Highly Cross-Linked Polymers Based on Acetylene Derivatives of Tetraphenyladamantane

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ABSTRACT: 1,3,5,7-Tetrakis(4-iodophenyl)adamantane was reacted with 2-methyl-3-butyn-2-ol and phenylacetylene under Pd-catalyzed Heck coupling conditions to give the two corresponding tetraacetylene derivatives. Deprotection of the first gave the derivative with free terminal acetylenes. Thermal cure of both acetylene-containing monomers was monitored by FTIR. The cure products were then characterized by solid-state ^{13}C cross-polarization magic-angle spinning (CP/MAS) nuclear magnetic resonance (NMR) spectroscopy. This technique was combined with dipolar dephasing, in which resonances that are protonated are differentiated from those which are nonprotonated, to help clarify product composition. Both NMR and FTIR confirmed the presence of adamantane in the otherwise all-aromatic structures. TGA analysis indicated that these highly cross-linked materials began to degrade at ca. 450 and 490 °C, respectively, in air, confirming their excellent thermooxidative properties.

Introduction

The synthesis of high carbon content polymers that mimic or can lead to the structure and properties of diamond has been a goal of chemists for years. Diamond's attributes include high electrical resistivity, high thermal conductivity, a low coefficient of friction, transparency to infrared radiation, and extreme hardness.[1] The major obstacle to the incorporation of diamond into devices has been the difficulty in obtaining diamond in any form other than that of a crystal or collection of microcrystals. This has been overcome somewhat by the discovery that diamond films can be formed by the chemical vapor deposition of various hydrocarbons in a reducing plasma.[2] Still needed is a way to form all-carbon sheets, wires, and solid parts that possess some of diamond's desirable properties. One possibility may involve the synthesis of three-dimensional all-hydrocarbon polymer precursors which can be thermalized and/or treated with a hydrocarbon plasma to give diamond or diamond-like structures.

Several approaches have been taken in the synthesis of diamond precursors. Since adamantane can be thought of as the "repeat unit" of diamond (Figure 1), several attempts have been made to directly polymerize adamantane itself.[3] The most successful of these was an iterative polymerization of 1,3,5,7-tetrabromoadamantane which involved a repetitive two-step treatment with sodium metal (Wurtz coupling) followed by bromine (H–Br exchange).[4] In this manner, polyadamantane was obtained that, according to IR and X-ray analysis, consisted of adamantane units linked by saturated C–C bonds in a three-dimensional network.

An alternative synthetic approach to diamond-like materials was based on the synthesis and polymerization of tetraethynylmethane.[5] Theoretically, this compound should first form an expanded adamantane-like structure followed by additional reaction to a "superdiamond" network.[6] A full report on the polymerization of tetraethynylmethane has yet to be published.

Other avenues that have been explored include the synthesis and polymerization of the mono-, di-, and triacetylene derivatives of adamantane,[7,8] biadamantane,[9] and diadamantane.[10] All of these acetylene derivatives cure to give high carbon content polymers, though none have been converted to diamond. The polymerization of 1,3,5,7-tetraethynyladamantane may offer a path to a diamond-like material, although its synthesis is not trivial.[11]

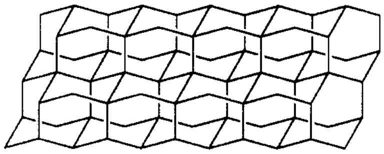

Figure 1. Schematic of diamond structure.

In addition to use of acetylene-containing materials as potential diamond precursors, monomers and reactive oligomers containing terminal acetylene and phenylacetylene moieties have been developed for generating high-performance polymers and composites. A number of recent reports confirm the utility of this approach. For example, NASA researchers have examined acetylene-terminal oligoimides as reactive composite matrices and are now exploring the phenylacetylene analogs of these materials. While the acetylene-terminated monomers do cure to cross-linked systems, the phenylacetylene analogs give improved processing and final properties.[12]

Our approach to new materials of related structures has been to use the readily available tetraphenyladamantane as a starting point for the synthesis of three-dimensional, all-hydrocarbon polymers which can serve as precursors to consolidated and cross-linked networks. Here we describe our results with two members of a new family of all-hydrocarbon reactive materials capable of thermal cure, one with terminal phenylacetylene units and the other with diphenylacetylene end groups. We compare the properties of both types of derivatives based on the tetraphenyladamantane core.

