Tetrahedrally-Oriented Four-Armed Star and Branched Aramids

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Received May 20, 1994; Revised Manuscript Received August 19, 1994[⊗]

ABSTRACT: Palladium-catalyzed carbonylation of 4-iodoaniline in the presence of 1,3,5,7-tetrakis(4-iodophenyl)adamantane and 1,3,5,7-tetrakis(4-aminophenyl)adamantane cores gave the corresponding four-armed star polybenzamides. Tetraphenyladamantane incorporation was confirmed by ^{13}C solution and solid-state CP/MAS NMR and FTIR. The stars exhibited the same thermal stability as linear polybenzamide synthesized by the same route. The star with the amine core exhibited the highest intrinsic viscosity in sulfuric acid ([η] = 0.74 dL/g), and films could be cast from dilute DMAC–5% LiCl solutions. Tetraphenyladamantane incorporation (confirmed by solid-state CP/MAS ^{13}C NMR and FTIR) significantly increased solubility. Branched aramids synthesized from 3,5-dibromoaniline under Pd-catalyzed carbonylation conditions were compared to a branched system based on 1,3,5,7-tetrakis(4-iodophenyl)adamantane. The former were insoluble, while the adamantane materials were slightly soluble in DMAc and H_2SO_4; both hyperbranched polymers tenaciously held residual solvent and could not be completely dried. These results confirm both the incorporation of the tetrasubstituted adamantyl core into both star and hyperbranched polymers and the possibility of property modification through disruption of chain packing and enforced tetrahedral arm orientation at the core.

Introduction

Multiarmed star and branched polymers have yet to be reported with constrained or enforced three-dimensional distribution of star arms. Such materials should posses unique properties since a three-dimensional geometry enforced by the core would greatly increase the hydrodynamic radii of the polymers obtained and perturb the close chain packing around the core. We have been examining derivatives of adamantane for use in novel polymer synthesis. Our goal is to incorporate rigid, tetrafunctional adamantane cores with intrinsic tetrahedral symmetry into rigid-rod polymer systems to study their effect on polymer viscosity, thermal behavior, and ultimate physical properties.

Aramids are a class of high-performance polymers that have been well studied to give a broad base of synthetic and physical data for a variety of linear[1,2] as well as cross-linked[3] (gel) systems. Rigid-rod aramids such as Kevlar and poly(*p*-benzamide) (PBA) are mainly used in fiber form due to their thermal stability, chemical resistance, and excellent tensile properties. Recently, much attention has been given to the preparation of aramid dendrimers and hyperbranched systems as a new class of potentially useful high-performance polymers. These highly branched aromatic systems possess unique properties and may find application as compatibilizers, rheological modifiers, and high-temperature composite matrices.[4,5]

Well-defined first- and second-generation dendrimers with a planar 1,3,5-benzenetricarboxamide core and 3,5-dicarboxamidophenyl repeat units have been prepared with phenyl[5] and/or carboxylate termini[6] through a stepwise controlled synthesis. The core was a crystalline molecule with a melting point of 317–321 °C, while the first-generation dendrimer displayed a broader melting transition of 295–309 °C.[5] No thermal data were published on the second-generation system.

Similar but structurally less well-defined branched aramids have been prepared via a one-pot synthetic approach.[4] Derivatives of 3,5-dicarboxyaniline and 3,5-diaminobenzoic acid were homopolymerized by conventional step-growth techniques to give two branched polymers, one with carboxylic acid terminal groups and the other with amine end functionality. Both AB_2 monomers gave polymers that were soluble in amide solvents, with the acid end-group polymer exhibiting a lyotropic liquid crystalline phase in 1-methyl-2-pyrrolidinone (NMP). Both polymers, and the methyl ester of the carboxylic acid terminal polymer, were shown to form aggregates in *N*,*N*-dimethylformamide (DMF) which were broken up by the addition of salts such as lithium chloride.

It has been known for some time that organic halides undergo palladium(0)-catalyzed carbonylation reactions.[7] By this route, aryl, benzyl, vinyl, and heteroaromatic halides are converted to esters in the presence of methanol, to amides in the presence of primary amines, and to aldehydes in the presence of hydrogen. Imai and co-workers[8] have shown that aramids can be formed by this route when aromatic dibromides are carbonylated in the presence of aromatic diamines. Moderate molecular weight aramids were isolated (η_{inh} = 0.3–0.78 dL/g) at low pressures of carbon monoxide. It was observed that, when excess diamine (ca. 5%) was used, polymers with higher viscosities were obtained.

