

# Environmentally Stable Conductive Polymers from Bis(Ethynylstyryl) Benzene Monomers

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## SYNOPSIS

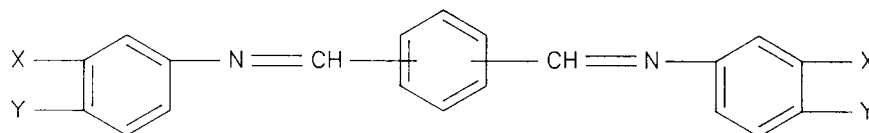
Several completely conjugated, all-carbon-hydrogen acetylene-terminated monomers, bis(ethynylstyryl)benzenes, were synthesized using the Wittig reaction with ethynylbenzaldehyde and xilyldiphosphonium salts. These prepolymers were thermally polymerized in the melt phase into thermally stable materials that can be further processed into conductive polymers having high stability to aggressive environments. Conductivity can range from that of an insulator to  $10^{+2}$  s/cm. The room temperature conductivity is unchanged by extended exposure to boiling water or 500°C in an inert atmosphere. With proper design of the monomers' structures, they will melt sufficiently below the polymerization temperature to provide an adequate time in the liquid state for ease of processing. Once cured into the solid form, the materials are intractable and exhibit high stability to aggressive environments.

## INTRODUCTION

We have undertaken the synthesis and study of highly conjugated polymers that do not require the addition of a dopant to make them electrically conducting. The approach has been to synthesize completely conjugated monomers or prepolymers that can be melt (thermally) cured through reactive terminal groups that form conjugated/aromatic linking structures to generate an "infinitely" conjugated polymer network. This approach has resulted in stable, intrinsically conducting polymers

with conductivities as high as  $10^{+2}$  s/cm. Exposure of these materials to boiling water for 1000 h or temperatures as high as 500°C for 500 h in an inert atmosphere does not decrease conductivity.<sup>1,2</sup> To develop the extended conjugation necessary for conductivity, the polymers must be processed at 400–700°C. Although the high-temperature processing results in some weight loss and shrinkage, the mechanical properties (tensile strength, modulus) are not degraded. In fact, these properties increase with higher processing temperatures.<sup>3</sup>

Structure I illustrates some of the prepolymers described in our earlier work:



where X = Y = CN or X = C≡CH and Y = H

Structure I

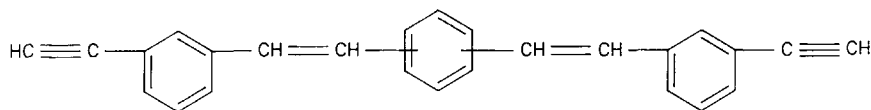
In the present work, we will describe the synthesis, characterization, polymerization, conductivity, and stability of a new system in which the imine groups (—N=CH—) in Structure I were replaced by —CH=CH— as illustrated by Structure II:

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**Structure II** 1,3-isomer**Structure III** 1,4-isomer

## EXPERIMENTAL

### Measurements

Infrared spectra were measured on a Perkin-Elmer model 1800 FTIR spectrophotometer. Solid samples were dispersed in anhydrous KBr and pressed into a pellet in a minidie, and liquid samples or melts were deposited as films on KBr plates. Nuclear magnetic resonance (NMR) measurements were obtained on a Varian EM-390, 60 MHz, instrument using tetramethylsilane (TMS) as reference and  $\text{DCCl}_3$  as the solvent.

Thermal analyses were measured on a Dupont 2100 system using a Model 910 DSC (differential scanning calorimeter) and a Model 951 TGA (thermogravimetric analyzer) and either compressed nitrogen or air at a flow rate of 75 mL/min. Heating rates were  $10^\circ\text{C}/\text{min}$ .