Results and Discussion

Monomer Synthesis. Friedel–Crafts reaction of 1-bromoadamantane and benzene with $AlCl_3$ and *tert*-butyl bromide as cocatalysts gave good yields of 1,3,5,7-tetraphenyladamantane.[13] Iodination of this key intermediate by [bis(trifluoroacetoxy)iodo]benzene occurred exclusively at the *para* positions to give 1,3,5,7-tetrakis(4-iodophenyl)adamantane[14] (**1**). This material was used as

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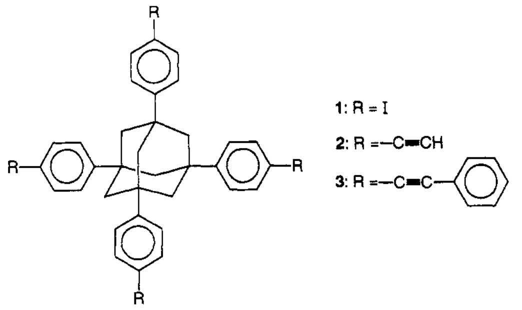
the starting material for the synthesis of the tetraacetylene derivatives 2 and 3 (structures given below show correct positions of attachment; in the rest of the paper, abbreviated structures of these compounds are used to indicate identity and carbon peak assignments).



The protected tetraacetylene was prepared by palladium-catalyzed coupling of 1 with 2-methyl-3-butyn-2-ol. The yields of the protected derivative were moderate (40–45%). Elemental analysis, FTIR, and ^{1}H and ^{13}C NMR were used to confirm product identity. Deprotection was carried out with NaH to give 2 in nearly quantitative yield (96–98%). The free acetylene groups of 2 were found to be quite stable, and no special precautions were taken with storage and handling of this compound.

Compound 3 was prepared in a similar manner by reaction of 1 with excess phenylacetylene in the presence of $Pd(PPh_3)_2Cl_2$. Yields were somewhat higher (55–62%) than those of the intermediate for 2. Compound 3 was soluble enough in chloroform that a ^{1}H NMR spectrum could be obtained, although acquisition times were so long it was impractical to obtain a solution ^{13}C NMR spectrum. Solid-state ^{13}C NMR and FTIR were used to confirm the identity of this product as described in a later section.

Cure Chemistry. Differential scanning calorimetry of 2 (Figure 2) indicated that the acetylenes began to react at 160 °C, with the maximum in the exotherm occurring at 190 °C; the small endotherm at ca. 90 °C is apparently due to loss of retained solvent. No transitions were observed during a second heating to 450 °C, which seems to suggest that complete cure had occurred. However, as discussed in the NMR section below, this was not the case. A step-cure process with a final cure temperature of 300 °C for 2 was required, and the IR discussion refers to completely cured material.

Acetylenes have very characteristic absorbances in the IR, which makes FTIR the method of choice for monitoring the cure. Figure 3 shows the FTIR spectra for 2 before and after complete curing. The free acetylenes in 2 are identified by the strong terminal C–H stretch at 3284 cm^{-1} and the weak sp carbon–carbon stretch at 2108 cm^{-1} (arrows indicate peaks in the lower spectrum, Figure 3). These stretches are absent in the FTIR spectrum of the cured compound (top trace, Figure 3), and new sp^2 C–H peaks are seen at 3000–3100 cm^{-1}.

