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Thermally Stable Acetylenic Adamantane Polymers

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ABSTRACT: 1,3-Diethynyladamantane (4) was synthesized from adamantane in 67% yield and polymerized thermally at 210 °C or in the presence of catalysts at 160–190 °C. After postcure at 320 °C, the resulting clear thermoset polymer exhibited an onset of major decomposition at 476 °C in air and 475 °C in helium (TGA). The polymer did not show thermal transitions in the DSC between 25 and 450 °C, but exhibited a weak glass transition in DMTA at 260 °C. Soluble oligomers were prepared by either thermal or bis(benzonitrile)palladium chloride catalyzed oligomerization and characterized by thermal analysis and molecular weight determinations. The catalyzed oligomers contained cyclotrimerized acetylene groups, whereas thermal oligomers contained linear polyene structures. 1-Ethynyladamantane (6), which formed no thermal homopolymer, formed copolymers with 4.

Introduction

Adamantane ($C_{10}H_{16}$) is a polycyclic cage hydrocarbon that has been incorporated into polymers, such as polyurethanes and polyacrylates, to increase the thermal stability and glass transition temperatures.[1] The increased stability of these polymers has been attributed to the unique "diamond-like" cage structure of adamantane, which inhibits degradation reactions, such as those resulting from backside attack or elimination.[2-4] The large steric size of the adamantane ring increases the rigidity of the polymer chains, which, in turn, gives high glass transition temperatures.[5]

Thermally and oxidatively stable polymers have been prepared from acetylenic derivatives of poly(phenyl ethers) and -sulfones.[6-8] The acetylenic groups on these monomers react during thermal polymerization without evolution of volatile byproducts to form a void-free thermoset. For certain applications the presence of heteroatoms is undesirable, and hydrocarbon polymers prepared from aliphatic acetylenes would be valuable if thermal stability is not compromised.

Only a few examples of wholly hydrocarbon polymers based on adamantane are known. Polymerization of 1-vinyladamantane with Friedel–Crafts catalysts[1] or the reaction of adamantane with benzene[9] gave only low molecular weight oligomers, whereas, Wurtz-type coupling of dibromoadamantane derivatives gave a crystalline polymer (polyadamantane) that melted above 420 °C.[10,11] The metathesis reaction of 1-ethynyladamantane with molybdenum or tungsten salts gave amorphous, insoluble powders, which decomposed at 200 °C in air and 240 °C in nitrogen.[12] In the absence of the catalyst, 1-ethynyladamantane did not polymerize and could be recovered in a good yield after vacuum pyrolysis at 800 °C.[13] In this paper, we report the synthesis of 1,3-diethynyladamantane[14] (4) and its unexpectedly facile thermal polymerization to give a hydrocarbon polymer with high thermooxidative stability.

Experimental Section

Warning: 1,3-Diethynyladamantane may undergo exothermic decomposition above 200 °C.

Instrumentation and Materials. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Varian T-60 and ^{13}C NMR spectra on a Bruker AC-200 MHz spectrometer. The chemical shifts are reported in ppm downfield from tetramethylsilane. Infrared spectra were recorded in CH_2Cl_2 on a Perkin-Elmer 700 spectrometer. GLC analyses were performed using a Perkin-Elmer 3920 chromatograph with a 4-ft OV-17 column at 150 °C. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on an Omnitherm or Du Pont 990 thermal analyzer system. DSC measurements were made at a heating rate of 10 °C/min in air, whereas TGA measurements were made at a heating rate of 20 °C/min in air or helium at a flow rate 20 mL/min. Dynamic mechanical thermal analysis (DMTA) was conducted at 30 Hz and 10 °C/min on a Polymer Laboratories MkII analyzer, and number-average molecular weights (M_n) were determined in ethyl acetate solution at 37 °C with a Mecrolab Model 301A vapor osmometer. Melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Adamantane was purchased from Dixie Chemical Co., Inc. Catalysts were purchased (Aldrich Chemical Co.) and used as received. Solvents were purified in the usual manner.

