br m, 8H, Ar***H***OCO), 8.12 and 8.20 (2 s, 1H, ArHO***H***, exchangeable with D_2O) ppm. ^{13}C NMR (THF-d_8): δ 31.2 ($Ar_3C\boldsymbol{C}H_3$), 52.0−52.4 ($Ar_3\boldsymbol{C}CH_3$), 115.2−115.5 (Ar***C***OH), 120.7−121.4 (Ar***C***OCO), 130.4−130.6 (Ar***C***OCO and Ar***C***OH), 140−140.5, 147.5−148, 150−151, 152−152.5, 157−157.5 (Ar***C*** and carbonyl ***C***) ppm. Anal. Calcd for $C_{21}H_{16}O_4$ (332.36): C, 75.89; H, 4.85. Found: C, 74.30; H, 4.50.

***tert*-Butyldimethylsilyl Ether-Terminated Hyperbranched Polycarbonate (10).** To a solution of **1** (0.2221 g, 0.6682 mmol) in pyridine (6 mL) was added *tert*-butyldimethylsilyl chloride (0.5012 g, 3.325 mmol) and triethylamine (0.7 mL, 5 mmol). The reaction mixture was allowed to react at 48 °C with stirring under N_2 overnight. The salts were removed by filtration and washed with THF. Most of the solvent was removed in vacuo, and the products were isolated by precipitation into methanol: yield 0.2233 g (75%). M_w = 82 000, M_n = 11 000 from GPC based upon polystyrene standards; M_w = 83 000, M_n = 17 000 from GPC and LALLS; M_w = 88 000, M_n = 14 000 from GPC and SEC^3 with dn/dc = 0.170; T_g 200 °C. TGA in air: 60−200 °C, 5% mass loss; 300−540 °C, 51% mass loss. IR: 3060−2858, 1777, 1606, 1503, 1472, 1463, 1230, 1196, 1164, 1066, 1014, 917, 839, 806 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.20 (s, 6H, SiC$\boldsymbol{H}_3$), 0.98 (s, 9H, Si(C$\boldsymbol{H}_3$)$_3$), 2.12−2.21 (br m, 3H, Ar$_3$CC$\boldsymbol{H}_3$), 6.7−6.8 and 6.9−7.0 (br m, 4H, Ar$\boldsymbol{H}$OSi), 7.09−7.27 (br m, 8H, Ar$\boldsymbol{H}$OCO) ppm. ^{13}C NMR ($CDCl_3$): δ −4.24 (Si$\boldsymbol{C}$H$_3$), 18.13 (Si$\boldsymbol{C}$(CH$_3$)$_3$, 25.63 (SiC($\boldsymbol{C}$H$_3$)$_3$), 30.76 (ArC$\boldsymbol{C}$H$_3$), 51.31 (Ar$\boldsymbol{C}$CH$_3$), 119.14−119.34 (Ar$\boldsymbol{C}$OSi), 119.90−120.33 (Ar$\boldsymbol{C}$OCO), 129.52−130.01 (Ar$\boldsymbol{C}$OCO and Ar$\boldsymbol{C}$OSi), 140.90−154.1 (Ar$\boldsymbol{C}$OCO (ipso), Ar$\boldsymbol{C}$OSi (ipso), and ArCO$\boldsymbol{C}$O) ppm. Anal. Calcd for $C_{27}H_{30}O_4Si$ (446.62): C, 72.61; H, 6.77. Found: C, 72.09; H, 6.19.

Conclusions

Hyperbranched aryl polycarbonates, based upon 1,1,1-tris(4′-hydroxyphenyl)ethane as the repeat unit, were synthesized through polymerization of an A_2B monomer. These polymers are structurally and compositionally different from bisphenol A polycarbonate, due to their high degree of branching and large number of phenolic chain ends. The hyperbranched polycarbonates are expected to find application as soluble, thermally-stable polymers that are applicable as prepolymers for the creation of unique engineering materials. In order to determine the effects of branching upon the properties of the aryl polycarbonate, the preparation of the analogous linear polymer, which bears a phenolic group at each repeat unit, is in progress. Comparisons between the macroscopic mechanical properties and microscopic dynamics of molecular motion (determined by solid-state NMR experiments) for the hyperbranched and linear polycarbonates will be used to gain further information as to the overall structure of these unique macromolecules.

Acknowledgment. The authors acknowledge Dr. Jon M. Goetz (Department of Chemistry, Washington University) for solid-state NMR measurements and interpretation, and Dr. André d'Avignon for solution-state 2-D NMR studies. Financial support for this work from the National Science Foundation (DMR-9458025) and the U.S. Army Research Office (DAAH04-96-1-0158) is gratefully acknowledged. A fellowship (for D.H.B.) from the Department of Education, Graduate Assistance in Areas of National Need (P200A4014795), is also acknowledged with thanks.

References and Notes

(1) Clagett, D. C.; Shafer, S. J. *Comprehensive Polymer Science: The Synthesis, Characterization, Reactions, and Applications of Polymers*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: Oxford, England, 1989; Vol. 5, Step Polymerization; pp 345−356.

(2) Schnell, H. *Chemistry and Physics of Polycarbonates, Polymer Reviews*, Bd. 9; Interscience Publishers: New York, 1964.

