Macromolecules 1991, 24, 5266-5268

New High-Temperature Polymers Based on Diamantane

A. A. Malik,* T. G. Archibald, and K. Baum

Fluorochem, Inc., 680 South Ayon Avenue, Azusa, California 91702

M. R. Unroe

Wright Laboratories, WRDC/MLBP, Air Force Materials Laboratory,
Wright-Patterson AFB, Ohio 45433-6533

Received January 9, 1991; Revised Manuscript Received April 10, 1991

ABSTRACT: 1,4-, 4,9-, and 1,6-diethynyldiamantanes (**3a–c**) were prepared from diamantane and polymerized at 250–275 °C to give clear thermoset resins that showed onsets of degradation between 518 and 525 °C in air or helium (TGA). Nickel(II) acetylacetonate or tetrakis(triphenylphosphine)palladium catalysts lowered the polymerization temperature to 210 °C. A copolymer prepared from a mixture of **3a** (35%), **3b** (58%), and **3c** (7%) exhibited onset of major degradation at 476 °C in air.

Introduction

Recently, we reported the first example of polymerization of an acetylene-terminated cage hydrocarbon, 1,3-diethynyladamantane. The polymer was a thermoset resin that was stable to 475 °C in air and exhibited less than 5% weight loss in air after 100 h at 301 °C.[1] This unusually high thermal stability for an aliphatic hydrocarbon polymer presumably results from the presence of adamantane units in the polymer backbone, which due to their "diamond-like" structure retard degradation reactions resulting from either nucleophilic or electrophilic attack, or from elimination reactions.[2,3] Although 1,3-diethynyladamantane gives a polymer with good thermal and thermooxidative stability, the high content of acetylenic groups in the monomer results in an exothermic polymerization and a high cross-link density.

Diamantane is a cycloaliphatic cage hydrocarbon ($C_{14}H_{20}$) containing an "extended cage" adamantane structure.[2,4-6] We postulated that replacement of adamantane units in poly(1,3-diethynyladamantane) with an extended cage diamantane unit would reduce the acetylenic content of the monomer and give a polymer with a lower cross-link density without compromising thermal stability. Although diamantane has been of interest to synthetic chemists for many years,[7-10] its use in polymers has not been reported. In this paper we report the synthesis of acetylenic derivatives of diamantane and their thermal polymerization to give materials with thermooxidative stabilities significantly greater than those of the corresponding adamantane polymers.

Experimental Section

Instrumentation and Materials. ^{13}C and ^{1}H NMR spectra were recorded in $CDCl_3$ with a Bruker, AC-200 FT NMR spectrometer and the chemical shifts are reported in ppm downfield from tetramethylsilane. IR spectra were recorded in CH_2Cl_2 by use of a Perkin-Elmer Model 700 spectrometer. Thermal analyses (DSC and TGA) were performed on an Omnitherm or a 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 of 20 mL/min. GLC analyses were conducted using a Shimadzu Model GC-14A chromatograph employing a 30-m SE-30 column. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Diamantane was prepared by a literature procedure from norbornadiene in three steps.[11,12] Aluminum bromide, purchased from Alfa, and vinyl bromide, potassium *tert*-butoxide, and DMSO, purchased from Aldrich, were used as received.

$AlBr_3$-Catalyzed Bromination of Diamantane. The procedure for the synthesis of dibromodiamantanes, by Vodicka et al.,[10] was modified as follows. Diamantane (50 g, 266 mmol) was added over 1 h to stirred liquid bromine (200 mL) at 0 °C. Next, aluminum bromide (5.4 g, 20 mmol) was added and the mixture was stirred at 0 °C for 3 h and at ambient temperature for 16 h. Bromine was removed under reduced pressure and the residue was dissolved in CH_2Cl_2. The solution was washed with 10% aqueous Na_2SO_3 solution, water, and brine, dried ($MgSO_4$), and stripped of solvent under reduced pressure. The residue was triturated with pentane, filtered, and dried to give 67 g (73%) of a mixture of dibromodiamantanes, which contained (by GLC analysis) 33% 1,4-dibromodiamantane (**1a**), 57% 4,9-dibromodiamantane (**1b**), and 10% 1,6-dibromodiamantane (**1c**).