Preparation of 1,3-Diethynyladamantane (4). Aluminum chloride (150 g, 1.1 mol) was added in 1–5-g portions over 2 h to a stirred solution of vinyl bromide (900 mL, 12.8 mol) and 1,3-dibromoadamantane[15] (2; 1000 g, 3.4 mol) in CH_2Cl_2 (6 L) at −15 °C. After 0.5 h, water (1 L) was added dropwise at −15 °C, and the mixture was warmed to ambient temperature and poured into 10% aqueous HCl (3 L). The aqueous layer was separated and extracted with CH_2Cl_2 (1.5 L). The combined organic layers were washed with water (2 L), dried ($MgSO_4$), and concentrated to give 1722 g (99%) of 85% pure 1,3-bis(2,2-dibromoethyl)adamantane (3). Chromatography of an aliquot over silica gel (85:15 hexane/CH_2Cl_2), followed by recrystallization from hexane, provided analytically pure 3: mp 55–56.5 °C; IR 2950, 1430, 1340, 1260, 1150 cm^{-1}; ^{1}H NMR δ 5.80 (t, J = 6 Hz, 2 H) 2.56 (d, J = 6 Hz, 4 H), 2.10 (m, 2 H), 1.63 (m, 12 H). Anal. Calcd for $C_{14}H_{20}Br_4$: C, 33.11; H, 3.97; Br, 62.92. Found: C, 33.26; H, 3.97; Br, 62.68.

Solid potassium *tert*-butoxide (1820 g, 16.2 mol) was added to a stirred solution of crude 3 (1720 g, 3.4 mol) in DMSO (6 L) at 50 °C over 1 h. The mixture was stirred at ambient temperature for 20 h, diluted with water (6 L), and extracted with CH_2Cl_2 (2 × 3 L). The combined organic layers were washed with water and brine, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was distilled (85 °C (0.1 Torr)) to give 452 g (72%) of 99% pure 4, mp 43–45 °C. This material was recrystallized from methanol to give 350 g (56%) of analytically pure 4: mp 45–46 °C; purity >99.5% by GLC (R_T 1.47 min); IR 3350, 2950, 2150 cm^{-1}; ^{1}H NMR δ 1.60 (m, 2 H), 1.80 (s, 10 H), 1.95 (s, 2 H), 2.08 (s, 2 H); ^{13}C NMR δ 91.25, 67.27, 46.93, 41.34,

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34.72, 29.27, 27.52. Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 90.96; H, 8.87.

Preparation of 1-Ethynyladamantane (6). Ferric chloride (3 g, 18 mmol) was added to a solution of 1-bromoadamantane (10 g, 46 mmol) in 1:1 hexane/CH_2Cl_2 (30 mL) at -10 °C. Next, a solution of vinyl bromide (8 mL, 113 mmol) in 3:1 hexane/CH_2Cl_2 (20 mL) was added, dropwise, over 30 min at -5 °C. The mixture was stirred for 10 min and quenched into 10% aqueous HCl (100 mL). The aqueous layer was separated and extracted with CH_2Cl_2. The organic extracts were combined and washed with water, dried ($MgSO_4$), filtered, and solvent-stripped under reduced pressure. The residual oil was dissolved in DMSO (100 mL), and potassium *tert*-butoxide (14 g, 125 mmol) was added over 10 min. The mixture was stirred at ambient temperature for 48 h, diluted with 200 mL of water, and extracted with CH_2Cl_2 (2 × 100 mL). The organic extracts were washed with water (2×), dried ($MgSO_4$), evaporated, and distilled (110 °C (0.1 Torr)) to give 6.1 g (83%) of 95% pure 6. This material was recrystallized from hexane to give 4.0 g (54%) of >99.5% pure (GLC) 6: mp 82–83 °C (lit.[16] mp 83 °C); IR 3350, 2950, 2140, 1060, 960 cm^{-1}; ^1H NMR δ 2.0 (s, 1 H), 1.82–1.67 (m, 15 H); ^{13}C NMR δ 92.76, 66.54, 42.66, 36.21, 29.25, 27.82.

Polymerization. Samples of 4 (1–5 g) were sealed in glass tubes and heated at 210 °C without catalysts or at 180 °C with catalysts until gelation occurred (24–50 h). The gelled samples were then step-cured to 320 °C over 16–24 h in increments of 10–25 °C to give clear, light brown polymeric rods.

