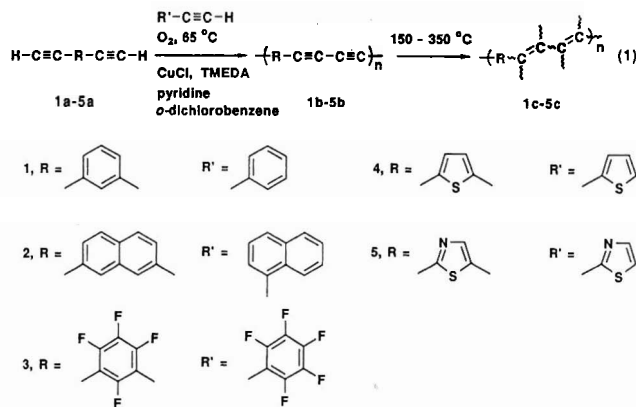


Hypercross-Linked Organic Solids: Preparation from Poly(aromatic diacetylenes) and Preliminary Measurements of Their Young's Modulus, Hardness, and Thermal Stability

We are engaged in a program intended to establish relationships between the microscopic structure of highly cross-linked organic solids and the Young's modulus, thermal stability, and hardness of these solids. This program was stimulated by an interest in the physical properties of diamond.¹ Diamond is the hardest substance known, is the best thermal conductor, and has the highest known Young's modulus. These properties undoubtedly reflect, in some way, the high volume density of strong, directional carbon-carbon bonds that characterize the structure of diamond. Our objective is to prepare organic solids with a high and controllable density of carbon-carbon bonds, to characterize the bonding in these solids, to establish their physical and materials properties (especially Young's modulus, thermal stability, and hardness), and to correlate their microscopic structures with these macroscopic properties.

Our approach has been to prepare organic oligomers containing a high proportion of acetylenic groups capable of forming carbon-carbon bonds, to mold these oligomers into macroscopic objects, and to cause the cross-linking

reaction to occur in the solid state (eq 1). It was our



hypothesis that a high ratio of carbon to hydrogen in these oligomers and, thus, a high density of carbon-carbon bonds in the solids derived from them, would result in a high modulus and thermal stability. This paper summarizes the preparation of polymers from five aromatic diacetylenes (1a-5a)² and the conversion of these polymers to highly cross-linked solids (1c-5c). These structures were chosen to survey the response of the physical properties of the final cross-linked solid to variation in the structure

Table I
Density (ρ), Young's Modulus (E), Shear Modulus (S), Poisson's Ratio (ν), and Electrical Contact Resistance Measurement of Vickers Hardness (H_{VR})

sample	ρ , g/cm ³	E , ^a MN/m ²	S , MN/m ²	ν	H_{VR} ^b			E/H_{VR} ($L = 1.0$ kg)
					$L = 0.5$ kg (MN/m ²)	$L = 1.0$ kg (MN/m ²)	$L = 2.0$ kg (MN/m ²)	
1c	1.60	24 800	9640	0.286	11000	14000	7400	1.8
2c	1.61	25 700	10000	0.241	10000	12000	5900	2.6
3c	1.66	10 000	3850	0.306	5900	4100	2400	2.4
4c	1.34	24 000	9410	0.277	31000	12000	6100	2.0
5c	1.35	23 200	9280	0.251	20000	8100	6500	2.9
glassy carbon ^c	1.46	29 400	12000	0.233		6400	4900	4.6
graphitic carbon ^d	1.89	13 900	5860	0.185	420	450	480	31.0
diamond ^e	3.51	1 050 000	437 000	~0.200		~80000		13.0
Kerimid 601 ^f	1.29	4 460	1610	0.389	620	620	550	7.2
Thermid-600 ^g	1.33	4 650	1690	0.378	550	670	590	6.9
ABS ^h	1.04	2 640	954	0.385	240	180	190	15.0
poly(methacrylate)	1.05	3 590	1340	0.338	420	330	340	11.0
polystyrene	1.04	3 680	1370	0.343	360	370	360	10.0
polyethylene	0.94	2 540	908	0.396	49	44	46	58.0
sapphire	3.99	358 000	136 000	0.318		18 000		20.0
aluminum	2.70	69 100	25 800	0.338		1400		49.0
gold	17.00	76 300	26 900	0.420		630		120.0
copper	8.92	120 000	44 500	0.345		880		140.0
steel (soft)	7.86	204 000	78 700	0.294		1500		140.0
steel (hard)	8.20	237 000	92 900	0.276		7200		33.0

