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

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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.

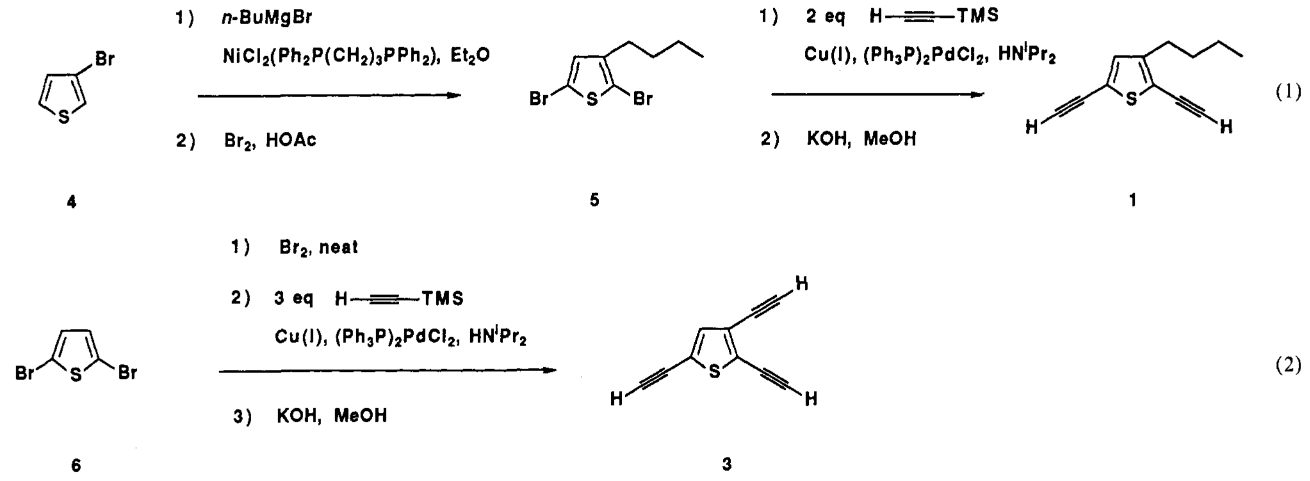
Scheme I outlines the syntheses of **1** and **3**. The nickel-catalyzed[6] coupling of 3-bromothiophene (**4**) with *n*-butylmagnesium bromide in ether, followed by treatment of the resulting 3-*n*-butylthiophene with bromine in acetic acid,[8] gave 3-*n*-butyl-2,5-dibromothiophene (**5**) in an overall 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.

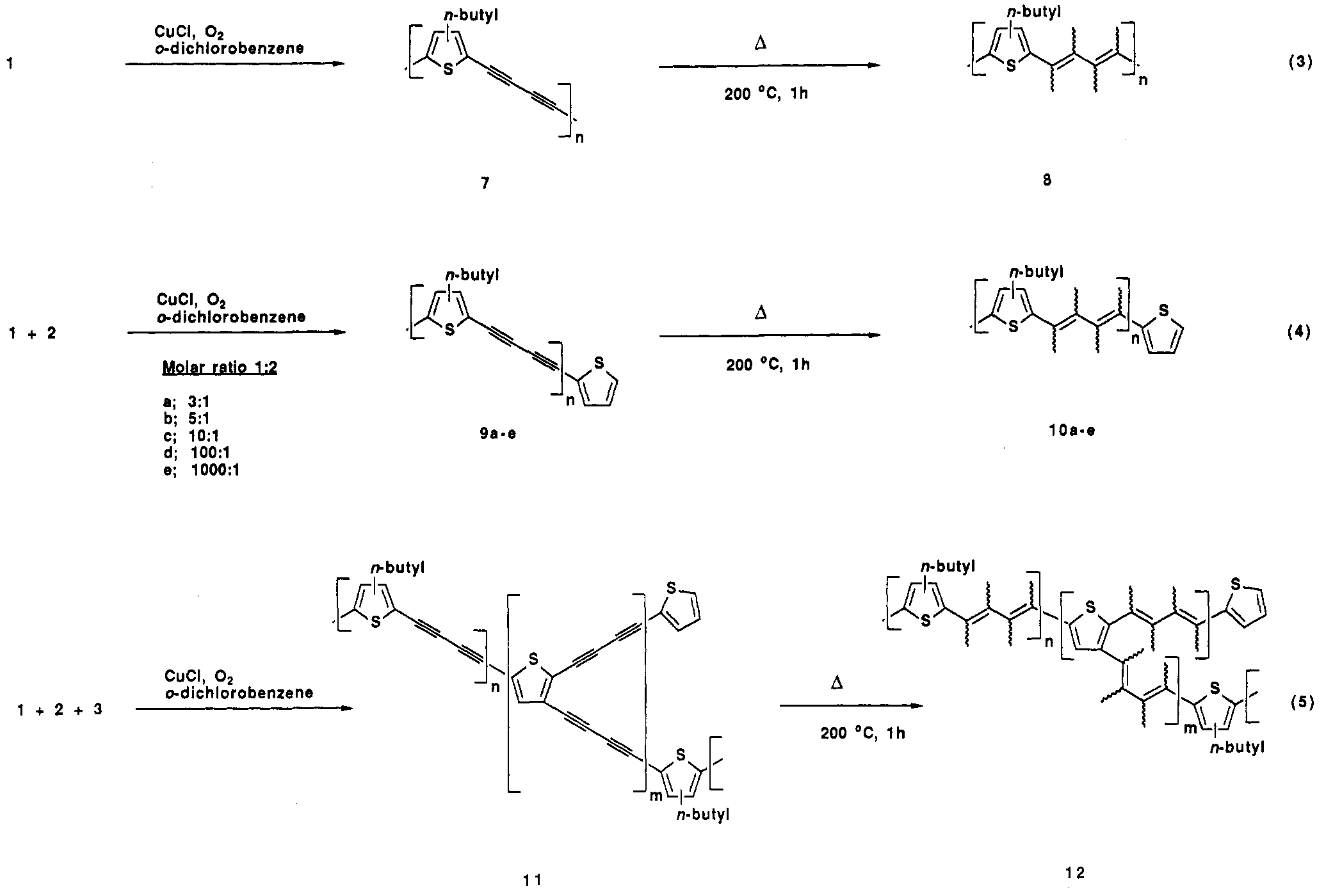
Examination of **9a** by ^{1}H NMR spectroscopy clearly showed resonances assignable to the end-capping groups. At molar ratios of **1**:**2** > 10:1, resonances of the end-capping groups were no longer observed in the ^{1}H NMR spectrum. Infrared spectral analysis did not show acetylenic C-H stretching 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** ($\bar{M}_n$ = 13000; Z = 2.1); **9e** ($\bar{M}_n$ = 16000; 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 (10000 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