Synthesis of 1,4-, 1,6-, and 4,9-Diethynyldiamantanes. Aluminum bromide (0.6 g, 2.2 mmol) was added, portionwise, to a solution of a mixture of dibromodiamantanes **1a–c** (2.0 g, 5.8 mmol) in vinyl bromide (25 mL) at −30 °C. The mixture was stirred at −30 °C for 1 h, diluted with CH_2Cl_2, and slowly added to 2% aqueous HCl (200 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3×). The combined organic layers were washed with 2% aqueous HCl, water, and brine, dried ($MgSO_4$), filtered, and stripped of solvent under reduced pressure to give 3.3 g of a colorless oil. The oil was dissolved in DMSO (25 mL) and potassium *tert*-butoxide (3.1 g, 28 mmol) was added. The resulting mixture was stirred at room temperature for 3 days, diluted with CH_2Cl_2, and slowly added to an ice/water mixture. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water (5×) and brine, dried ($MgSO_4$), filtered, and stripped of solvent under reduced pressure to give a brown semisolid residue. The residue was chromatographed over silica gel (90% hexane/CH_2Cl_2) to give, in order of elution, 500 mg (37%) of 4,9-diethynyldiamantane, 45 mg (3%) of 1,6-diethynyldiamantane, and 350 mg (26%) of 1,4-diethynyldiamantane.

4,9-Diethynyldiamantane (3b): IR ($CDCl_3$) 3350, 2950, 2150, 1400, 1360 cm^{-1}; ^{1}H NMR δ 2.03 (s, 2 H), 1.80 (s, 12 H), 1.71 (s, 6 H). Anal. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.60; H, 8.50.

1,6-Diethynyldiamantane (3c): IR 3350, 2975, 2150, 1360 cm^{-1}; ^{1}H NMR δ 2.25 (s, 4 H), 2.19 (s, 2 H), 1.85 (br s, 12 H), 1.55 (s, 2 H). Anal. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.79; H, 8.44.

1,4-Diethynyldiamantane (3a): IR 3350, 2950, 2150, 1450, 1260 cm^{-1}; ^{1}H NMR δ 2.43 (br s, 1 H), 2.30 (br s, 1 H), 2.13 (s, 1 H), 2.03 (s, 2 H), 1.92 (br s, 2 H), 1.79 (m, 13 H). Anal. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.65; H, 8.39.

Polymerization of 4,9-Diethynyldiamantane: Typical Procedure. A sample of 4,9-diethynyldiamantane (275 mg) was sealed in a glass tube and heated at 220 °C for 6 h, 230 °C for 4 h, 240 °C for 2 h, 250 °C for 6 h, and 275 °C for 16 h to give

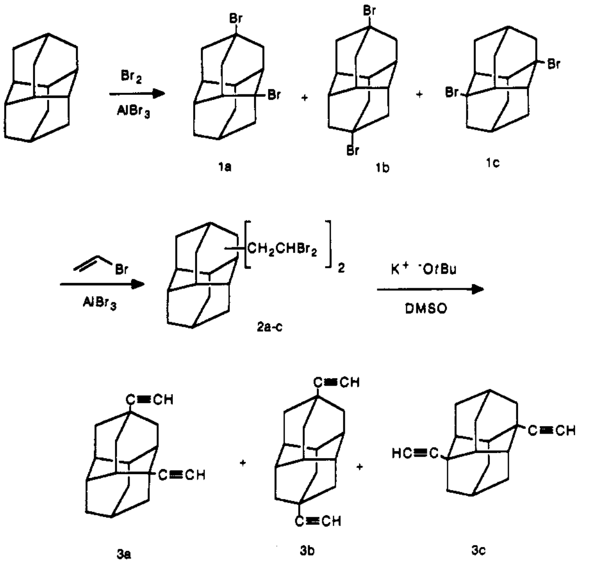
Table I
^{13}C NMR and Melting Point Data of Diethynyldiamantanes

compound	mp, °C	^{13}C NMR, ppm: C≡CH	^{13}C NMR, ppm: ring carbons
1,4-diethynyldiamantane (**3a**)	88	92.1, 69.7, 90.7, 67.1	43.7, 43.4, 40.6, 39.9, 37.1, 37.1, 36.4, 35.6, 35.2, 26.3
4,9-diethynyldiamantane (**3b**)	196	92.2, 67.1	42.9, 36.0, 27.4
1,6-diethynyldiamantane (**3c**)	176	90.8, 69.6	44.1, 40.3, 35.5, 33.8, 25.9

a transparent, light brown polymeric rod. The polymer was postcured in air at 300 °C for 16 h.