Thermal Oligomerization of 1,3-Diethynyladamantane. Neat 4 (60 g, 0.3 mol) was placed in a 250-mL round-bottomed flask and heated without stirring at 210 °C for 48 h. The mixture was cooled to room temperature, transferred to a mortar, and crushed to give 60 g (100%) of a yellow powder: mp 35–40 °C; M_n = 600. Unreacted monomer (45%) was removed by bulb-to-bulb distillation (120 °C (0.5 Torr)) and the residue was extracted with hexane (1 L) for 16 h. The insoluble solid was filtered, washed with hexane, and dried under reduced pressure to give 12 g (20%) of oligomeric 4: mp >250 °C; M_n = 1200; IR 3350, 3050, 2950, 2150, 1200, 1080 cm^{1-}; ^1H NMR δ 5.1 (m), 1.0–2.3 (m).

Bis(benzonitrile)palladium Chloride Catalyzed Oligomerization of 1,3-Diethynyladamantane. A solution of 4 (2 g, 11 mmol) and bis(benzonitrile)palladium chloride (150 mg, 0.4 mmol, 3.6 mol %) in CH_2Cl_2 (10 mL) was stirred at room temperature for 16 h. The mixture was diluted with CH_2Cl_2 (10 mL) and hexane (35 mL), and the precipitated catalyst was removed by filtration. The filtrate was concentrated under reduced pressure, and the residual oil was triturated with hexane (100 mL). The hexane-insoluble solid was filtered, washed with hexane (50 mL), and dried under reduced pressure to give 0.40 g (20%) of oligomeric 4: mp 235 °C (softens); M_n = 1160; IR 3350, 3100, 2975, 2150, 1600, 1200, 1080, 920 cm^{-1}; ^1H NMR δ 7.2 (m), 2.0 (br m).

Results and Discussion

Synthesis. Monomers 4 and 6 were prepared in three steps from adamantane (1). Bromination of adamantane with neat bromine at reflux gave 1-bromoadamantane (5) in 89% yield, whereas, iron-catalyzed bromination of adamantane with bromine in Freon 113[15] gave 1,3-dibromoadamantane (2) in 93% yield. Reaction of 1,3-dibromoadamantane (2) with vinyl bromide in the presence of a Friedel–Crafts catalyst gave 1,3-bis(2,2-dibromoethyl)adamantane (3), which, in turn, was dehydrohalogenated with potassium *tert*-butoxide in DMSO to give 4 in 72% yield. Similarly, 1-ethynyladamantane (6) was prepared in 83% yield from 1-bromoadamantane (5). The monomers were purified by distillation followed by recrystallization. In the synthesis of 1-ethynyladamantane (6) from 1-bromoadamantane, substantial amounts of adamantane, 4, and 1,3,5-triethynyladamantane were formed when the reaction temperature, type of solvent, and catalyst concentrations were not controlled. 1-Bromoadamantane has been reported to disproportionate in the presence of Lewis acids and, when reacted with vinyl bromide and catalytic aluminum bromide, gives, after dehydrohalogenation, a low yield of 1,3-diethynyladamantane.[14]

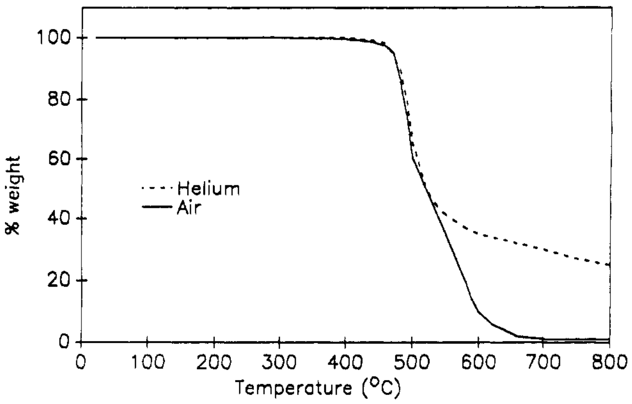
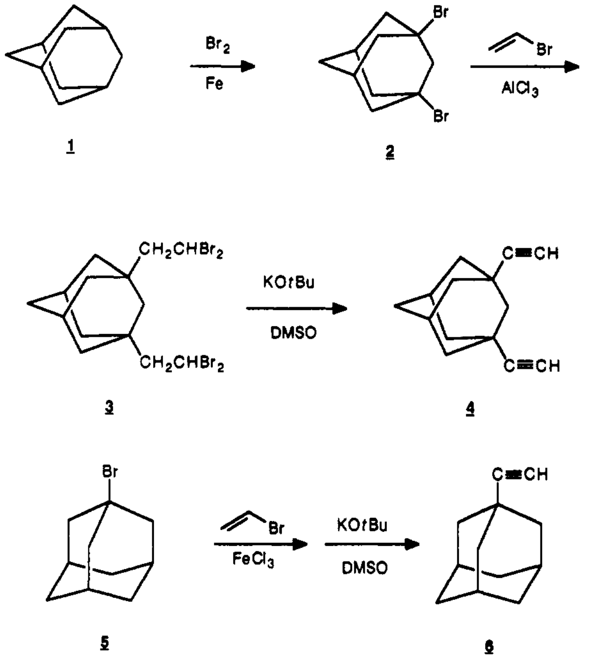