^aThe Young's modulus was determined by the ultrasonic method described in ref 6. Uncertainty in the measurement is <5%. ^bThe hardness H_{VR} was determined by the method in ref 8. The values for the metals was taken from this reference. Uncertainty in the measurement is approximately $\pm 20\%$ for $L = 0.5$ kg and $\pm 10\%$ for $L = 1$ and 2 kg. The hardness values for diamond (Knoop indenter) and sapphire (Vickers indenter) were obtained from ref 1. ^cV10, Atomergic Co. ^dCarbon P03, Pure Carbon Co., St. Mary's, PA. ^eThe values were obtained from ref 1. ^fBis(4-aminophenyl)methane- N,N' -(diphenylmethyl)bismaleimide copolymer. ^gBenzophenonetetracarboxylic dianhydride-1,3-bis(3-aminophenoxy)benzene copolymer, 3-aminophenyl acetylene terminated. ^hAcrylonitrile-butadiene-styrene copolymer.

of a constituent of this solid (the group R). We have prepared 1a-5a, oxidatively coupled^{3,4} these monomers in the presence of monoacetylenes $R'C\equiv CH$ to control the degree of polymerization to form low molecular weight oligomers 1b-5b, molded the oligomers under pressure into disks (ca. 1 cm in diameter and 0.25 cm thick), and heated the oligomers in the disks to give the black, hypercross-linked solids 1c-5c (eq 1).⁵ All samples used in Tables I and II were prepared by the same procedure.

The Young's moduli of these materials⁶ (Table I) indicate that the hypercross-linked solids 1c-5c more closely resemble glassy carbon ($\rho = 1.35$ g/cm³, $E = 29 000$ MN/m²) than diamond ($\rho = 3.51$ g/cm³, $E = 1 050 000$ MN/m²) in properties. The density and Young's modulus of the materials increase on thermal treatment. For example, 4b ($\rho = 1.18$ g/cm³, $E = 3100$ MN/m²) when heated to 150 °C for 6 h forms 4c with a density of 1.31 g/cm³ and a Young's modulus of 12 400 MN/m². Further heating at 350 °C for 16 h forms 4c with a density of 1.35 g/cm³ and a Young's modulus of 24 000 MN/m².

Our efforts to measure the hardness of materials 1c-5c by the conventional Vickers microindentation technique⁷ were inconclusive. It was difficult to characterize the indentations in these darkly colored materials by microscopy; they also suffered microcracking and fracture around the indentations. One of us has recently described a method for measuring hardness of solids by a method based on electrical contact resistance.⁸ For metals of widely differing hardness, values obtained by this method (H_{VR}) correlate well with values determined by conventional Vickers indentation (H_V). Table I summarizes values of H_{VR} . Materials 1c-5c show remarkably high hardness by this technique, but the values of H_{VR} do not correlate closely with values of E . Table I includes values for the ratio E/H_{VR} ; these values are lower for the brittle materials than the ductile ones. Thus, direct comparison of the hardness values of 1c-5c to those of metals is probably not appropriate. We do, however, find that 1c-5c are scratched by

Table II
Thermal Gravimetric Analysis of Materials 1c-5c^a

sample	atmosphere			
	argon		air	
	$T_{10\%}$, °C	$T_{50\%}$, °C	$T_{10\%}$, °C	$T_{50\%}$, °C
1c	875	(13%) ^b	420	510
2c	605	(19%) ^b	350	410
3c	530	950	394	505
4c	541	(27%) ^b	328 ^c	405 ^c
5c	620	(21%) ^b	333 ^c	402 ^c

