ternational, Lexington, MA, and Dr. Owen Webster of E. I. du Pont deNemours and Co. for helpful discussions. We thank Dr. Timothy M. Miller (Massachusetts Institute of Technology) for assistance. We thank Professor Richard R. Schrock, Gui Bazan, and Steven A. Krouse (Massachusetts Institute of Technology) for allowing us to use the GPC equipment and computer programs in their laboratory to characterize these polymers. We also thank Professor John K. Stille (Colorado State University) for discussions concerning this class of polymers. Thermal analysis was carried out by using an apparatus at Hyperion Catalysis International.

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

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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.*
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(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]
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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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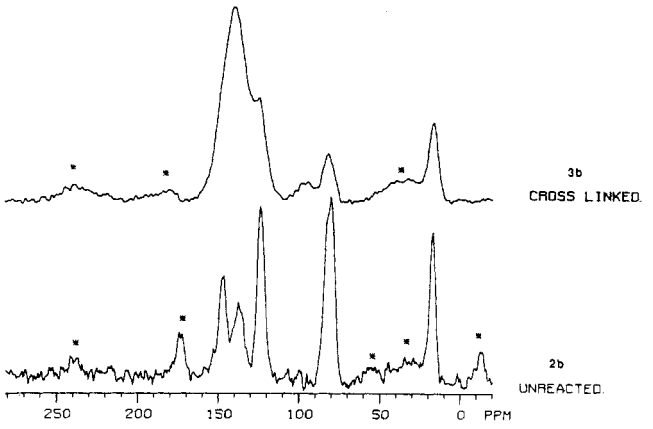
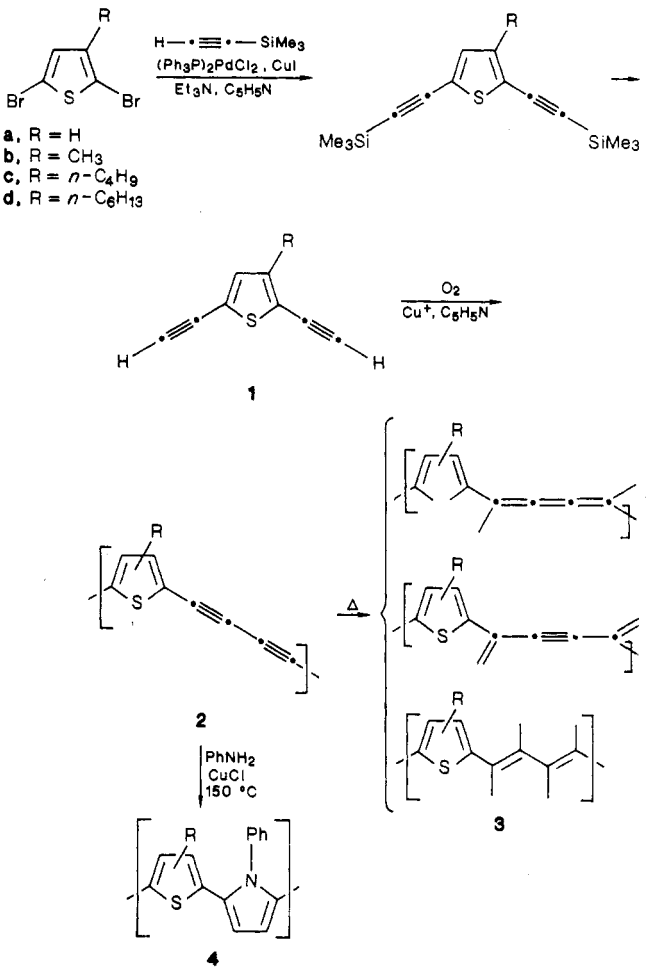


Figure 1. ^{13}C CPMAS spectra of **2b** and **3b**: *, spinning sideband.