Figure 1. TGA of poly(1,3-diethynyladamantane).



(1)

In contrast to adamantane[17] and most disubstituted adamantane derivatives, 4 is a relatively low melting solid (mp 46 °C). When heated at temperatures above 200 °C, 4 was converted to a clear, brown, void-free polymeric resin; at 210 °C gelation occurred in 24–50 h. Freshly gelled samples, containing 40–45% unreacted monomer, were step-cured by incremental temperature increases to 320 °C. Samples heated at 250 °C for several days were incompletely cured, as indicated by DSC exotherms above 300 °C. When samples that were heated above 320 °C were cooled and rescanned, no DSC transitions were observed. The fully cured sample exhibited an onset of major degradation (TGA) at 476 °C in air and 475 °C in helium (TGA) (Figure 1). Isothermal aging studies were conducted on 10–15-mg pieces of the polymer in air. At 315 °C, the adamantane-containing polymer lost 8% of its weight after 100 h and was more stable than the polymer prepared from the aromatic diacetylene 4,4′-bis(3-ethynylphenoxy)diphenyl sulfone (*m*-ATS), which lost 12% of its weight after a simlar period.[8] Weight losses of 5% and 20% were observed for the adamantane polymer at 301 and 325 °C after 100 h in air (Figure 2).

Although no thermal transitions were observed in the DSC between 25 and 450 °C (Figure 3), poly(1,3-diethy-

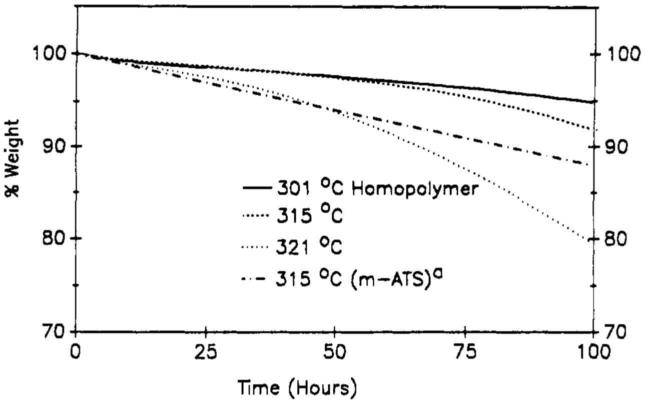


Figure 2. Isothermal aging in air of poly(1,3-diethynyladamantane) and *m*-ATS.

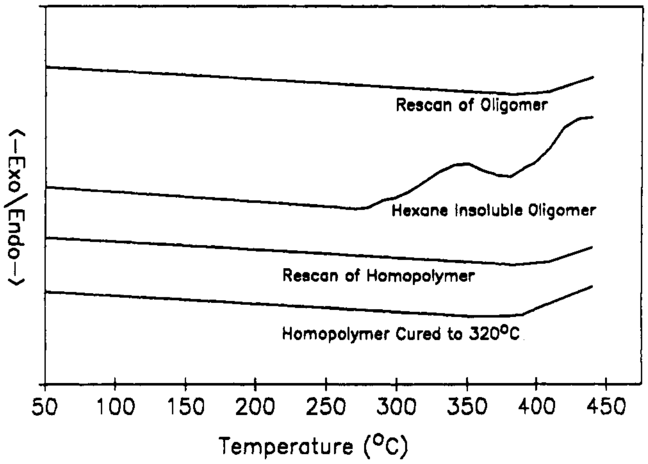


Figure 3. DSC of poly(1,3-diethynyladamantane) and M_n = 1200 oligomer.