Perry and co-workers[9] have shown that aromatic diiodo compounds are more susceptible to this aminocarbonylation reaction than the dibromides to give high molecular weight aramids. The enhanced reactivity of aryl iodides is illustrated by the observation that, even for an AB monomer (iodoaniline), moderate molecular weight polymer was isolated. As in Imai's case, an excess of the diamine was necessary for the formation of high molecular weight aramids from AA–BB systems. These results have been reviewed recently.[10]

The effect of carbon monoxide pressure on aromatic dibromides is quite dramatic.[9] At high carbon monoxide pressures (20–90 psig), carbonylation is inhibited and no or only low molecular weight aramids were isolated. For aryl bromides, the rate-determining step is oxidative addition of the Pd(0) to the aryl bromide.[9] This is inhibited by high CO pressures which enhance CO coordination to the Pd(0), rendering the palladium less nucleophilic and slowing the oxidative addition step. In contrast, the rate-determining step for iodoaromatics is CO insertion,[9]

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1994.

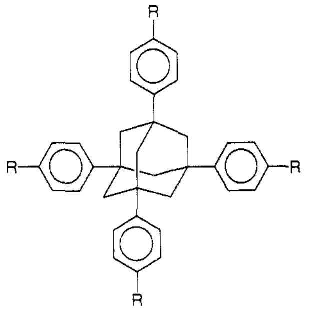
0024-9297/94/2227-7024$04.50/0

and increasing CO pressure increases the rate of reaction and the rate of high molecular weight polymer formation. This pressure-sensitive behavior provides a useful method for controlling halide selectivity.

Appropriate derivatives of 1,3,5,7-tetraphenyladamantane are ideal three-dimensional core units for rigid-rod aramid star and branched systems due to their high symmetry and thermal stability. We describe here use of a tetraiodide and a tetraamine to give isomeric aramids through tail-linked and head-linked polymerizations from the cores using 4-iodoaniline in the Pd-catalyzed carbonylation reaction to give three-dimensional star aramids. Similarly, use of 3,5-dibromoaniline gives highly branched polymers under the same conditions.

Results and Discussion

Monomer Synthesis. The key intermediate used in the polymerizations described here is 1,3,5,7-tetrakis(4-iodophenyl)adamantane (1) whose synthesis was described previously.[11] Overall yields of ca. 50% were obtained for this material in a two-step process starting from commercially available 1-bromoadamantane. Important to the present study is the high regioselectivity that occurs in the iodination reaction to give pure para substitution at all four phenyl groups. This leads to polymers with well-defined architecture, especially when the high-yield carbonylation reaction is employed to give aramids.



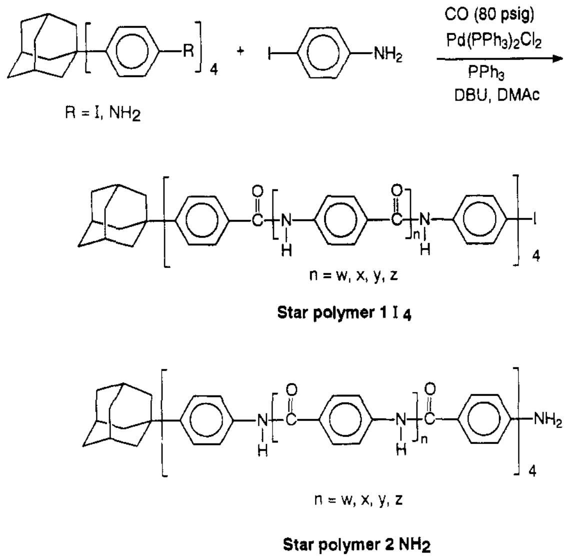
1: R = I

2: R = NH_2

The second key monomer used in this project was obtained in two steps from 1. A modified literature procedure was developed that gave excellent yields in the copper-catalyzed coupling reaction between 1 and potassium phthalimide. Hydrazinolysis of the four imide groups gave essentially pure 1,3,5,7-tetrakis(4-aminophenyl)adamantane (2).

Four-Armed Star Aramids. The star aramids were prepared from the tetraiodide 1 and 4-iodoaniline via the palladium-catalyzed carbonylation reaction[9] shown in Scheme 1. Polymers were purified by precipitating the reaction mixtures into methanol, and this may explain the less-than-quantitative yields; i.e., the star structures of these materials greatly enhance their solubility, even to the extent that low molecular weight products are soluble in the precipitation solution. Molecular modeling results illustrate the three-dimensional structure of these materials. Figure 1 is the Polygraph-minimized structure of the amino-terminated four-armed aramid **Star 2NH$_2$**, which shows the difficulty the arms would have packing in ordered or crystalline domains.