Results and Discussion

Monomer Synthesis. Diethynyldiamantanes were prepared from diamantane in three steps. Diamantane was reacted with bromine in the presence of aluminum bromide at 0 °C to give a mixture of 33% 1,4-dibromodiamantane (**1a**), 57% 4,9-dibromodiamantane (**1b**), and 10% 1,6-dibromodiamantane (**1c**) in 73% yield.[10] The mixed dibromodiamantanes **1a–c** were reacted with vinyl bromide and catalytic aluminum bromide to give the corresponding bis(2,2-dibromoethyl) adducts **2a–c** in a quantitative yield. High dilution and low temperatures (−30 °C) in the alkylation reaction were used to suppress the disproportionation/isomerization of dibromodiamantanes.[10] The bis(2,2-dibromoethyl) compounds **2a–c** were dehydrohalogenated with potassium *tert*-butoxide in DMSO to give a mixture of isomeric diethynyldiamantanes **3a–c** in 66% yield. This mixture contained 1,4-diethynyldiamantane (**3a**; 39%), 4,9-diethynyldiamantane (**3b**; 56%), and 1,6-diethynyldiamantane (**3c**; 5%) and was separated by column chromatography. The melting point and ^{13}C NMR data of the diethynyldiamantanes are presented in Table I. The number of differentiated ethynyl groups and ring carbons in ^{13}C NMR is consistent with the symmetry properties of each isomer. The high symmetry of 4,9-diethynyldiamantane (**3b**) is reflected by its relatively high melting point and the presence of three ring carbon signals in the ^{13}C NMR.



(1)

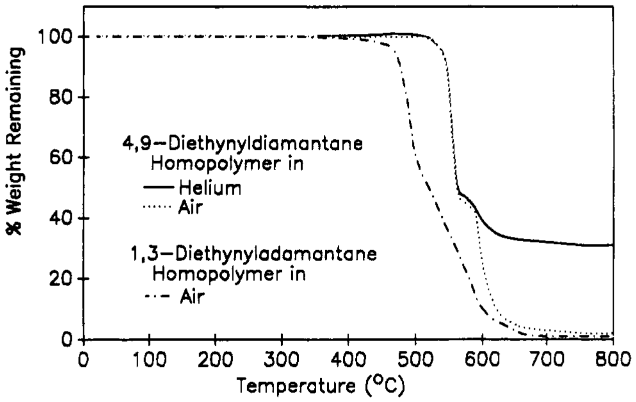


Figure 1. TGA of poly(4,9-diethynyldiamantane).

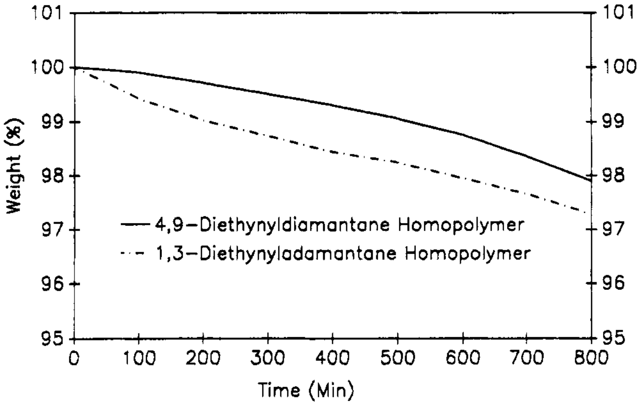


Figure 2. Isothermal aging of poly(4,9-diethynyldiamantane) and poly(1,3-diethynyladamantane).

Polymer Synthesis and Characterization. The melting points of pure diethynyldiamantanes **3a–c** (Table I) are lower than the onsets of their thermal polymerization (250 °C), and thus, samples of **3a**, **3b**, or **3c** could be thermally polymerized as melts at 250–275 °C to give transparent, light brown, voidless polymers. Polymers that were heated at 275 °C for several days were incompletely cured, as indicated by DSC analysis. Samples that were postcured at 300 °C for 16 h, however, did not exhibit any detectable DSC transitions between 25 and 450 °C. The fully cured samples exhibited onsets of major degradation (TGA) between 522 and 526 °C in air and 518 and 522 °C in helium. A typical thermogravimetric trace is shown in Figure 1. Comparable values for the adamantane-based polymers were 475–476 °C for the onset of major decomposition in air or helium.[1] The diamantane polymers underwent a continuous weight loss above 525 °C, with residues at 750 °C ranging from 1.1 to 2.4% in air and 16 to 57% in helium, respectively. An isothermal aging study, conducted on a 20-mg sample of the polymer derived from 4,9-diethynyldiamantane, exhibited a 2.1% weight loss at 325 °C after 800 min in air (Figure 2). Under similar conditions, a fully cured sample of poly(1,3-diethynyladamantane) lost 2.7% of its weight (Figure 2). The polymers were insoluble in common organic solvents, such as dichloromethane, acetone, and hexane, and showed no measureable weight gain in water at room temperature. However, in boiling water the polymers gained between 0.2 and 0.3% by weight after 24 h. The low moisture uptake of these materials is noteworthy and reflects the wholly hydrocarbon nature of these polymers.