^aMeasurements were obtained on a Du Pont 9900 Series thermal analyzer. The heating rate was 10 °C/min. $T_{10\%}$ is the temperature at which the sample has lost 10% of its mass at this heating rate; $T_{50\%}$ is the corresponding temperature for loss of 50% of the sample mass. Samples were prepared as described.⁵

^bFor these cases, $T_{50\%}$ exceeded the upper temperature limit of the thermal analyzer (1100 °C). The values reported are the percent mass of the sample lost at 1000 °C. ^cThese samples underwent a 6-8% gain in weight on heating in air at temperatures of 200-250 °C. We attribute this weight gain to surface oxidation of sulfur atoms.

steel but not by aluminum. The significant difference between the Young's modulus and hardness of 3c and the other hypercross-linked solids suggests that it may be possible to control the macroscopic properties of the organic solids by choice of the structure of the monomer. Comparison of the values of H_{VR} at indenter loads of 0.5, 1.0, and 2.0 kg indicates that the observed hardness depends on load. The hardness of a material should, in principal, be independent of load, but a number of materials, including single-crystal, aggregate, and hard materials, deviate from this theoretical independence.^{9,10}

Table II summarizes the thermal stabilities observed for 1c-5c under argon and under air.¹¹ All display exceptional (for organic polymers) thermal stability. The broad similarity between the thermal properties of these five materials suggests that these properties are dominated by the network of bonds derived from the diacetylene moieties,

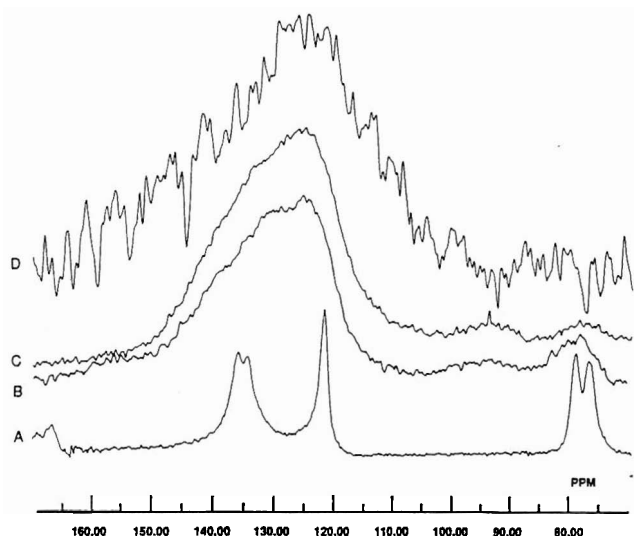


Figure 1. ^{13}C CPMAS NMR spectra of samples of **4b** at (A) room temperature and after heating at (B) 100 °C for 1 h, (C) 150 °C for 1 h, and (D) 350 °C for 6 h. For (B) and (C) a ramp rate of 1 °C/min was used to reach the final temperature. For (D) the sample was heated at 150 °C (ramp rate of 1 °C/min) for 1 h followed by heating for 6 h at 350 °C.

rather than by the aromatic groups present in the original monomers.

We have begun to explore the processes that occur in the formation of **1c–5c** from **1b–5b** using solid-state ^{13}C NMR spectroscopy.^{12,13} Figure 1 shows a representative series of spectra taken at different stages during thermal cross-linking of a sample of oligomer **4b**. These spectra establish that the initial stages of the cross-linking process involves conversion of the sp carbon centers to sp² centers. The resonances at approximately 75–80 ppm, assigned to the diacetylenic carbons,¹⁴ diminish in intensity and are replaced in part by resonances at 90–100 ppm (acetylenic carbons). Eventually both diacetylenic and acetylenic resonances are incorporated into a broad envelope of signals in the 120–150 ppm region. These spectra are consistent with the generation of a polyaromatic and/or polyolefinic solid.¹⁵ We did not observe resonances attributable to sp³ carbon atoms.