Scheme 1. Star Aramid Formation from Core Units 1 and 2 with 4-Iodoaniline



Assigning the amine group the "tail" designation, the product obtained from the tetraiodide 1 represents a tail-linked polymerization of the 4-iodoaniline. Similar conditions were used to polymerize 1,3,5,7-tetrakis(4-aminophenyl)adamantane (2) and 4-iodoaniline to give the head-linked star polymer. In each case, the core molecule was reacted in a 1:20 ratio with 4-iodoaniline (5 mol % of core). Ideally, this would give star polymer in which $w = x = y = z = 5$; i.e., the DP of each arm should be 5, and the polymer would have a total DP of 20. Even realizing that ideal reaction is improbable, the well-known molecular weight narrowing that occurs with multiarm polymers should give products with distributions of ca. 1.25 (polydispersity index $X_w/X_n = 1/f_{\#arms}$).[12]

The intrinsic viscosities, decomposition temperatures and observed thermal transitions of the star and linear PBA's are listed in Table 1. Plots of inherent viscosity and reduced viscosity versus concentration for **Star 2NH$_2$** polymer were linear with large positive slopes (0.54 and 1.1, respectively). For **Star 1I$_4$**, the slopes were also positive (0.36 for inherent viscosity and 0.37 for reduced viscosity plots). Such viscosity behavior indicates that the star PBA's do not behave as rigid rods in sulfuric acid solutions, in contrast to linear aramids. This behavior is not unexpected given the ball-like structure that should result from tetrahedral arm orientation and the relatively low molecular weights of these samples.

The fact that the star aramid based on core 2 gave the highest viscosity is, we believe, due to two factors. First, incorporation of adamantane allows the growing polymer to remain soluble longer in the DMAc polymerization media. The latter may also explain the higher viscosity of the star aramid that contains 1 than that of the linear polymer obtained under otherwise identical conditions. Second, since the core contains amine groups, the stoichiometric balance is skewed toward amines. According to both Imai and Perry's observations, excess amine favors formation of higher molecular weight polymers, perhaps due to a decrease in side reactions. In any event, it is apparent that, while identical polymers were expected based on the two different cores with identical linkage groups, the amine core actually gave a higher molecular weight product. This observation is important for extending this approach to other star and branched aramids.

Adamantane incorporation in the star polymers was verified by FTIR, solid-state ^{13}C NMR, and solution ^{13}C NMR. Figure 2 gives the FTIR results showing the weak adamantyl CH_2 peaks at 2919 and 2849 cm^{-1} in the spectra of both **Stars 1I$_4$** and **2NH$_2$**. Otherwise, the IR spectra of the stars were identical to that of the linear polybenzamide (bottom) prepared using the same synthetic technique.

Solid-state ^{13}C NMR even more clearly confirmed the presence of adamantane. Figure 3 shows the ^{13}C CP/MAS

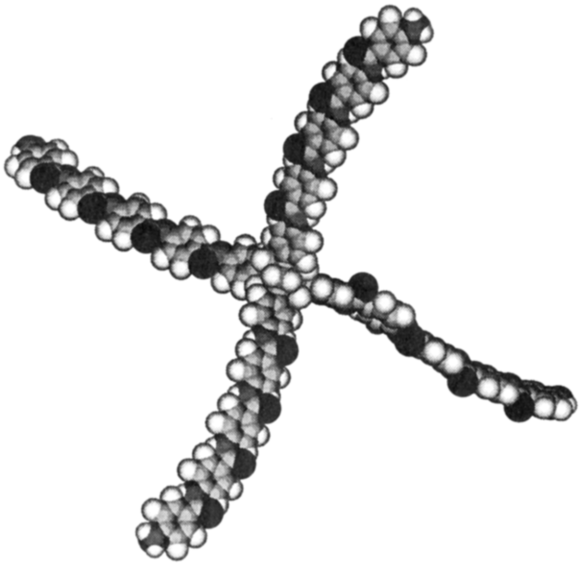


Figure 1. Polygraph-minimized structure for star aramid 1.