Terminal acetylenes can cure by cyclotrimerization, biradical mechanisms, Glaser coupling, and Straus coupling.[15] Solid-state NMR has proven to be a valuable tool for characterization of insoluble materials and has been used to identify the products formed during the cure of acetylene-terminated polyimides.[15,16] Figure 4 shows the CP/MAS ^{13}C NMR spectra of 2 as the free acetylene (lowest spectrum), after partial cure (1 h at 200 °C, middle trace), and after complete curing (three-step cure, top trace). The free acetylene carbons are present at 78 and 84 ppm. The peaks seem to merge during thermal treatment, broadening slightly for the partially cured material and forming a single broad peak at 79 ppm for the fully cured material. Based on this data, it would seem that the cure mechanism (or one of the mechanisms) involves the formation of an acetylene-containing intermediate and/or product struc-

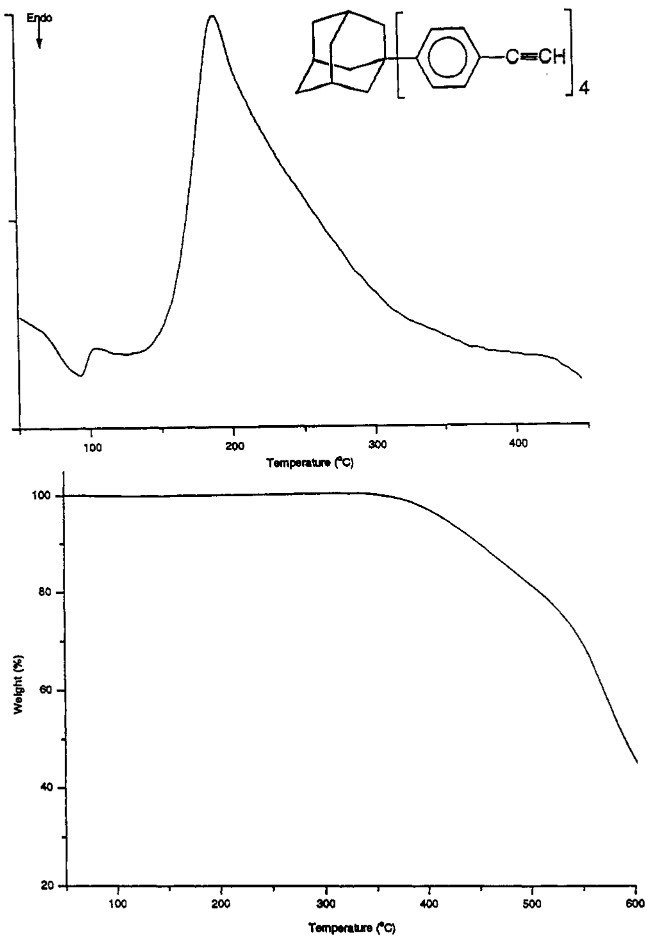


Figure 2. DSC thermogram of 2 (20 °C/min) (top trace); TGA trace of 2 after step-curing, T_d onset = 450 °C (air) (bottom trace).

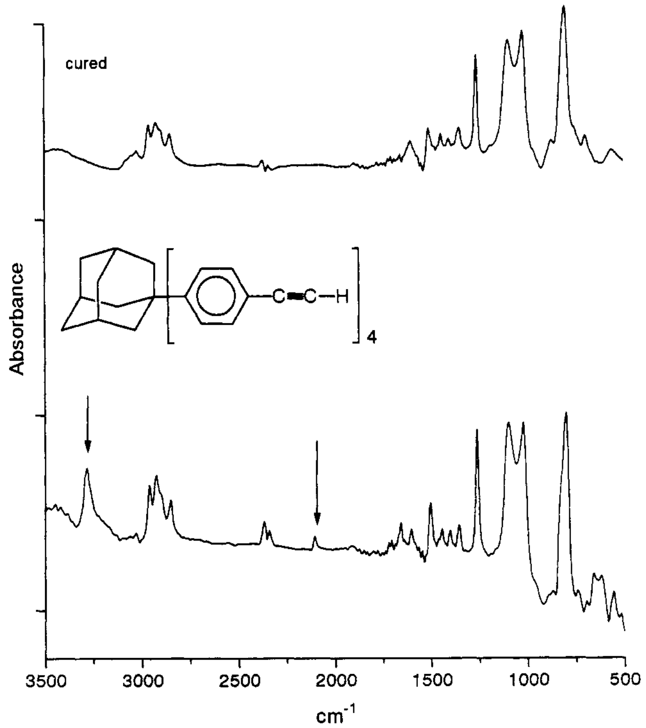


Figure 3. FTIR (KBr) spectrum of 2 before reaction (bottom) and after curing (top).