Scheme I



Scheme II



10% of their weight was $T_{10\%} \approx 470$ °C; the corresponding temperature for 50% weight loss was $T_{50\%} \approx 950$ °C. Under air, all had a $T_{10\%} \approx 425$ °C and a $T_{50\%} \approx 525$ °C. These values are similar to those observed for analogous nonbutylated materials.[2] For example, the organic solid derived from the thermal cross-linking of **13**, poly(2,5-diethynylthiophene), derived from the oxidative polymerization of **14** and **2**, exhibited, under argon ($T_{10\%} = 540$ °C, $T_{50\%} > 1100$ °C[15]) and air ($T_{10\%} = 330$ °C, $T_{50\%} = 400$ °C), thermal stability similar to those of **8**, **10a–e**, and **12**.[2]

Although the disks that we prepared from **8**, **10d**, **10e**, and **12** were extremely brittle and had surprisingly low densities: $\rho \approx 1.2$ g/cm^3,[16] those from **10a–c** formed solids having good mechanical properties. The black, shiny disks formed from **10a–c** had $\rho \approx 1.34$ g/cm^3 and Young's moduli (~14 000 MN/m^2) clearly indicative of a highly cross-linked organic solid.[16,17] We have also found that smooth, noncracking, yellow films can be cast on glass from toluene or tetrahydrofuran solutions. When thermally treated at 200 °C the resultant adherent, shiny, black films cracked due to shrinkage.

The solubility, Young's modulus and thermal stability of poly[ethynylene(3-*n*-butyl-2,5-thiophenediyl)ethynylene] and related oligomers and polymers provide an attractive system for the exploration of the properties of hypercross-linked solids. We are continuing to investigate these materials.

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Registry No. 1 (homopolymer), 116954-15-5.

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(3) We refer to these materials—solids designed to maximize the volume densities of the bonds linking the chains of the polymeric precursors—as hypercross-linked solids.

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(9) Spectral and elemental analyses of **5**, the trimethylsilyl-protected ethynylated monomers [3-*n*-butyl-2,5-bis[(trimethylsilyl)ethynyl]thiophene and 2,3,5-tris[(trimethylsilyl)ethynyl]thiophene], and the polymers (**7**, **9a–e**, **11**) were satisfactory. The deprotected monomers (**1–3**) have spectral analyses consistent with the assigned structures.

(10) **Caution**: *Compound 3 was isolated only in small (milligram) amounts. Only limited quantities should be stored or manipulated as pure (undiluted) material. Although we have had few incidents with these substances, all deprotected ethynyl aromatics and oligomeric and polymeric materials mentioned in this paper should be treated as potentially explosive materials.*

(11) Rosenberg, J. *Chem. Ber.* **1885**, *18*, 1773–1778.