In the presence of nickel acetylacetonate or tetrakis(triphenylphosphine)palladium catalyst, polymerization occurred below 210 °C. In contrast to the clear polymers obtained from thermal polymerization, materials obtained from the metal-catalyzed polymerizations were opaque

Table II
Thermogravimetric Analysis of Poly(diethynyldiamantanes)

polymer	onset, °C		wt residue (750 °C), %	
	air	helium	air	helium
1,4-	524	519	2.4	57
4,9-	526	518	1.1	34
1,6-	522	522	1.2	16
copolymer[a]	476		1.2	

[a] Copolymer of 35% 1,4-diethynyldiamantane, 56% 4,9-diethynyldiamantane, and 9% 1,6-diethynyldiamantane.

with a dark metallic luster. Thermal properties (DSC and TGA) of these polymers, however, were similar to those of uncatalyzed polymers.

A copolymer of **3a** (35%), **3b** (58%), and **3c** (7%) was prepared by stage-heating a mixture of diethynyldiamantanes **3a–c** in a sealed tube to 275 °C and then postcuring the copolymer in air at 300 °C for 16 h. The copolymer was similar in appearance to the uncatalyzed homopolymers, and like the homopolymers did not exhibit any DSC transitions between 25 and 450 °C and was insoluble in common organic solvents. The thermal stability of the copolymer, however, was lower than that of the homopolymer, with the onset of major degradation (TGA) at 476 °C in air.

Conclusion

We have demonstrated that acetylene groups on highly hindered cage compounds, such as adamantane and diamantane, can be polymerized thermally to give thermoset polymers. The presence of diamantyl groups enhances the thermal stability of the resulting thermoset resins by nearly 50 °C (TGA) over the corresponding adamantane-based polymers. Further studies are under way to determine the source of this increased stability and on the synthesis of other diamantane-based polymers.

Acknowledgment. This work was performed under Contract F33615-86-C-5154, which was funded by the Air Force Materials Laboratory, Wright Laboratories, Wright-Patterson AFB, OH 45433-6533. We thank Mr. Francis Bonsu and Mr. Thomas Roberts for assistance with the synthesis work.

References and Notes

(1) Archibald, T. G.; Malik, A. A.; Baum, K.; Unroe, M. R. *Macromolecules*, preceding article in this issue.
(2) Olah, G. A.; Prakash, G. K. S.; Shih, J. G.; Krishnamurthy, V. V.; Mateescu, G. D.; Liang, G.; Sipos, G.; Buss, V.; Gund, T. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1985**, *107*, 2764.
(3) Fort, R. C., Jr.; Schleyer, P. v. R. *Chem. Rev.* **1964**, *64*, 277. Moon, S.; Schwartz, A. L.; Hecht, J. K. *J. Polym. Sci., Part A1* **1970**, *8*, 3665.
(4) Diamantane is correctly named decahydro-3,5,1,7-[1,2,3,4]butanetetraylnaphthalene.
(5) Fort, R. C., Jr. *Adamantane. The Chemistry of Diamond Molecules*; Marcel Dekker: New York, 1976.
(6) Vogl, O.; Anderson, B. C.; Simons, D. M. *Tetrahedron Lett.* **1966**, 415.
(7) Gund, T. M.; Osawa, E.; Williams, V. Z.; Schleyer, P. v. R. *J. Org. Chem.* **1974**, *39*, 2979.
(8) Gund, T. M.; Schleyer, P. v. R.; Unruh, G. D.; Gleicher, G. J. *J. Org. Chem.* **1974**, *39*, 2995.
(9) Gund, T. M.; Nomura, M.; Schleyer, P. v. R. *J. Org. Chem.* **1974**, *39*, 2987.
(10) Vodicka, L.; Janku, J.; Burkhard, J. *Collect. Czech. Chem. Commun.* **1983**, *48*, 1162.
(11) Gund, T. M.; Williams, V. Z., Jr.; Osawa, E.; Schleyer, P. v. R. *Tetrahedron Lett.* **1970**, 3877.
(12) Gund, T. M.; Thielecke, W.; Schleyer, P. v. R. *Org. Synth.* **1973**, *53*, 30.

Registry No. **1a**, 32401-09-5; **1b**, 30651-02-6; **1c**, 32401-10-8; **3a**, 134334-28-4; **3a** (homopolymer), 134334-29-5; **3b**, 134334-26-2; **3b** (homopolymer), 134334-31-9; **3c**, 134334-27-3; **3c** (homopolymer), 134334-30-8; (**3a**)(**3b**)(**3c**) (copolymer), 134334-32-0; $H_2C{=}CHBr$, 593-60-2; diamantane, 2292-79-7; nickel acetylacetonate, 3264-82-2; tetrakis(triphenylphosphine)palladium, 14221-01-3.