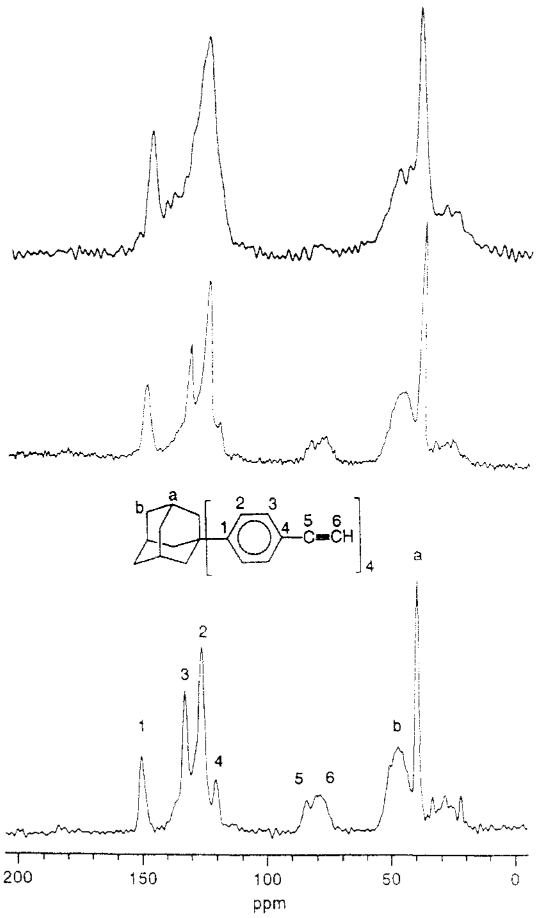


Figure 4. CP/MAS ^{13}C NMR spectra of 2 as the free acetylene (lowest trace), after heating at 150 °C for 2 h (partially cured material, middle trace) and after fully curing (top trace).

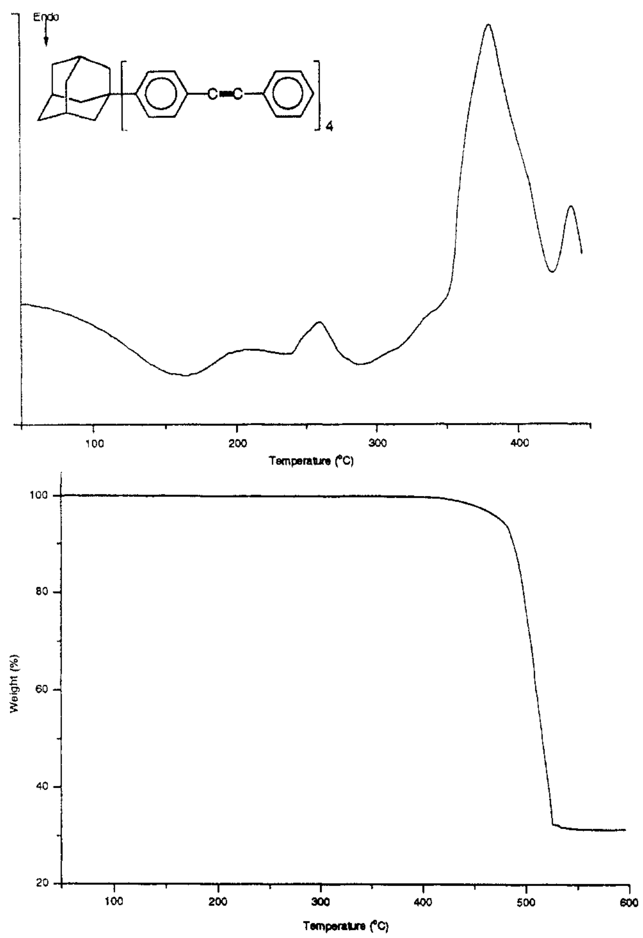


Figure 5. DSC thermogram of 3 (20 °C/min) (top trace) and TGA trace of 3 after step-curing (bottom trace), T_d onset = 490 °C (air).