Scheme I



linked density. Reaction exotherms (DSC, maxima) were observed at 179 °C (121 cal/g), 206 °C (108 cal/g), 210 °C (66 cal/g), and 222 °C (24.3 cal/g) for **2a–d**, respectively, with **2b–d** exhibiting secondary exotherms at 352 °C (28 cal/g), 375 °C (57 cal/g), and 350 °C (28.8 cal/g), respectively. These secondary exotherms are associated with decomposition reactions that can be attributed to the alkyl side chains and are the temperatures at which some weight loss (TGA, nitrogen atmosphere) takes place. Crystalline diyne monomers and layered diyne structures are known to undergo polymerization reactions to yield conjugated structures.[11] Thus pressing powders of **2a,b** at these reaction temperatures (30 000 psi) produces black pellets having a metallic luster, and heating films of **2c** and **2d** yields shiny black films. All of these cross-linked materials are thermally stable, exhibiting only 5% weight loss at ~600 °C (TGA) and 10% weight loss at ~700 °C under argon.

The solid-state ^{13}C spectrum (CP/MAS) of **3b** was quite different than that exhibited by **2b**. The strong sp carbon peak at ~80 ppm disappears in the spectrum of the pyrolyzed product (**3b**) and the intensity of the sp^2 peaks in the 110–160 ppm region increases. The absence of the absorption (Figure 1 shows a spectrum of partially thermally converted material) in the sp region for acetylenic carbons and the absence of absorption in the allenic carbon region (~200 ppm) suggest that the structure of the cross-linked product corresponds to neither of the first two representations of **3**, structures that have been written as the product of polymerization of certain conjugated diynes,[11a-c] but instead corresponds to the third representation which contains (with the exception of the methyl group) all sp^2 carbons.[10f,g] This material also exhibits a broad EPR signal centered at 3477 G.

Polymers containing the 1,3-butadiyne units also undergo reactions with primary amines and hydrogen sulfide.[12] The reaction of **2d**, for example, with aniline yields the unique, chloroform-soluble polymer (**4d**) containing alternating thiophene and pyrrole units. Polymer **4** contains a 1:1 ratio of sulfur and nitrogen (elemental analyses) and shows no DSC exotherm and the correct ratio of aryl to alkyl protons in the ^1H NMR spectrum.

Concentrated solutions of the soluble polyacetylenes, for example, **2c** in tetrachloroethane, are anisotropic. Coherent films could be cast from these solutions, and pyrolysis at 200 °C produced a shiny, metallic film (**3c**). The electrical properties of these materials will be reported in due course.

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Registry No. **1a**, 79109-72-1; **1b**, 116954-12-2; **1c**, 116954-14-4; **1d**, 116954-16-6; **2a**, 84154-54-1; **2b**, 116954-13-3; **2c**, 116954-15-5; **2d**, 116954-17-7; $PhNH_2$, 62-53-3; 2,5-dibromothiophene, 3141-27-3; 2,5-dibromo-3-methylthiophene, 13191-36-1; 2,5-dibromo-3-butylthiophene, 116971-10-9; 2,5-dibromo-3-hexylthiophene, 116971-11-0.

Supplementary Material Available: Physical characteristics, ^1H and ^{13}C NMR, and elemental analyses of 2,5- and 2,5,3-substituted thiophenes and **1a–d**, **2a–d**, and **4d** (2 pages). Ordering information is given on any current masthead page.

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Fluorescence Evidence of Shear Flow-Induced Miscibility in a Blend of Polystyrene and Poly(vinyl methyl ether)

Introduction. Flow may cause molecular mixing of an otherwise phase-separated polymer blend, at least at temperatures near the coexistence temperature. It has been observed that polymer blends become transparent in shear[1] and in planar extension.[2] This was attributed to a transition from a phase separated to a molecularly mixed state. However, the optical transition can be equally well-explained by a size reduction of the composition fluctuations instead of mixing on a molecular scale. This question will be resolved in this study, using the fluorescence quenching technique[3,4] with PS/PVME as a model polymer blend.

