suggested by experimental evidence are proton dipole–dipole relaxation and proton relaxation by unpaired electrons that are not involved in the DNP. Proton dipole–dipole relaxation requires molecular motion in polyethylene with correlation times $\sim(60\ \mathrm{MHz})^{-1}$; such motion is well documented at ambient temperatures.[11] Leakage due to other mechanisms becomes important at low temperatures where we have also measured very small enhancements ($\epsilon = +1.4$ at 90 K) and where the motions so crucial to dipole–dipole relaxation are quenched. At these temperatures, we believe that relaxation of the protons by unpaired electrons in pockets of unreacted catalyst is the dominant source of leakage.

The source of the small but reproducible enhancement found in the composite containing deuteriated polyacetylene (Figure 2c) is intriguing. There are three possible explanations for this signal: (1) direct surface polarization of polyethylene protons by electrons in polyacetylene due to electronic overlap between the two components; (2) residual protons in the deuteriated polyacetylene; (3) enhancement of catalyst protons left in the polyacetylene during sample preparation.

This investigation shows that it is indeed possible to use DNP to polarize the nuclei in a matrix surrounding clusters which contain unpaired electrons. In the particular composite we have studied, rapid ^1H spin diffusion in the polyethylene matrix propagates the polarization induced by the DNP, thus reducing the initially selective interfacial polarization transfer from the polyacetylene clusters. Possibilities for overcoming this limitation include restricting the extent of spin diffusion either by polarizing for short times or by using rotating-frame DNP.[12] Another alternative is to probe with rare nuclei, such as ^{13}C, for which spin diffusion is very slow. Experiments are currently under way to explore these alternatives.

Acknowledgment. We thank T. C. Clarke, J. R. Lyerla, and D. J. VanderHart for fruitful discussions and R. A. Wind for suggesting the role of spin duffusion. The support of IBM Germany for a World Trade Postdoctoral Fellowship (G.G.M.) is gratefully acknowledged.

Registry No. Polyacetylene, 25067-58-7; polyethylene, 9002-88-4; deuteriated polyacetylene, 28265-43-2.

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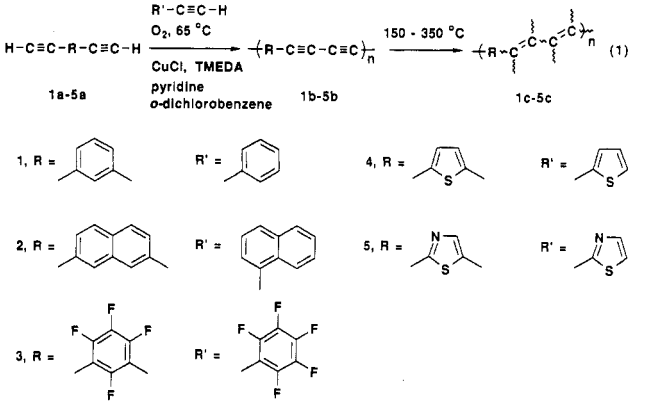
Received June 21, 1988;
Revised Manuscript Received September 20, 1988

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

0024-9297/88/2221-3525$01.50/0

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] L = 0.5 kg (MN/m^2)	H_{VR}[b] L = 1.0 kg (MN/m^2)	H_{VR}[b] L = 2.0 kg (MN/m^2)	E/H_{VR} (L = 1.0 kg)
1c	1.60	24800	9640	0.286	11000	14000	7400	1.8
2c	1.61	25700	10000	0.241	10000	12000	5900	2.6
3c	1.66	10000	3850	0.306	5900	4100	2400	2.4
4c	1.34	24000	9410	0.277	31000	12000	6100	2.0
5c	1.35	23200	9280	0.251	20000	8100	6500	2.9
glassy carbon[c]	1.46	29400	12000	0.233		6400	4900	4.6
graphitic carbon[d]	1.89	13900	5860	0.185	420	450	480	31.0
diamond[e]	3.51	1050000	437000	~0.200		~80000		13.0
Kerimid 601[f]	1.29	4460	1610	0.389	620	620	550	7.2
Thermid-600[g]	1.33	4650	1690	0.378	550	670	590	6.9
ABS[h]	1.04	2640	954	0.385	240	180	190	15.0
poly(methacrylate)	1.05	3590	1340	0.338	420	330	340	11.0
polystyrene	1.04	3680	1370	0.343	360	370	360	10.0
polyethylene	0.94	2540	908	0.396	49	44	46	58.0
sapphire	3.99	358000	136000	0.318		18000		20.0
aluminum	2.70	69100	25800	0.338		1400		49.0
gold	17.00	76300	26900	0.420		630		120.0
copper	8.92	120000	44500	0.345		880		140.0
steel (soft)	7.86	204000	78700	0.294		1500		140.0
steel (hard)	8.20	237000	92900	0.276		7200		33.0