The high hardness, Young's modulus, and thermal stability of **1c–5c** indicates that the class of organic solids obtained by solid-state cross-linking of poly(aromatic diacetylenes) (and, we assume, other structurally related polymers) provide an attractive system with which to explore relationships between microscopic structure and macroscopic structural properties. The density of cross-links and the character of the group R can be controlled conveniently in these solids by synthesis; at least certain of the important reactions occurring in the solid state can be monitored by ^{13}C solid-state NMR spectroscopy; a range of physical properties can be measured.

Acknowledgment. We are grateful to the National Science Foundation for support of this research (Grant CHE-85-08702). The solid-state NMR spectrometer was purchased under NSF Grant CHE-86-12910 (to G.M.W. and Mark Wrighton, Massachusetts Institute of Technology). We thank Craig Baird and Dr. H. J. Goldsmid of the Department of Applied Physics, The University of New South Wales, Kensington, New South Wales, Australia, for making the hardness measurements and Dr. R. R. Paxton of the Pure Carbon Co., St. Mary's, PA, for the donation of carbon materials. We also thank Drs. Jim Barber, Howard Tennant, and Larry Truesdale of Hyperion Catalysis International, Lexington, MA, and Dr.

Owen Webster of E. I. du Pont de Nemours and Co. for helpful discussions. Dr. Shaw Huang provided essential help with the solid-state NMR experiments. Thermal analysis was carried out by using an apparatus at Hyperion Catalysis International.

Registry No. **1a** (homopolymer), 25359-90-4; **2a** (homopolymer), 117024-50-7; **3a** (homopolymer), 116998-06-2; **4a** (homopolymer), 84154-54-1; **5a** (homopolymer), 116998-08-4.