Table 1. Properties of Aramid Star and Linear Polymers

polymer	[η] (dL/g)[a]	T_d (°C)[b]	transition (°C)
linear	0.24	450	none
star 1I_4	0.27	450	355
star 2NH_2	0.74	445	none

[a] 0.25 g/dL of H_2SO_4, 30 °C. [b] 10% weight loss in air.

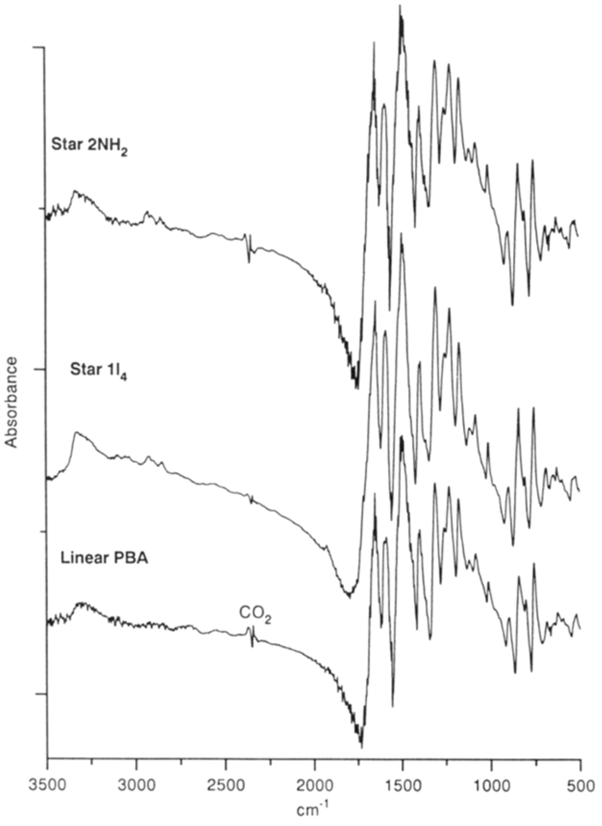


Figure 2. FTIR spectra of linear PBA (bottom), star aramid from 1 (middle), and star aramid from 2 (top).

NMR spectrum of the star and linear PBA's. The spectrum of each of the stars shows resonances at ca. 40 (sharp) and 49 ppm (broad) which correspond to the quaternary and secondary carbons, respectively, of the adamantane core. These peaks are also present in the solution NMR spectrum of each (not shown) but with the latter peak shifted upfield due to loss of local environment effects in the solid state plus solvent effects in the highly polar and hydrogen bonding solvent (sulfuric acid). In any case, both the IR and NMR results clearly confirm similarity of the overall composition for the aramid segments of these three polymer samples plus the incorporation of the adamantane core into both the tail- and head-linked derivatives.