ture which would result in additional peaks for the sp carbons between 75 and 85 ppm. The adamantane carbons are found at 39.5 and 50.8 ppm and the phenyl peaks are seen at 120–132 and 148 ppm. The former show little change on cure, while the latter broaden and show additional peaks at ca. 135–145 ppm. This information points to the formation of a mostly-aromatic structure that has adamantane incorporated in it. This also correlates well with the FTIR spectrum of the fully cured material which showed complete loss of the terminal acetylene hydrogen.

Thermogravimetric analysis of the cured material (Figure 2) indicated that weight loss began at ca. 450 °C. For comparison, poly(1,3,5-triethynyladamantane) began to decompose at 477 °C in air and the polymer of 1,3-diethynyl-5-phenyladamantane exhibited a T_d of 460 °C in air.[9]

Disubstituted acetylenes require higher curing temperatures than terminal acetylenes. For example, poly(phenylquinoxalines) that have pendant phenylethynyl groups randomly incorporated cure between 430 and 450 °C,[17] while phenylethynylaniline-terminated polyimides were found to cure at 380 °C.[18] Differential scanning calorimetry analysis of the tetra(phenylethynyl) derivative 3 (Figure 5) indicated a small exotherm at 259 °C followed by a large exotherm with a maximum at 390 °C. Again, a multi-step cure was used that ended at 400 °C.

TGA analysis of the cured material (Figure 5) indicated that decomposition began at 490 °C (in air). For comparison, phenylethynyl-containing poly(phenylquinoxalines) exhibited initial weight loss at 460 °C followed by catastrophic weight loss at 600 °C[17] and were stable to ca. 450 and 490 °C in air, respectively. This difference in thermal properties indicates the importance of comparing the mono- and disubstituted alkynes as reactive groups for thermally curable materials and confirms the value of the diphenylacetylene moieties as a functionality that requires higher cure temperatures but gives significantly more stable products.

The FTIR spectra of 3 before and after step-curing are shown in Figure 6. Disubstituted acetylenes are characterized by a very weak IR peak at ca. 2200 cm^{-1}, which is present in 3 (bottom spectrum, Figure 6) at 2214 cm^{-1}. This peak is much stronger in the FT–Raman spectrum of 3 (not shown). The FTIR spectrum of the cured material (top spectrum, Figure 6) is similar to that of the monomer except that the peaks are much broader and the absorbance at 2214 cm^{-1} is absent. This peak is also absent in the FT–Raman spectrum of the fully cured material. Besides the IR resonances associated with an aromatic structure, peaks are present at 2931, 2849, and 1443 cm^{-1} which are characteristic of tetraphenyladamantane.

The products of the thermally induced reaction of phenylethynyls have not been clearly identified yet but are thought to consist of a complex mixture of components.[17] In an attempt to elucidate the structure of the cured material, solid-state ^{13}C NMR was employed. The CP/MAS ^{13}C NMR spectra of 3, in monomeric form and after curing, are shown in Figure 7. For the monomer, the acetylene carbons are present at 89 ppm. After step-curing, the CP/MAS ^{13}C NMR spectrum consists of two broad aromatic resonances at 148 and 127 ppm and broadened adamantane peaks at 47 and 39 ppm. The spectrum obtained from the dipolar dephasing experiment (Figure 8) displayed nonprotonated carbons at 39 (adamantane),