[a] The Young's modulus was determined by the ultrasonic method described in ref 6. Uncertainty in the measurement is <5%. [b] The 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 ±20% for L = 0.5 kg and ±10% for L = 1 and 2 kg. The hardness values for diamond (Knoop indenter) and sapphire (Vickers indenter) were obtained from ref 1. [c] V10, Atomergic Co. [d] Carbon P03, Pure Carbon Co., St. Mary's, PA. [e] The values were obtained from ref 1. [f] Bis(4-aminophenyl)methane-*N*,*N*'-(diphenylmethyl)bismaleimide copolymer. [g] Benzophenonetetracarboxylic dianhydride-1,3-bis(3-aminophenoxy)benzene copolymer, 3-aminophenyl acetylene terminated. [h] Acrylonitrile–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≡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 materials[6] (Table I) indicate that the hypercross-linked solids **1c–5c** more closely resemble glassy carbon (ρ = 1.35 g/cm^3, E = 29000 MN/m^2) than diamond (ρ = 3.51 g/cm^3, E = 1050000 MN/m^2) in properties. The density and Young's modulus of the materials increase on thermal treatment. For example, **4b** (ρ = 1.18 g/cm^3, E = 3100 MN/m^2) when heated to 150 °C for 6 h forms **4c** with a density of 1.31 g/cm^3 and a Young's modulus of 12400 MN/m^2. Further heating at 350 °C for 16 h forms **4c** with a density of 1.35 g/cm^3 and a Young's modulus of 24000 MN/m^2.

Our efforts to measure the hardness of materials **1c–5c** by the conventional Vickers microindentation technique[7] 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 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
Thermal Gravimetric Analysis of Materials 1c–5c[a]

sample	atmosphere: argon $T_{10\%}$, °C	argon $T_{50\%}$, °C	air $T_{10\%}$, °C	air $T_{50\%}$, °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]

[a] Measurements 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] [b] For 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. [c] These 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.

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,

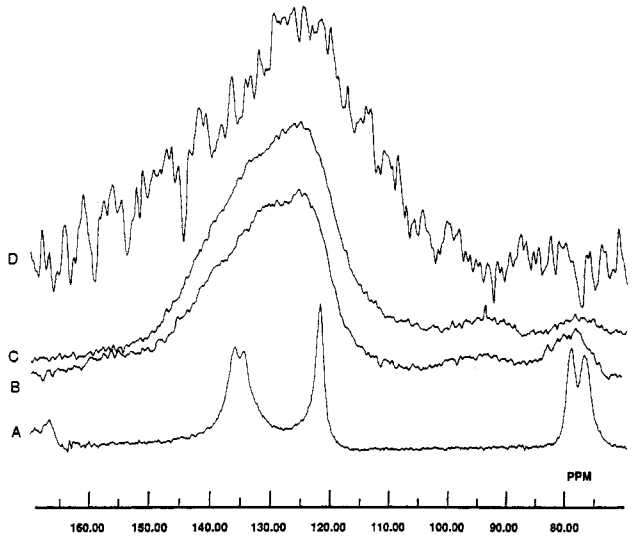


Figure 1. ^{13}C CPMAS NMR spectra of samples of **4b** at (A) room temperature and after heating at (B) 100 °C for 1 h, (C) 150 °C for 1 h, and (D) 350 °C for 6 h. For (B) and (C) a ramp rate of 1 °C/min was used to reach the final temperature. For (D) the sample was heated at 150 °C (ramp rate of 1 °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 sp^2 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 diacetylic 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 sp^3 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.

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(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 10 000 psi. The pressure was released and the sample was heated under nitrogen at 1 atm for 16 h at 350 °C.
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(8) The electrical contact resistance method measures the resistance to deformation under load using an adaptation of the traditional Vickers indentor. 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 $H_{VR} = CLR^2 = 1.8544LR^2/(0.083)^2$ 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: Wieczorek, L.; Howes, V. R.; Goldsmid, H. J. *J. Mater. Sci.* **1986**, *21*, 1423–1428.
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ppm, diacetylenic carbons; 122 ppm, C-2 and C-5; band centered at 135 ppm, C-3 and C-4) by using nonquaternary suppression[13] with a decoupling window of 40 μs. 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.

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(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-workers[11] have examined the thermal treatment of poly(*m*-diethynylbenzene) by infrared spectroscopy.

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Received May 23, 1988; Revised Manuscript Received September 13, 1988

Poly[ethynylene(3-*n*-butyl-2,5-thiophenediyl)ethynylene]: A Soluble Polymer Containing Diacetylene Units and Its Conversion to a Highly Cross-Linked Organic Solid

We are engaged in a program directed at the synthesis and study of highly cross-linked organic solids. Our approach has been to prepare low molecular weight polymers and oligomers consisting of aromatic moities linked by diacetylene units, to cross-link the diacetylenic units thermally, and to examine the properties of the resulting solids. Our initial efforts were directed toward the preparation of monomers having as high a ratio of carbon to hydrogen as possible.[1,2] Although this approach yielded materials with interesting properties (high Young's modulus, hardness, and thermal stability) the oligomeric/polymeric intermediates had poor solubility and high cure energies (in some cases exceeding 500 J/g); these values of cure energy made the preparation of large pieces difficult.