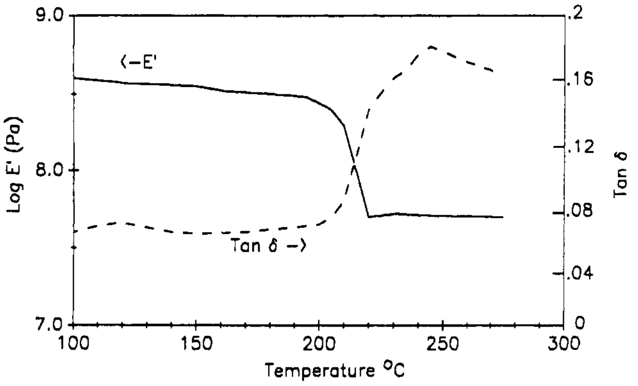


Figure 4. DMTA of poly(1,3-diethynyladamantane).

nyladamantane) exhibited a glass transition temperature near 260 °C in DMTA (Figure 4). The density of the polymer was 1.08 g/cm^3, similar to that of the parent hydrocarbon, adamantane (1.09 g/cm^3). The relatively high density of the polymer, as compared to conventional aliphatic hydrocarbon polymers ($d < 1.0$ g/cm^3), suggests that the adamantane ring remained intact during polymerization. The polymer showed no measurable weight gain in water or 10% aqueous HCl at room temperature over several weeks. The equilibrium weight gain in water at 71 °C after 30 days was 0.7%. The polymer was insoluble in organic solvents, such as hexane and ethanol, but was swelled slightly by ethyl acetate and showed an equilibrium weight gain of 1.4% in DMF and 0.5% in DMSO at 20 °C.

Table I
Thermal Properties of Ethynyladamantane Polymers

reactant	catalyst	step start, °C	cure end, °C	Tpoly[a] first scan onset	Tpoly[a] first scan max	onset of major dec air	onset of major dec helium
4	none	210	320	none	none	476	475
4[b]	none	210	210	160	380	283 476	
4	AIBN	100	250	264	353 405	389	484
4	*c*	175	200	243	417 466	433	471
4	*d*	155	250	280	345	478	473
50% 4 50% Olig[e]	*d*	160	230	280	345 423	478	473
50% 4 50% Olig[e]	*f*	160	230	266	339 410	474	473
60% 4 40% 6	none	210	275	343	430	445	453
70% 4 30% 6	none	210	250	260		424	469
77% 4[b] 23% 6	none	210	210	180	350 447	457	454

[a] All samples showed no thermal transition upon rescan from 25 to 450 °C. [b] Hexane-insoluble oligomer, 24-h cure. [c] $Ni(PhCN)_2(CO)_2$ (0.1%). [d] $Pd(PhCN)_2Cl_2$ (3.6%). [e] Oligomer prepared with palladium catalyst and redissolved in 4. [f] Pd/C.

Table II
Thermal Oligomerization of 1,3-Diethynyladamantane

temp, °C	time, h	M_n[a]	conversn, wt %[a]	mp, °C
201	44	968	7	128–158
201	52	643	14	126–134
201	68	532	22	127–137
201	76	663	27	146–162
205	32	405	5	130–150
205	48	664	9	124–140
205	52	486	15	124–135
205	72	860	54	189–210[b]
210	17	603	20	130–140
210	20	649	36	134–139
210	23	700	21	150–156
210	26	629	51	151–158[b]

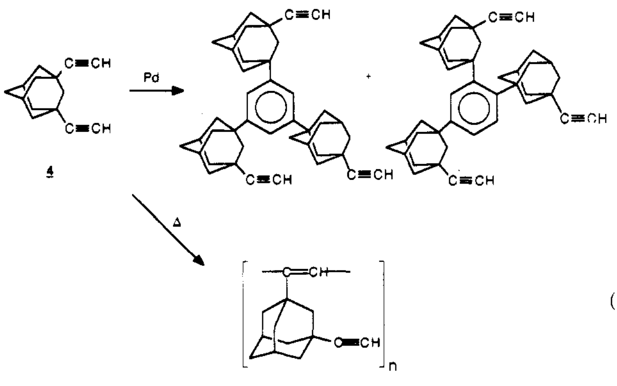
[a] Average of three samples. [b] Sample reached gel point.