Conductivities were measured by the four-point probe technique with an Alessi four-point probe head, a Keithley 225 current source, and a 616 digital electrometer (Ref. 1, p. 975). The voltage drop was measured at several different currents (e.g., 1, 2, 4, 8 mamp) and at forward and reverse polarity to ensure that the measurements obeyed Ohm's law. Since the samples were large compared to the spacing between the probes, the following equation<sup>9</sup> was used to calculate the conductivity from the current and voltage:

$$\sigma = \frac{I}{2\pi SV}$$

where  $\sigma$  = conductivity in  $\text{s}/\text{cm}$  or  $(\Omega\text{-cm})^{-1}$ ,  $I$  = current,  $V$  = voltage, and  $S$  = spacing between probes (0.1 cm).

### Thermal Cure/Processing

Samples were usually cured in air up to  $300^\circ\text{C}$  for 50 h. Samples were postcured at higher temperatures ( $400$ – $900^\circ\text{C}$ ) in an argon atmosphere that was first passed through an Altech Associates oxygen ab-

sorber (Oxy-Trap, Catalog No. 002). Heating and cooling rates were  $0.5^\circ\text{C}/\text{min}$  and controlled by a microprocessor.

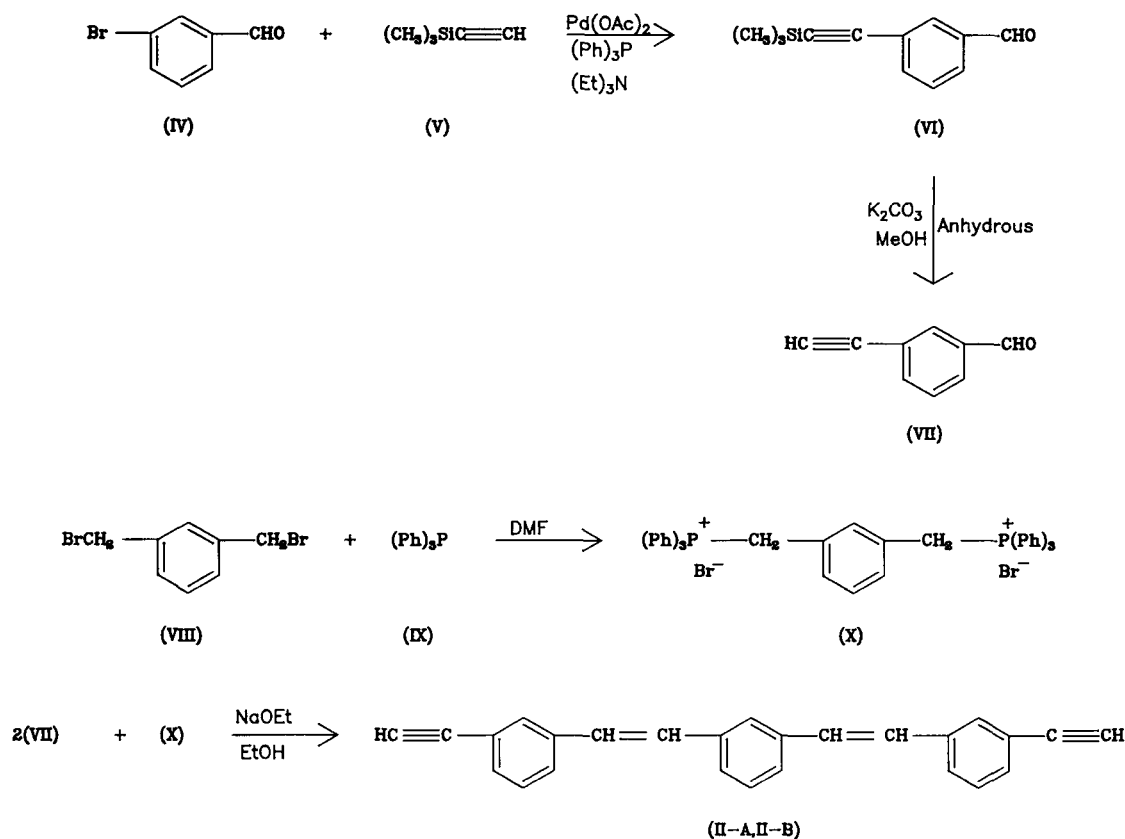
### Synthesis/Characterization

The prepolymers, 1,3- and 1,4-bis(3-ethynylstyryl)benzene, **II** and **III**, were prepared by the classical Wittig reaction for the synthesis of olefins.<sup>4</sup> Scheme 1 illustrates the preparation for the 1,3-isomer.