(12) For the cuprous chloride catalyzed oxidative coupling of *m*- and *p*-diethynylbenzene in acetone, see: Hay, A. S. *J. Org. Chem.* **1960**, *25*, 1275–1276.

(13) We estimate the limits of detection by infrared analysis to be approximately one free acetylene per 125 3-*n*-butyl-2,5-diethynylthiophene units.

(14) Number-average molecular weights ($\bar{M}_n$) and polydispersities of these polymers were measured in tetrahydrofuran and referenced to polystyrene standards by using a Polymer Laboratories PLgel 10-μm polystyrene mixed-bed resin column with a range of $\bar{M}_n$ of 500–(4×10^6). Because the reference standards are of polystyrene polymer, the absolute values of molecular weights reported here are probably less accurate than the relative values. The chromatograms were analyzed by using software developed in the laboratories of Professor Richard R. Schrock at the Massachusetts Institute of Technology.

(15) For this case, $T_{50\%}$ exceeded the upper temperature limit of the thermal analyzer (1100 °C). At 1100 °C, 70% of the mass of the organic solid derived from the polymer **13** was retained.

(16) Densities of typical organic polymers range from 0.94 g/cm^3 (polyethylene) to ~1.33 g/cm^3 (Thermid-600, a polyimide thermoset polymer) with Young's moduli from 2450 MN/m^2 (polyethylene) to 4650 MN/m^2 (Thermid-600).[2]

(17) Young's moduli were measured by using an ultrasonics method with a Panametrics 5055 pulser–receiver; 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.

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Poly(ethynylene-2,5-thiophenediylethynylenes). Processable, Reactive Polymers That Thermally Cross-Link

A polymer cross-linking reaction that proceeds without the evolution of volatiles is especially useful, providing a means of processing void-free parts and devices. If the reaction also is one that maintains π-conjugation in the product, the system can be designed to generate a material possessing unique properties.

To accomplish this, we have synthesized a series of 2,5-diethynylthiophenes (**1**) and effected their polymerizations to poly(ethynylene-2,5-thiophenediylethynylenes) (**2**), utilizing the oxidative coupling procedure introduced by Hay[1] for the polymerization of *m*- and *p*-diethynylbenzenes (Scheme I).[2] The parent monomer, 2,5-diethynylthiophene (**1a**), and 2,5-diethynyl-3-methylthiophene (**1b**) were obtained by the palladium-catalyzed coupling[3] of (trimethylsilyl)acetylene[4] with 2,5-dibromothiophene and 2,5-dibromo-3-methylthiophene[5] followed by deprotection.[6] The 3-butyl and 3-hexyl monomers (**1c,d**) were obtained by the nickel-catalyzed cross-coupling reaction between 3-bromothiophene and butyl- or hexylmagnesium bromide,[7] followed by bromination,[5] ethynylation,[3] and deprotection.[6]

In the course of the oxidative polymerization of **1a,b**, both polymers **2a,b** precipitated from solution. The dark brown and red precipitates, respectively, were partially soluble in hot nitrobenzene and hot chlorobenzene. Although polymers **2c,d** (purple) precipitated toward the end of the polymerization reaction, they were completely soluble in hot nitrobenzene and hot chlorobenzene and nearly completely soluble in tetrachloroethane, from which films could be cast. This solubility behavior is analogous to that exhibited by the polymer obtained from *m*-diethynylbenzene[1b] and poly(2,5-thiophenediyls).[8] Both the ^{1}H and ^{13}C NMR spectra (taken at 120 °C in $C_6D_5NO_2$ and $CHCl_2CHCl_2$, respectively) were consistent with structure **2c**.[9] Polymers **2b–d** could be expected to possess a random orientation of the substituent groups (head-to-head and head-to-tail). The solid-state CP/MAS ^{13}C spectrum of **2b** (Figure 1) shows five peaks, due to CH_3 (16.1 ppm), the 2- and 5-carbons (122 ppm), acetylenic carbons (78–80 ppm), the 4-carbon (136 ppm), and the 3-carbon (145 ppm). A sample of **2d**, $[\eta] = 2.95$ ($CHCl_3$), exhibited a broad molecular weight distribution (GPC) with $\bar{M}_w = 23\,143$, $D = 3.72$.

The reactivity of **2** and the large number of reactions available for its transformation into other structures are somewhat unique. An important feature is that the diyne unit is subject to both thermal and photochemical reactions; the thermolysis of poly(butadiynylene-1,3-phenylene) is an example.[10] Thermolysis of **2** at moderate temperatures (180–225 °C) generated **3** containing a high cross-

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