The temperature required to initiate polymerization of 4 was lowered to below 200 °C by the use of certain catalysts (Table I). Azobis(isobutyronitrile) (AIBN) and benzoyl peroxide lowered the onset of polymerization to 185 °C. Nickel(II) acetylacetonate, at a concentration of 50 ppm, caused 4 to undergo a violent, exothermic decomposition at 160 °C. Cobalt(II) and chromium(III) acetylacetonates did not catalyze the polymerization, but 0.14% molybdenyl(VI) acetylacetone lowered the cure temperature to 170 °C. Bis(benzonitrile)nickel dicarbonyl and bis(benzonitrile)palladium(II) chloride at 0.1% concentrations lowered the polymerization temperature to 180 °C. At 210 °C, copper metal caused darkening of the monomer but did not increase the rate of polymerization, whereas at 210 °C iron metal caused gelation. No effects were observed at 210 °C with nickel, aluminum, Monel, or 304 stainless steel. The thermal polymerization of 4 was also accelerated by the presence of air, since samples cured in containers pressurized with nitrogen showed no reaction below 230 °C.

Oligomer Formation. Thermal polymerization of 4 appears to proceed through formation of a complex mixture of oligomers. Thermal oligomers of 4 were prepared by heating the monomer in a glass container at varying reaction times and temperatures (Table II). Unreacted monomer was removed by distillation and the residue was characterized by melting point and number-average molecular weight (M_n) determination. The data indicate that although the rate of oligomerization is much faster at higher temperatures, the number-average molecular weight of the oligomers is not changed significantly.

The residue obtained after the distillation of unreacted monomer was extracted with hexane to give a methylene chloride soluble, hexane-isoluble material with a melting point in excess of 250 °C and $M_n = 1200$. Reverse-phase HPLC showed that the material consisted of a broad spectrum of oligomers with number-average molecular weights ranging from 184 to 10 000 (detection limit of the column). The IR and ^1H and ^{13}C NMR spectra of the hexane-insoluble material were consistent with a polyene structure containing acetylenic and vinyl groups but no aromatic groups. The signals corresponding to the adamantane ring carbons in the ^{13}C NMR spectrum of the oligomers had similar chemical shifts but were more complex than those of the monomer, indicating that the adamantane ring remained intact (Figure 5). These data suggest that the thermal oligomerization proceeds by the reaction of acetylene groups to form a linear polyene structure containing adamantane rings with terminal acetylene groups and are consistent with the mechanism reported for the polymerization of aromatic acetylenes.[18-20]

Diacetylene 4 could also be oligomerized in methylene chloride at room temperature with 3.6 mol % bis(benzonitrile)palladium chloride or in refluxing THF with palladium on carbon or palladium(II) chloride and trimethylsilyl chloride, to give hexane-insoluble, methylene chloride soluble oligomers in 20% yield. The hexane-insoluble material softened at 235 °C and had $M_n = 1160$. The material was a complex mixture (TLC) similar to the thermal oligomers, except that the ^1H NMR spectrum of the palladium-catalyzed material exhibited an absorbance at δ 7.2 corresponding to aromatic protons; vinyl protons were not detected. The presence of free acetylenic groups in the hexane-insoluble material was indicated by IR absorbances at 3350 and 2150 cm^{-1}. The palladium-catalyzed oligomerization may proceed through the cyclotrimerization of acetylene groups to give benzene rings that are substituted with acetylene-terminated adamantanes. This result is consistent with the known tendency for this catalyst to cyclotrimerize acetylene groups to aromatic rings.[21,22]



(2)

The oligomers obtained from palladium-catalyzed reactions did not melt in a range useful for melt processing, but were soluble in toluene and could be solvent-cast into films. In addition, the hexane-insoluble oligomers (5–50% by weight) could be dissolved in 1,3-diethynyladamantane (4) to form mixtures that could be cured in open tubes or molds at 160–200 °C to gelation without a significant loss of the monomer. The gelled material, in turn, could be step-cured to 320 °C to give polymers that were indistinguishable by TGA and DSC from the polymers obtained by thermal polymerization of 4.