We chose to introduce an alkyl group into the aromatic portion of the monomer to increase the solubility and to lower the cure energy of the polymer derived from it. This paper reports our results of a study of poly[ethynylene-(3-*n*-butyl-2,5-thiophenediyl)ethynylene] and related oligomers and polymers: preparation of these diacetylenic oligomers and polymers in soluble form, conversion of the oligomers to hypercross-linked[3] organic solids with high carbon content, and characterization of these solids. An accompanying paper by Rutherford and Stille describes related work.[4] Our studies demonstrate that the properties of poly[ethynylene(3-*n*-butyl-2,5-thiophenediyl)-ethynylene] derived from the oxidative coupling of 3-*n*-butyl-2,5-diethynylthiophene (**1**) can be controlled by the addition of 2-ethynylthiophene (**2**)[5,6] as an end-capping agent. We have also prepared 2,3,5-triethynylthiophene (**3**) and carried out the oxidative copolymerization of **1**, **2**, and **3** in a 10:1:1 molar ratio to investigate the properties of a diacetylene network[7] polymer.

Scheme I outlines the syntheses of **1** and **3**. The nickel-catalyzed[6] coupling of 3-bromothiophene (**4**) with *n*-butylmagnesium bromide in ether, followed by treatment of the resulting 3-*n*-butylthiophene with bromine in acetic acid,[8] gave 3-*n*-butyl-2,5-dibromothiophene (**5**) in an overall yield of 87%. The palladium- and copper-catalyzed coupling of the dibromide with (trimethylsilyl)acetylene followed by deprotection of 3-*n*-butyl-2,5-bis[(trimethylsilyl)ethynyl]thiophene with potassium hydroxide in methanol gave **1** in >99% yield.[9] We prepared 2,3,5-triethynylthiophene (**3**)[10] from 2,3,5-tribromothiophene (**6**)[11] in 74% overall yield using a procedure analogous to that used for the conversion of **5** to **1**.

Polymerization of **1** by oxidative coupling of the acetylenes with dioxygen and catalytic amounts of cuprous chloride in *o*-dichlorobenzene for 10 min at 65 °C followed by cooling over 2 h to room temperature gave a completely homogeneous solution of the polymer represented by the structure **7** (Scheme II, eq 3).[12] Copolymerization of **1** and **2** (added as an end-capping agent) in molar ratios of **1**:**2** = 3:1, 5:1, 10:1, 100:1, and 1000:1 all gave completely homogeneous solutions in *o*-dichlorobenzene of the polymers **9a–e** (eq 4). The oxidative copolymerization of **1**, **2**, and **3** in molar ratios of 10:1:1, respectively, gave the network polymer **11** (eq 5), also soluble in *o*-dichlorobenzene.

Examination of **9a** by ^{1}H NMR spectroscopy clearly showed resonances assignable to the end-capping groups. At molar ratios of **1**:**2** > 10:1, resonances of the end-capping groups were no longer observed in the ^{1}H NMR spectrum. Infrared spectral analysis did not show acetylenic C–H stretching vibrations in any of the polymers prepared.[13] Analysis by GPC confirms that added **2** does indeed decrease the molecular weight.[14] The number-average molecular weights ($\bar{M}_n$) and polydispersities (Z) of **9a–e** decrease with increasing amount of end capping: **9a** ($\bar{M}_n$ = 3700; Z = 1.9); **9b** ($\bar{M}_n$ = 4500; Z = 2.1); **9c** ($\bar{M}_n$ = 6000; Z = 2.3); **9d** ($\bar{M}_n$ = 13 000; Z = 2.1); **9e** ($\bar{M}_n$ = 16 000; Z = 2.2). The addition of the triacetylenic monomer **3** for the preparation of **11** resulted in an increase in both molecular weight ($\bar{M}_n$ = 9000) and polydispersity (Z = 2.7) relative to **9c**. The polymers **9a–e** are soluble in solvents such as tetrahydrofuran and toluene. The lower molecular weight materials, **9a** and **9b**, are also soluble in methylene chloride. The solubilities of **7**, **9a–e**, and **11** are remarkable in comparison to that of the oligomer **13** derived from the oxidative polymerization of 2,5-diethynylthiophene (**14**).[2] We found that **13** was soluble only at low molecular weights, when formed by coupling of a 1:1 molar ratio of **14** and **2**.

The hypercross-linked solids **8**, **10a–e**, and **12** were prepared by molding the oligomers/polymers under pressure (10 000 lb/in.^{2}) into disks (ca. 1 cm in diameter and 0.25 cm thick) and heating to 200 °C for 1 h. The cross-linking processes of the oligomers and polymers, **7** and **9a–e**, are characterized (DSC, ramp rate = 5 °C/min) by a cure onset temperature of ~160 °C, a cure maximum temperature of ~180 °C, and a cure energy of ~300 J/g. As expected, **11** had a lower cure onset temperature of 110 °C, a lower cure maximum temperature of 137 °C, and a higher cure energy of 350 J/g reflecting the higher reactivity of the triacetylinic monomer unit. The thermal stabilities (TGA, ramp rate = 10 °C/min) of **8**, **10a–e**, and **12** were virtually indistinguishable: under argon, the characteristic temperature ($T_{10\%}$) at which they had lost

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