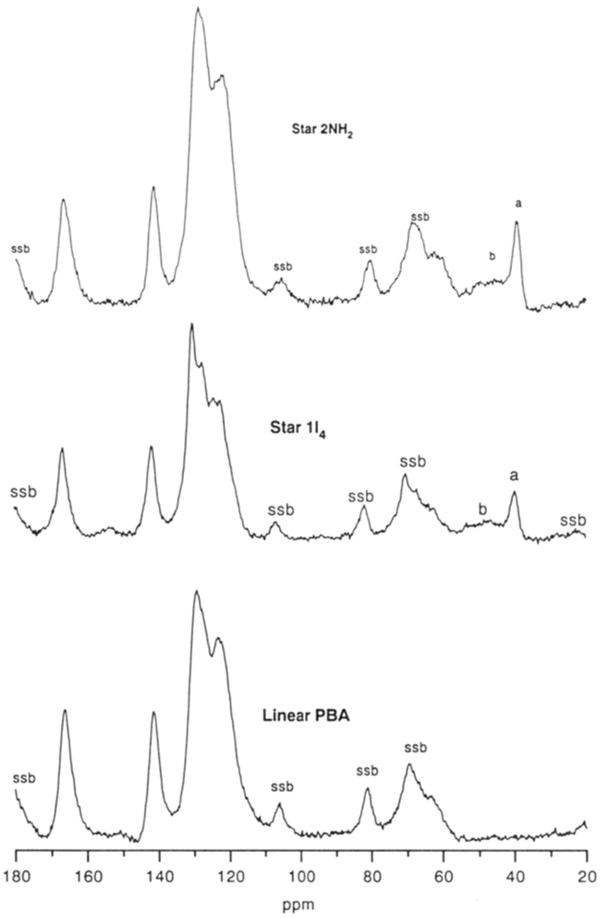


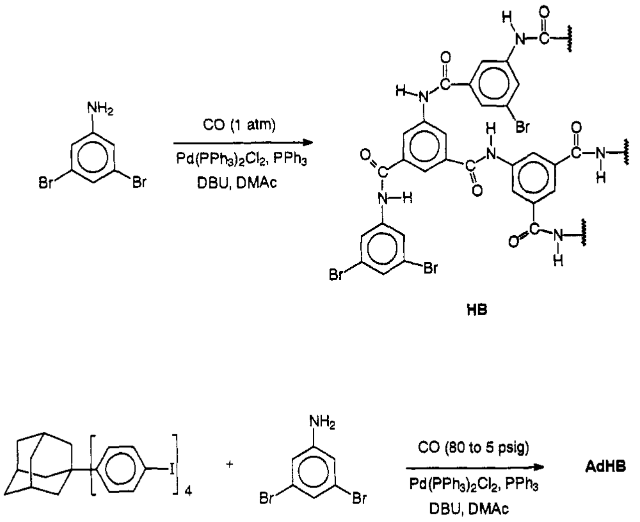
Figure 3. Solid-state ^{13}C NMR spectra of linear PBA (bottom), star aramid from 1 (middle), and star aramid from 2 (top). "ssb" indicates spinning sidebands which should be ignored.

The star and linear polymers exhibited similar thermal stability in that all began to degrade at ca. 450 °C. As-precipitated samples of PBA synthesized by different routes also decompose at ca. 450 °C.[13] **Star 1I_4** also showed a weak endothermic transition at ca. 355 °C (which we cannot explain; possibly a solid-state reorganization process of some kind) on the first DSC heating run only. No melting was observed for either star polymers or the linear PBA before decomposition.

All three PBA polymers were found to be soluble in DMAc–5% LiCl as well as in concentrated sulfuric acid. Films of **Star 2NH_2** were cast from dilute solutions in DMAc–5% LiCl; concentrated solutions formed gels, probably due to strong interaction between the arms combined with the impossibility of these polymers having all of their arms aligned in liquid crystalline arrays. **Star 1I_4** and the linear PBA did not form films or gels, probably due to lower molecular weights and the absence of entanglement.

Hyperbranched Aramids. The highly branched aramids were synthesized by the routes shown in Scheme 2. In the case of the branched polymer from 3,5-dibromoaniline and 1 (**AdHB**), we took advantage of the difference in reactivity of aryl bromides and iodides toward carbonylation to insure incorporation of all four adamantane

Scheme 2. Formation of Hyperbranched Aramids from 3,5-Dibromoaniline Alone and with Core Initiator 1



core arms. The reaction was allowed to proceed under conditions that favor aryl iodide carbonylation (i.e., high pressures of CO) for 2 h before the CO pressure was lowered to ca. 1 atm to favor carbonylation of the aryl bromides. **AdHB** was directly compared to the polymer that resulted from the carbonylation of 3,5-dibromoaniline, **HB**.

HB is structurally similar to the branched aramid systems reported by Kim[4] except that **HB** (as well as **AdHB**) should have bromine end groups instead of acid or amine moieties. The previously reported branched aramid systems were soluble in amide solvents such as DMF, DMAc, and NMP. **HB** was found to be insoluble in these solvents as well as insoluble in DMAc–5% LiCl and sulfuric acid. This may be due to cross-linking through coupling of the reactive intermediates and end groups. Another possibility (less likely) is that, for these branched aramid systems, the end-group functionality dictates or modifies the overall solubility of the molecules. Surface functionality has been shown to play a major role in determining physical properties and solubility in other dendrimer systems.[14] Because of the insolubility of this polymer, solid-state NMR was used to confirm product structure. Figure 4 contains the solid-state ^{13}C NMR spectrum of this insoluble polymer, clearly showing aramid carbonyls at ca. 165 ppm. Strong spinning sidebands are seen from 20 to 110 ppm, as indicated in the spectrum. Surprisingly, even after extensive extraction and vacuum drying, peaks for residual solvent (DMAc and/or CH_2Cl_2) are seen at ca. 50 ppm.

When tetraphenyladamantane was incorporated into the highly branched aramid structure (**AdHB**), partial solubility was observed in DMSO and amide solvents such as DMF and DMAc. Again, it appears that adamantane incorporation disrupts crystalline packing and leads to a more open and molecularly-porous branched structure that is capable of taking up and holding solvent. Additionally, the two-step carbonylation process used for this polymer may have reduced possible cross-linking reactions.