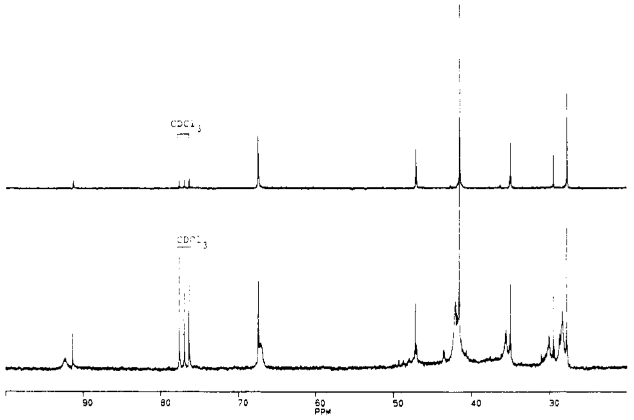


Figure 5. ^{13}C NMR spectra of 1,3-diethynyladamantane (top) and $M_n = 1200$ oligomer (bottom) in $CDCl_3$.

Table III
Oligomers of Mono- and Diethynyladamantane[a]

wt % of 6 at start	wt % of 6 in distillate	% conversn to oligomer	M_n (oligomer)	oligomer mp, °C
9.0	12.8	19	533	124–140
17.0	16.4	16	482	121–146
23.0	21.6	21	468	124–143
29.0	29.1	6	461	90–120
0.0	0.0	45	629	130–150

[a] Mixtures were heated at 210 °C for 24 h.

Copolymers. 1-Ethynyladamantane (6) remained unchanged after it was heated at 250 °C for 24 h, and it was partially decomposed after several days of heating above 300 °C. Although 6 did not form a homopolymer, it did copolymerize with the diacetylene 4. Copolymers (5 mm × 80 mm rods), containing 10–47% weight of 6, were prepared by step-curing mixtures of 4 and 6 to 320 °C. Complete incorporation of 6 into the copolymer was observed when less than 50% by weight of 6 was used. However, at concentrations exceeding 50% by weight of 6, incorporation of 6 into the polymer matrix was not observed and unreacted monomer (6) was recovered. It is not known why the monoacetylene does not form a homopolymer but readily forms copolymers.[23]

Cooligomers were prepared by heating mixtures of monomers 4 and 6 at 210 °C for 24 h. (Table III). The unreacted monomers were removed by distillation, and the ratio of 4 and 6 in the distillate was determined by quantitative GLC. The rate of cooligomerization was slower than that observed for the homooligomerization of 4, but the incorporation of the monoacetylene into the oligomer corresponded to the starting monomer ratio.

Homopolymer rods of 4 (5 mm × 50 mm) exhibited a linear thermal expansion of 2% over the range of 20–250 °C. By comparison, copolymer rods (containing 23% 6) expanded less than 1% from 20 to 100 °C and then showed no further expansion to 250 °C.

Conclusion. Hydrocarbon polymers that were comparable in thermooxidative stabilities to polymers derived from acetylene-terminated aromatic compounds were prepared by thermal polymerization of acetylenic adamantane derivatives. These materials show good moisture resistance, and since they can be prepared free of metals and heteroatoms, they hold promise for advanced applications, such as polymeric dielectric materials.

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(23) The failure of **6** to polymerize is underlined by the fact that 3,3′-diethynyl-1,1′-biadamantane, which also contains only one acetylenic group per adamantane ring, forms a thermally catalyzed homopolymer. The properties of this and other alkyl- and aryl-substituted ethynyladamantane derivatives will be published later.

Registry No. **2**, 876-53-9; **3**, 106325-31-9; **4**, 106325-28-4; **4** (homopolymer), 124767-93-7; (**4**)(**6**) (copolymer), 124848-32-4; **5**, 768-90-1; **6**, 40430-66-8; AIBN, 78-67-1; $H_2C{=}CHBr$, 593-60-2; $Ni(PhCN)_2(CO)_2$, 97376-82-4; $Pd(PhCN)_2Cl_2$, 14220-64-5; Pd, 7440-05-3; nickel(II) acetylacetonate, 3264-82-2; molybdenyl(VI)-acetylacetone, 17524-05-9.