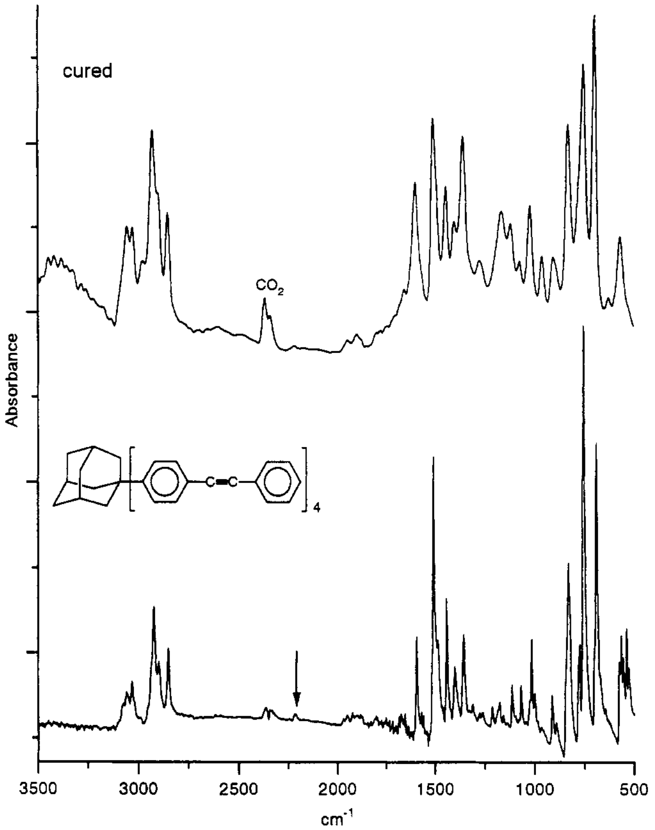


Figure 6. FTIR (KBr) spectrum of 3 before curing (lowest trace) and of 3 after curing (top trace).

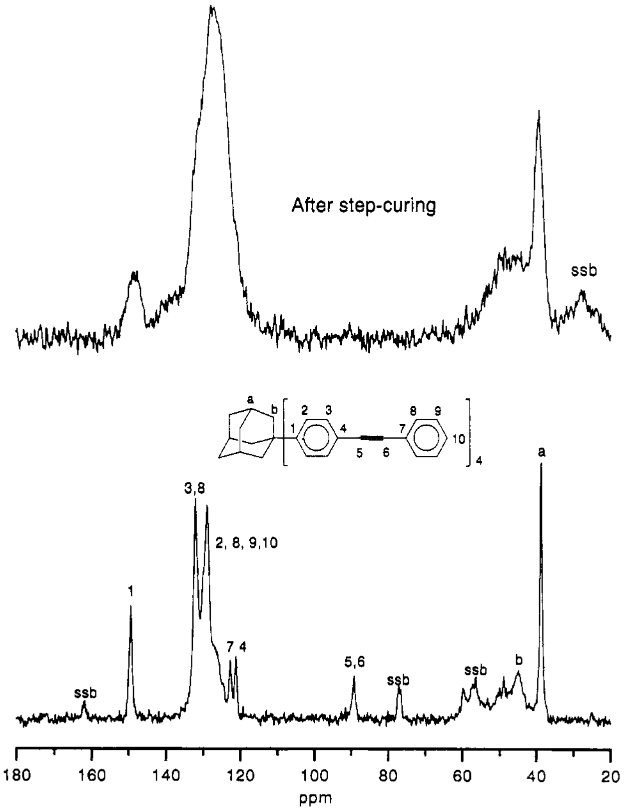


Figure 7. CP/MAS ^{13}C NMR spectra of 3 before curing (bottom trace) and after step-curing (top trace).

148 (phenyl carbon attached to adamantane), and additional overlapping peaks between 125 and 144 ppm (nonprotonated carbons resulting from cure reactions). These data suggest that an all-aromatic and/or extended polyacetylene structure has formed that contains adamantane cores. Further work with model compounds and ^{13}C-labeled models and monomers is needed to elucidate the cure mechanism and final product structures.