References and Notes

- (1) Field, J. E., Ed. *The Properties of Diamond*; Academic: New York, 1979.
- (2) Neenan, T. X.; Whitesides, G. M. *J. Org. Chem.* 1988, **53**, 2489–2496.
- (3) In a typical procedure, oligomer **1b** was prepared in *o*-dichlorobenzene by the Cu(I) catalyzed oxidative coupling of 1,3-diethynylbenzene containing phenylacetylene as the end-capping agent.⁴ Oligomers **2b–5b** were prepared analogously. **Caution:** Compound **1a** and all other volatile polyethynyl aromatics should be distilled at high vacuum and at temperatures of less than 60 °C in well-shielded equipment. Only limited quantities should be distilled, stored, or manipulated as pure (undiluted) material. A sample of **4b** decomposed violently on handling on one occasion. Although we have had few incidents with these substances, all deprotected ethynyl aromatics and oligomeric materials mentioned in this paper should be treated as potentially explosive materials.
- (4) Hay, A. S. *J. Org. Chem.* 1960, **25**, 1275–1276.
- (5) Approximately 350 mg of oligomer **1b–5b** was heated from room temperature to 250 °C over the course of 2 h in a temperature-controlled, 1-cm diameter die at 10000 psi. The pressure was released and the sample was heated under nitrogen at 1 atm for 16 h at 350 °C.
- (6) These measurements were made by using a nondestructive analysis based on ultrasonics; see: McSkimin, H. J. In *Physical Acoustics, Principles and Methods*; Mason, W. P., Ed.; Academic: New York, 1964; pp 271–334. Papadakis, E. P. In *Physical Acoustics, Principles and Methods*; Mason, W. P., Thurston, R. N., Eds.; Academic: New York, 1976; pp 277–374. Krautkramer, J.; Krautkramer, H. *Ultrasonic Testing of Materials*; Springer-Verlag: New York, 1977. Fitting, D. W.; Adler, L. *Ultrasonic Spectral Analysis for Nondestructive Evaluation*; Plenum: New York, 1981. McMaster, R. C., Ed. *Nondestructive Testing Handbook*; Ronald: New York, 1959.
- (7) For a general discussion, see: Tabor, D. *Hardness of Metals*; Clarendon: Oxford, 1951.
- (8) The electrical contact resistance method measures the resistance to deformation under load using an adaptation of the traditional Vickers indenter. The indentation area is measured by the electrical constriction resistance between the indenter and the sample at the indent. This method requires that the indenter be electrically conductive (SiC is used) and that the specimen be coated with a thin film of gold to make the surface electrically conductive. The resistance is measured between the indenter and the sample. The indentation area is inversely proportional to R^2 where R is the measured constriction resistance. The hardness is given by $H_{VR} = CLR^2 = 1.8544LR^2/(0.083)^2 \text{ kg/mm}^2$, where C is a constant, L is the load of the indenter, and R is measured in ohms. For a more thorough description of the method, see: Wiczorek, L.; Howes, V. R.; Goldsmid, H. J. *J. Mater. Sci.* 1986, **21**, 1423–1428.
- (9) The power law relationship between P , the load of the indenter, and d , the diagonal length of the indentation, has been expressed in the form: $P = Ad^n$, where A is a constant. For most metals and single crystals that demonstrate this behavior, n lies between 1.92 and 2.00.¹⁰ Examination of a fracture surface of **3c** by scanning electron microscopy found no evidence for inhomogeneity of the material.
- (10) Brookes, C. A. In *Science of Hard Materials*; Vizwanadham, R. K., Rowcliffe, D. J., Gurland, J., Eds.; Plenum: New York, 1983; pp 181–199.
- (11) The thermal degradation of **1** has been studied previously; see: Newkirk, A. E.; Hay, A. S.; McDonald, R. S. *J. Polym. Sci., Part A* 1964, **2**, 2217–2233.
- (12) Solid-state ^{13}C NMR were obtained on a Chemagnetics CMC-200A spectrometer using approximately 200 mg of **4b** or **4c** at 50 MHz with high-power proton decoupling. Magic angle spinning at approximately 4 kHz with a cross-polarization spin-locking (CP MAS) contact time of 3 ms and a pulse delay of 10 s provided the solid-state spectra. Chemical shifts were referenced externally to hexamethylbenzene (132.2 ppm). For **4b** (Figure 1, spectrum A), resonances were assigned (δ 75–80

- ppm, diacetylenic carbons; 122 ppm, C-2 and C-5; band centered at 135 ppm, C-3 and C-4) by using nonquaternary suppression¹³ with a decoupling window of 40 μ s. The spectra shown in Figure 1 were acquired by using approximately the same number of transients with pulse delays from 4 s (spectrum A) to 20 s (spectrum D).
- (13) Opella, S. J.; Frey, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5854-5856.
 - (14) Levy, G. C.; Lichter, R. L.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Wiley: New York, 1980.
 - (15) Economy and co-workers have suggested that the thermal cross-linking of the oligomer derived from 1,3,5-triethynylbenzene proceeds by a [2 + 4]-cycloaddition reaction of the diacetylenic linkage, giving an aryl biradical or benzyne intermediate. Internal hydrogen shifts aromatize the diacetylenic oligomer (Dawson, D. J.; Fleming, W. W.; Lyerla, J. R.; Economy, J. *Reactive Oligomers*; ACS Monograph 282; American Chemical Society: Washington, DC, 1982; pp 63-79). Newkirk and co-workers¹¹ have examined the thermal treatment of poly(*m*-diethynylbenzene) by infrared spectroscopy.

**Thomas X. Neenan, Matthew R. Callstrom,
Louis M. Scarmoutzos, Kevin Randall Stewart, and
George M. Whitesides***

*Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138*

V. R. Howes

*Department of Applied Physics
University of New South Wales
Kensington, N.S.W., Australia*

Received May 23, 1988;

Revised Manuscript Received September 13, 1988