The solid-state NMR spectrum of the **AdHB** sample is given in Figure 4 for comparison with that of the **HB** sample. Peaks due to the adamantane moiety are clearly seen at 40 ppm (sharp, quaternary carbons), 48 ppm (CH_2 groups), and 153 ppm (aromatic carbon attached to adamantane). The solution spectrum of a DMSO-soluble fraction of **AdHB** showed peaks with greater resolution and identical chemical shifts.

Thermal analysis of these two highly branched polymers showed no transitions below 500 °C by DSC, although the gradual changes in base line above 310 and 340 °C, respectively, correspond to the onset of weight loss seen in the TGA scans. Thermal decomposition began ca. 80 °C lower, and was more rapid above 350 °C, than for linear and star-branched polymers examined here. We can offer no explanation for this marked difference in stability between linear and highly branched aramids except to point out that, first, the branched polymers are much less crystalline than their linear counterparts and this may increase mobility and degradation at high temperatures and, second, that the branched polymers contain at least one unreacted aryl bromide group per repeat unit (on average) that may thermolyze or promote backbone degradation.

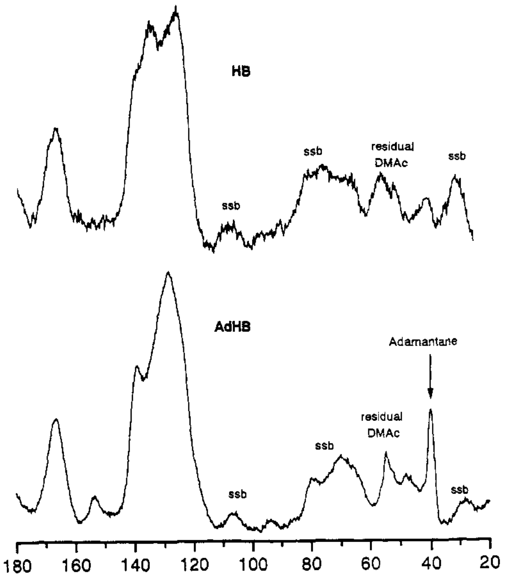


Figure 4. Solid-state ^{13}C NMR spectra of hyperbranched aramid (top) and adamantane-core hyperbranched aramid (bottom). "ssb" indicates spinning sidebands.

Conclusions

Key intermediates with tetrahedrally-arrayed terminal iodine and amine groups were synthesized in high yields. Conversion to aramid star structures by copolymerization with 4-iodoaniline occurred readily. Both solution and solid-state NMR, as well as FTIR analysis, confirmed adamantane incorporation. For the four-armed star aramids, incorporation of tetraphenyladamantane allowed the growing polymer to remain soluble longer in the polymerization media which apparently led to the formation of higher molecular weight polymers than for linear analogs. Moreover, the presence of 1,3,5,7-tetraphenyladamantane was found not to have an adverse effect on the thermal properties of the star PBA's. For the highly branched aramids, incorporation of adamantane was again confirmed by FTIR and solution and solid-state ^{13}C NMR. The presence of adamantane units as defects to prevent close packing did not maintain solubility in this case (probably due to crosslinking) and actually resulted in a decrease in the thermal stability of the polymer obtained.

Experimental Section

General Procedures. High-pressure (80–90 psig) carbonylation reactions were performed in a 200-mL stainless steel high-pressure reactor equipped with a pressure gauge, gas inlet, and pressure release valve. Carbonylation reactions at 1 atm were performed in a two-neck round-bottom flask that had been purged twice with CO and then kept under a carbon monoxide atmosphere (filled balloon). FTIR spectra were obtained using a Perkin-Elmer 1600 spectrometer. Solution ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AC300 spectrometer operating at 300.1 and 75.469 MHz, respectively. Solid-state ^{13}C NMR spectra were acquired on a Bruker MSL400 spectrometer operating at 100.614 MHz. A DuPont 9900 thermal analysis system was used to collect DSC and TGA data. Viscosities were obtained on 0.25 g/dL solutions in sulfuric acid at 30 °C using a 1B Cannon-Ubbelohde viscometer. Molecular modeling was carried out with the Polygraph program of Molecular Simulations on an IBM RISC R/S 6000.

Chemicals. 1,3,5,7-Tetrakis(4-iodophenyl)adamantane (1) was synthesized from 1,3,5,7-tetraphenyladamantane.[11,15] 3,5-Dibromoaniline was synthesized by diazotization[16] of 2,6-dibromo-4-nitroaniline (Aldrich) followed by reduction of the nitro group with tin under acidic conditions.[17] All other chemicals were purchased from Aldrich and used as obtained.