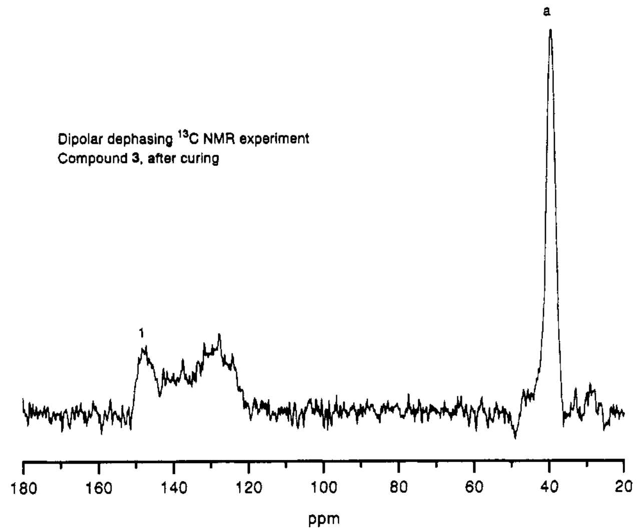


Figure 8. Solid-state ^{13}C NMR dipolar dephasing experiment of cured 3.

Conclusions

Two acetylene derivatives of adamantane were prepared from 1 in good yields, and their cure chemistry was studied. Solid-state ^{13}C NMR and FTIR were used in an attempt to determine the structures of the cured materials, while DSC and TGA were used to study the thermal properties of the fully cured all-hydrocarbon materials. On the basis of CP/MAS ^{13}C NMR spectra and dipolar dephasing experiments, as well as FTIR data, both acetylene derivatives cured to give essentially all-aromatic structures still containing adamantane cores that were stable to ca. 450 and 490 °C in air, respectively. Key findings of this research include the following:

(a) The use of the 1,3,5,7-tetrakis(4-iodophenyl)adamantane core provides a versatile entry to terminally reactive, multifunctional materials.

(b) Higher cure temperatures were needed for the disubstituted than for the monosubstituted acetylene derivatives.

(c) The disubstituted alkynes (diphenyleacetylene-containing) gave more thermally stable products after complete cure. We believe that further extention of these materials through alkyne and aryl coupling reactions can lead to more highly functionalized molecules possessing tetrahedrally arrayed terminal groups capable of similar cure.

Experimental Section

General Procedures. All reactions were performed under nitrogen unless otherwise specified. Solution NMR spectra were collected on a Bruker AC300 spectrometer (300.1 MHz for ^{1}H and 75.469 MHz for ^{13}C solution spectra). Solid-state CP/MAS ^{13}C NMR data were obtained on a Bruker MSL400 spectrometer (100.614 MHz for ^{13}C) using standard pulse sequences and delays. Dipolar dephasing experiments were also run on the Bruker MSL400. All FTIR spectra were obtained on a Perkin-Elmer 1600 spectrophotometer. A DuPont TA 9900 was used to collect DSC and TGA data. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ.

Chemicals. 1,3,5,7-Tetrakis(iodophenyl)adamantane[14] was synthesized through iodination of 1,3,5,7-tetraphenyladamantane. Phenylacetylene, 2-methyl-3-butyn-2-ol, copper iodide, Pd(PPh$_3$)$_2$Cl$_2$, and sodium hydride (dry, 98%) were used as received from Aldrich. Toluene (Fisher) was dried over magnesium sulfate prior to use. Triethylamine (Aldrich) was distilled from sodium hydride prior to use. 1-Methyl-2-pyrrolidinone (NMP), was obtained from Aldrich, distilled from calcium hydride, and stored over molecular sieves before use.