(3) Committee on Polymer Science and Engineering, National Research Council, *Polymer Science and Engineering: The Shifting Research Frontiers*; National Academy Press: Washington, DC, 1994; pp 68−70.

(4) Mark, V.; Hedges, C. V. U.S. Patent No. 4,469,861, 1984. Frietag, D.; Haberland, U.; Krimm, H. U.S. Patent No. 3,799,953, 1974.

(5) Stinson, S. C. *Chem. Eng. News* **1990**, May 7, 55.

(6) Krabbenhoft, H. O.; Boden, E. P. U.S. Patent No. 5,021,521, 1991. Boden, E. P.; Krabbenhoft, H. O. U.S. Patent No. 4,888,400, 1989.

(7) Hawker, C. J.; Chu, F.; Pomery, P. J.; Hill, D. J. T. *Macromolecules* **1996**, *29*, 3831. Gaynor, S. G.; Edelman, S.; Matyjaszewski, K. *Macromolecules* **1996**, *29*, 1079. Jikei, M.; Hu, A.; Kakimoto, M.; Imai, Y. *Macromolecules* **1996**, *29*, 1062. Zhang, Y.; Wang, L.; Wada, T.; Sasabe, H. *Macromol. Chem. Phys.* **1996**, *197*, 667. Fréchet, J. M. J.; Henmi, M.; Gitsov, I.; Aoshima, S.; Leduc, M.; Grubbs, R. B. *Science* **1995**, *269*, 1080. Hawker, C. J.; Fréchet, J. M. J.; Grubbs, R. B.; Dao, J. *J. Am. Chem. Soc.* **1995**, *117*, 10763. Fréchet, J. M. J.; Hawker, C. J. *React. Funct. Polym.* **1995**, *26*, 127. Kricheldorf, H. R.; Löhden, G. *J. M. S.--Pure Appl. Chem.* **1995**, *A32*, 1915. Wooley, K. L.; Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *Polym. J.* **1994**, *26*(2), 187. Percec, V.; Chu, P.; Kawsumi, M. *Macromolecules* **1994**, *27*, 4441. Turner, S. R.; Walter, F.; Voit, B. I.; Mourey, T. H. *Macromolecules* **1994**, *27*, 1611. Vicari, R.; Bodman, M. P. U.S. Patent No. 5,362,843, 1994. Chu, F.; Hawker, C. J. *Polym. Bull.* **1993**, *30*, 265. Miller, T. M.; Neenan, T. X.; Kwock, E. W.; Stein, S. M. *J. Am. Chem. Soc.* **1993**, *115*, 356. Johansson, M.; Malmstrom, E.; Hult, A. *J. Polym. Sci., Polym. Chem.* **1993**, *31*, 619. Spindler, R.; Fréchet, J. M. J. *Macromolecules* **1993**, *26*,4809. Kim, Y. H. *Adv. Mater.* **1992**, *4*(11), 764. Mathias, L. J.; Carothers, T. W. *J. Am. Chem. Soc.* **1991**, *113*, 4043. Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583.

(8) Bolton, D. H.; Wooley, K. L. *Polym. Prepr.* **1996**, *37*(2), 388. Bolton, D. H.; Wooley, K. L. *J. Polym. Sci., Part A: Polym. Chem.*, in press.

(9) It is important to note that this is not a direct hyperbranched analog to the well-studied linear material, since the two compounds have different overall compositions, and therefore, direct comparison between the two materials should not be made.

(10) Acetonitrile is well-known to be one of the most effective solvents for reactions of organic molecules with metal fluoride compounds and, therefore, was selected as one of the solvents for polymerization. Chambers, R. D. *Fluorine in Organic Chemistry*, Wiley: New York, 1973; p 21.

(11) Houlihan, F. M.; Bouchard, F.; Fréchet, J. M. J.; Willson, C. G. *Macromolecules* **1986**, *19*, 13.

(12) Hofmann, K. *Imidazole and Its Derivatives, Part I*; Interscience Publishers, Inc.: New York, 1953; pp 15−16.

(13) Kambouris, P.; Hawker, C. J. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2717.

(14) Kocienski, P. J. *Protecting Groups*, Georg Thieme Verlag: Stuttgart, Germany, 1994; p 33. Corey, E. J.; Jones, G. B. *J. Org. Chem.* **1992**, *57*, 1028.

(15) Phenol-terminated hyperbranched polyesters have been reported to experience difficulties with GPC due to affinity with the packing material of the GPC columns. Wooley, K. L.; Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *Polym. J.* **1994**, *26*, 187.

(16) Gillespie, D. T.; Hammons, H. K.; Bryan, S. R. results presented at the MOLMASS 1996 2nd International Conference on "Molecular Mass Characterization of Synthetic and Natural Polymers", Bradford University, Cunbria, U.K., April 1−4, 1996.

(17) Wooley, K. L.; Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *Polym. J.* **1994**, *26*, 187. Miller, T. M.; Neenan, T. X.; Zayas, R.; Bair, H. E. *J. Am. Chem. Soc.* **1992**, *114*, 1018. Hawker, C. J.; Chu, F. *Macromolecules* **1996**, *29*, 4370. Kim, Y. H.; Webster, O. W. *Macromolecules* **1992**, *25*, 5563.

(18) Schaefer, J.; Stejskal, E. O.; McKay, R. A.; Dixon, W. T. *Macromolecules* **1984**, *17*, 1479.

MA961746D