1,3,5,7-Tetrakis(4-aminophenyl)adamantane (2) from the Tetraphthalimide. Literature procedures for the copper-catalyzed substitution of aryl halides by potassium phthalimide[18] were modified as follows. 1,3,5,7-Tetrakis(4-iodophenyl)adamantane (0.5 g, 0.53 mmol), potassium phthalimide (0.39 g, 2.12 mmol), copper iodine (0.42 g, 2.2 mmol), and 10 mL of DMAc were placed in a 25-mL one-neck round-bottom flask and heated under a nitrogen atmosphere at reflux temperature overnight. After cooling, the reaction mixture was poured into 5% H_2SO_4 and a white/yellow solid was isolated and extracted with methylene chloride. The solvent was removed under reduced pressure and the yellow solid recrystallized from methanol/methylene chloride (1:4) to give the tetraphthalimide as a white microcrystalline solid; 0.43 g (79%); DSC 349 °C (endo), 408 °C (endo); IR (KBr) 3056, 2919, 2849, 1737, 1719, 1514, 1378, 1226, 1079, 720, 703 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.25 (br s, 12H), 7.50 (apparent d, 8H), 7.60 (apparent d, 8H), 7.80 (apparent d, 8BH), 7.90 (apparent d, 8H); ^{13}C NMR ($CDCl_3$) δ 39.3, 47.1, 123.7, 125.9, 126.4, 131.8, 134.3, 148.9, 167.3.

The tetraphthalimide (0.35 g, 0.343 mmol) and 10 mL of absolute ethanol were placed in a 25-mL round-bottom flask. The suspension was stirred under nitrogen for 4 h, and an excess of hydrazine (0.78 g, 2.45 mmol) was added. The reaction was heated at reflux temperature overnight. The ethanol was removed under reduced pressure, leaving a yellow solid which was separated from phthalhydrazide by Soxhlet extraction with chloroform. Removal of the chloroform under reduced pressure gave the product as a light yellow solid; 0.15 g (87%); DSC 373 °C (endo); IR (KBr) 3424, 3330, 3213, 3025, 2119, 2849, 1619, 1514, 1496, 1443, 1355, 826, 761, 697 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.81 (s, 12H), 4.78 (s, 8H), 6.50 (d, 8H), 7.11 (d, 8H); ^{13}C NMR (DMSO-d_6) δ 37.8, 47.7, 113.7, 125.3, 137.7, 146.2.

General Four-Armed Star Polymerization Procedure. 4-Iodoaniline (1.0 g, 0.46 mmol), core compound (0.023 mmol, 5 mol % based on 4-iodoaniline), $Pd(PPh_3)_2Cl_2$ (6 mol % based on aryliodo groups), PPh_3 (2 equiv to catalyst), and 15 mL of DMAc were placed in an oven-dried stainless steel pressure reactor containing a magnetic stirbar. The base, 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU; 2 equiv to NH_2 groups), was then added and the vessel purged three times with 40 psig of carbon monoxide. After the final purge, the vessel was charged with 80 psig of carbon monoxide, placed in an oil bath, and heated at 100–115 °C overnight with stirring. After cooling, the pressure was released and the reaction mixture poured into methanol. The crude polymer was isolated by vacuum filtration. It was then dissolved in a suitable solvent (DMSO or H_2SO_4) and reprecipitated into methanol. Extraction with methanol followed by drying gave 0.50–0.85 g of a light gray polymer.

Star polymer 1I_4: 0.55 g (52%); TGA 10% weight loss at 450 °C; intrinsic viscosity (0.25 g/dL, H_2SO_4, 30 °C) 0.27 dL/g; IR (KBr) 3336, 2919, 2849, 1654, 1602, 1502, 1402, 1318, 1238, 1182, 846, 762 cm^{-1}; ^{13}C NMR (H_2SO_4, referenced to DMSO-d_6 insert) δ 40.0, 43.0, 124.0, 129.9, 139.0, 171.7; CP/MAS ^{13}C NMR δ 40.0, 49.0, 122.9, 124.5, 141.6, 166.7.