1,3,5,7-Tetrakis(4-ethynylphenyl)adamantane (2) via the Protected Intermediate. A two-neck round-bottom flask was fitted with a reflux condenser, magnetic stirrer, and nitrogen inlet/outlet. Under a nitrogen flush, 1,3,5,7-tetrakis(4-iodophenyl)adamantane (1.0 g, 1.1 mmol), $Pd(PPh_3)_2Cl_2$ (0.02 g, 0.032 mmol), copper(I) iodide (0.01 g, 0.055 mmol), 2-methyl-3-butyn-2-ol (0.71 g, 8.5 mmol), and a solvent mixture consisting of 6.0 mL of NMP and 4.0 mL of triethylamine were added. The yellow reaction mixture was heated, with stirring, at 80 °C under a static nitrogen atmosphere for 6 h. After cooling, the mixture was poured into cold water and the yellow solid isolated via suction filtration. The crude product was recrystallized from ethanol: 0.40 g, 45% yield; DSC data 330.4 °C (endo), 331 °C (exo); IR (KBr) 3378, 2978, 2931, 2848, 2226, 1508, 1443, 1361, 1273, 1161, 1020, 961, 908, 838, 773 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.59 (s, 24H), 2.08 (s, 12H), 7.37 (s, 16H); ^{13}C NMR ($CDCl_3$) δ 31.5, 39.2, 46.8, 65.6, 81.9, 93.6, 120.7, 124.9, 131.7, 149.2. Anal. Calcd for $C_{54}H_{56}O_4$: C, 84.34; H, 7.34; O, 8.32. Found: C, 84.09; H, 7.13.

The protected intermediate (0.40 g, 0.52 mmol) was placed in a one-neck, 50-mL round-bottom flask along with 20 mL of toluene. The mixture was stirred under nitrogen and an excess of sodium hydride was added (ca. 0.25 g, 10 mmol). The reaction mixture was heated at reflux temperatures for 24 h. After cooling, the turbid mixture was poured into a 5% $NaHCO_3$ solution and stirred for 20 min. The layers were separated, and the organic layer was washed with water followed by a saturated NaCl solution. Removal of the toluene under reduced pressure gave 0.27 g (97%) of **2**: DSC 125–220 °C (broad exotherm); FTIR (KBr) 3284, 3083, 2931, 2848, 2108, 1684, 1608, 1508, 1443, 1355, 1261, 832, cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.1 (s, 12H), 3.03 (s, 4H), 7.4 (d, 8H), 7.46 (d, 8H); ^{13}C NMR ($CDCl_3$) δ 39.2, 48.6, 83.5, 120.5, 125.0, 132.2, 149.6.

1,3,5,7-Tetrakis(4-phenylacetylene)adamantane (3). Under a nitrogen purge, 1,3,5,7-tetrakis(4-iodophenyl)adamantane (0.78 g, 0.83 mmol), phenylacetylene (0.69 g, 6.8 mmol), $Pd(PPh_3)_2Cl_2$ (0.017 g, 0.024 mmol), copper(I) iodide (0.008 g, 0.042 mmol), and a solvent mixture consisting of 6 mL of NMP and 4 mL of triethylamine were added to a two-neck round-bottom flask, fitted with a condenser and magnetic stirrer. The mixture was heated at 80 °C under a static nitrogen atmosphere for 8 h. The reaction was cooled and poured into distilled water. A white solid was isolated via suction filtration. Drying gave 0.43 g (61%) of **3**; DSC 259 °C (exotherm), 350–425 °C (broad exotherm); FTIR (KBR) 3025, 2919, 2849, 2214, 1596, 1508, 1443, 1401, 1355, 1114, 1041, 914, 832, 779, 756, 691 cm^{-1}; ^1H NMR (300.1 MHz, $CDCl_3$) δ 2.17 (s, 12H), 7.31 (br s, 16 H), 7.50 (br s, 20 H); CP/MAS ^{13}C NMR δ 38.9, 45.0, 78.0, 89.4, 121.4, 122.8, 129.0, 132.4, 139.5, 149.8.

Thermal Cure Reactions. The tetraacetylene compounds **2** and **3** were sealed under nitrogen in a small thick-walled glass tube which was then cured in an oven in a step-cure process. Compound **2** was heated for 1 h at 200 °C, 1 h at 250 °C, and finally 30 min at 300 °C. Compound **3** required higher cure temperatures for complete reaction and was therefore heated at 300 °C for 30 min, 350 °C for 1 h, and finally 400 °C for 1 h. After curing, tubes were opened and the brittle, brown/orange powders removed and weighed; no apparent weight loss indicates complete conversion.

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