The few early studies of the effect of flow on polymer blends (without solvent) conclude that shear and extension increase blend miscibility. Mazick and Carr[1] observed that the lower critical solution temperature (LCST) of a PS/PVME blend increases by 2-7 K at shear rates of 0.1-20 s^{-1}. Katsaros et al.[2] stretched a similar blend in a planar stagnation flow and found that an extensional field at extension rates of about 1 s^{-1} induces miscibility up to 10 K above the cloud point. Lyngaae-Jörgensen and Söndergaard[5] found a homogeneous structure in a sheared blend of SAN and PMMA above the LCST. However, their shear rates were extremely high (>10^3 s^{-1}). The effect of flow seems to differ for polymer solutions, for which most of the reports[6-10] indicate that flow narrows the miscibility gap.

In our experiments, using flow between parallel disks, we have prepared transparent blends by shearing samples above the LCST where they were initially phase separated. However, the question remained whether shear flow actually mixed the blend on a molecular level or if it simply reduced the composition fluctuations to a small scale, too small to scatter light. The decisive answer will be given by applying a fluorescence quenching technique[3,4] to our experiment.

Experiment. Materials. Polystyrene, M_w = 348.000, polydispersity = 1.9, supplied by Monsanto (Lustrex 101) was blended with poly(vinyl methyl ether), M_w = 48 000, polydispersity = 1.9, at weight ratios between 15 and 85 wt % PS. A labeled polystyrene, PS*[11] (chains of molecular weight 300 000 contain dimethylanthracene fluorescent groups in their middle), was added for this study. The PS* chain concentration was less than 7 ppm of anthracenic units to prevent any undesired intermolecular energy transfer.

Shear Flow. Samples were sheared on a Rheometrics mechanical spectrometer using parallel disks with a diameter of $2R$ = 25 mm. Disposable disks were used so that the sample could be removed quickly (15-30 s after the cessation of shear) from the shaft and the quenched below the glass transition temperature. A shear rate of $\dot{\gamma}_R$ = 0.16 s^{-1} was applied for 4 min (sample A) and 12 min (sample B), 3 K above the cloud point temperature ("*" in Figure 2). In this geometry, the shear rate is a linear function of the radius:

$$\dot{\gamma}(r) = \dot{\gamma}_R r/R$$

The shear rate is maximum at the outer edge ($r = R$) and decreases to zero at the center of the disk ($r = 0$).

Digitized Image. White light transmission pictures of the samples were obtained on Kodak SO 163 film. This film was digitized with an array of 256 × 256 pixels on an Optronix digitizer with an aperture of 100 μm and digitized step of 100 μm.

Fluorescence Emission and Transmission. Fluorescence emission measurements were performed under continuous illumination on a microscope developed at Laboratoire PCSM. PS* excitation and fluorescence emission were probed at wavelengths around 365 and 440 nm, respectively, by means of filters. The diameter of the illuminating beam was 1 mm. Fluorescence intensities were measured at nine radial positions r/R = 0, 0.2, 0.4, 0.6, and 0.8 of the disk-shaped samples.

Transmittance measurements as a function of r/R were carried out on the same equipment, by inserting identical filters (365 nm) on both excitation and emission beams. Fluorescence intensities were normalized by the maximum value at $r = 0$ and were corrected in order to take into account the thereby observed changes in turbidity. Data were also corrected for the changes in specimen thickness along the diameter, but this effect is actually very small.

Results and Discussion. Cloud Point Temperature with Constant Shear Stress. In order to have a macroscopic idea about the influence of the shear flow on the apparent phase diagram, we use a cone and plate apparatus, keeping the shear stress constant. From the one-phase region (20 K below the cloud point temperature at quiescent state), the temperature was slowly increased, and the changing viscosity, η, at constant shear stress was measured. Phase separation results in an upturn of the viscosity-temperature curve. Additional information is given by optical clarity of the sample.

The viscosity-temperature plot changes its slope at the transition from phase separated to mixed state. Typical results for a 44/56 PS/PVME mixture are shown in Figure 1. Other compositions from 15% to 75% (wt) PS show a similar behavior, and the apparent "cloud points" depend on the stress level, as shown in Figure 2. These data were obtained with a slow heating rate of 0.3 K/min and a reproducibility of about ±1 K. The upward shift of the phase diagram increases with the applied shear stress.

Digitized Image Analysis. The optical density variation of the sample is presented in Figure 3, in terms of

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