Star polymer 2NH_2: 0.85 g (76%); TGA 10% weight loss at 445 °C; intrinsic viscosity (0.25 g/dL, H_2SO_4, 30 °C) 0.74 dL/g; IR (KBr) 3324, 2919, 2849, 1648, 1598, 1508, 1402, 1316, 1234, 1182, 844, 758 cm^{-1}; ^{13}C NMR (H_2SO_4 referenced to DMSO-d_6) δ 37.2, 44.0, 124.0, 126.0, 129.9, 138.3, 171.7; CP/MAS ^{13}C NMR δ 39.5, 49.5, 122.5, 130.2, 142.0, 167.0.

Linear Polybenzamide. Linear polybenzamide was synthesized by the same reaction route as above except the core molecule was not added. A dark gray-to-black solid was isolated: 0.50–0.60 g (40–55%); TGA 10% weight loss at 450 °C; intrinsic viscosity (0.25 g/dL, H_2SO_4, 30 °C) 0.24 dL/g; IR (KBr) 3312, 1648, 1596, 1508, 1402, 1318, 1236, 1180, 844, 764 cm^{-1}; ^{13}C NMR (H_2SO_4 referenced to DMSO-d_6) δ 124.0, 129.9, 134.0, 138.4, 171.8; CP/MAS ^{13}C NMR δ 122.2, 126.8, 130.2, 141.5, 166.7.

Polymerization of 3,5-Dibromoaniline To Give HB. A 50-mL two-neck round-bottom flask, equipped with a condenser, magnetic stirbar, and gas inlet and outlet, was charged with 3,5-dibromoaniline (1.0 g, 4.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.33 g, 0.48 mmol), PPh_3 (0.25 g, 0.96 mmol), and 20 mL of DMAc. The solution was heated at 50 °C with stirring and purged twice with carbon monoxide. DBU (1.2 g, 8 mmol) was then added, and the orange reaction mixture was heated at 115 °C under 1 atm of carbon monoxide (balloon fitted to reaction flask) overnight. The solution gelled after 8 h, though stirring was still possible. After cooling, the gelled mixture was poured into methanol. A yellow solid was isolated, stirred in boiling methanol for 4 h, and then Soxhlet extracted with methylene chloride overnight. After drying, a yellow solid was isolated: 0.75 g (60%); DSC, no transitions below 500 °C; TGA 10% weight loss at 310 °C; IR (KBr) 3260, 3060, 1672, 1578, 1531, 1437, 1314, 1284, 1232, 1102, 997, 879, 744, 685 cm^{-1}; CP/MAS ^{13}C NMR δ 124.1, 132.9, 165.7.

Formation of Hyperbranched Polymer from 3,5-Dibromoaniline and 1, AdHB. 3,5-Dibromoaniline (1.5 g, 6 mmol), 1 (0.28 g, 0.3 mmol), $Pd(PPh_3)_2Cl_2$ (0.26 g, 0.37 mmol), PPh_3 (0.2 g, 0.74 mmol), and 20 mL of DMAc were placed in a stainless steel pressure reactor equipped with a pressure gauge, gas inlet/outlet, and magnetic stirrer. The solution was stirred under a nitrogen atmosphere, and DBU (1.82 g, 12 mmol) was added. The vessel was then purged three times with carbon monoxide (40 psig). After the final purge, the vessel was pressurized to 85 psig and placed in a 100 °C oil bath. After 2 h, the carbon monoxide pressure was dropped to 5 psig and the reaction allowed to proceed at 100 °C for 14 h. After cooling to room temperature, the pressure was released, the reactor opened, and the orange, gelled contents poured into methanol. The rubbery polymer was chopped up and stirred in boiling methanol for 4 h. Soxhlet extraction with methylene chloride overnight followed by drying gave 0.70 g (65%): DSC, no transitions below 500 °C; TGA 10% weight loss at 340 °C; FTIR (KBr) 3260, 3072, 2931, 2849, 1654, 1578, 1531, 1437, 1279, 1237, 1096, 997, 867, 732, 691, 603 cm^{-1}; ^{13}C NMR (DMSO-d_6) δ 48.0, 52.0, 119.0, 121.4, 124.2, 125.5, 127.8, 128.0, 128.7, 128.9, 130.6, 131.4, 131.5, 132.0, 134.5, 136.6, 140.6, 153.0, 164.2, 165.6; CP/MAS ^{13}C NMR δ 39.8, 48.1, 128.1, 138.9, 153.5, 166.2.

Acknowledgment. This work was supported in part by a grant from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by a USDE Graduate Student Assistantship in Areas of National Need. We thank Dr. William L. Jarrett and Scott J. Steadman for collection of the solid-state NMR data and Michael J. Stewart for molecular modeling results.

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