Both the 1,3- and 1,4-diacetylenes are new compounds, but the intermediates to prepare them have been reported.<sup>4,5</sup>

The 3-ethynylbenzaldehyde (**VII**) was prepared by the method of Austin, et al.,<sup>6</sup> in which the bromine in 3-bromobenzaldehyde (**IV**) is displaced by trimethylsilylacetylene (**V**) (Petrarch Systems) in the presence of palladium acetate, triphenyl phosphine, and triethyl amine to give 3-[2-(trimethylsilyl)ethynyl]benzaldehyde (**VI**). The ethynylbenzaldehyde (**VII**) is obtained by removing the trimethylsilyl group with anhydrous  $\text{K}_2\text{CO}_3$  in anhydrous methyl alcohol. Overall yield was 71%; mp  $76$ – $78^\circ\text{C}$  (literature:  $76$ – $76.5^\circ\text{C}$ ); FTIR (KBr dispersion):  $\equiv\text{C}-\text{H}$   $3250\text{ cm}^{-1}$  (s),  $-\text{C}\equiv\text{C}-$   $2104\text{ cm}^{-1}$  (w),  $\text{C}=\text{O}$   $1698\text{ cm}^{-1}$  (s); NMR ( $\text{CDCl}_3$ , TMS):  $\equiv\text{C}-\text{H}$  3.15 ppm (s), Ar-H 7.40–7.98 ppm (m), Ar-C(O)H 10.01 ppm (s).

The bis-triphenylphosphonium salt of  $\alpha,\alpha'$ -dibromo-*m*-xylene (**X**) was prepared in 95% yield by reacting dibromoxylene (**VIII**) with a 5% excess of triphenylphosphine (**IX**) in refluxing DMF under argon. Approximately 80% of the DMF was stripped off under vacuum using a rotating evaporator, and the crude product precipitated by addition of toluene to the remaining solution. The product was isolated by filtration, washing with toluene, and vacuum drying at  $120^\circ\text{C}$ . A very strong absorption at  $1110\text{ cm}^{-1}$  is characteristic of this phosphonium salt. The 1,4-phosphonium salt was prepared from  $\alpha,\alpha'$ -dibromo-*p*-xylene (Eastman) by the same procedure with similar yields. Both the 1,3- and 1,4-phos-



Scheme 1

phonium salts have been previously reported by Friedrich and Henning.<sup>5</sup>

#### Typical Synthesis of 1,3-Bis(3-ethynylstyryl)Benzene (II)

A 500 mL, three-neck flask was fitted with a  $\text{N}_2$  inlet tube, a 125 mL dropping funnel, thermometer, a condenser open to the atmosphere, and a magnetic stirrer. The system was flushed with nitrogen, and this atmosphere was kept over the solution during the reaction. The dried bis-phosphonium salt (**X**, Scheme 1), (9.09 g,  $1.15 \times 10^{-2}$  mol), the ethynylbenzaldehyde (**VII**, Scheme 1), (3.30 g,  $2.54 \times 10^{-2}$  mol, 10% excess), and 150 mL anhydrous ethyl alcohol were placed in the flask. Sodium metal (0.64 g,  $2.78 \times 10^{-2}$  mol) was slowly added to 125 mL of anhydrous ethyl alcohol in the dropping funnel. After all sodium had dissolved, stirring was started and 50 mL of the EtOH–NaOEt solution added rapidly over a 1 min period. After the remaining NaOEt–EtOH solution was added dropwise over 15 min, stirring was continued at room temperature for 2 h. The reaction was followed by IR by observing

the disappearance of the aldehyde absorption at  $1698 \text{ cm}^{-1}$ , a shift in the  $\text{—C}\equiv\text{CH}$  absorption from  $3255 \text{ cm}^{-1}$  in the aldehyde to  $3290 \text{ cm}^{-1}$  in the product, and the appearance of triphenylphosphine oxide.

It should be noted that the bis-styrylbenzenes can exist in three isomeric forms, a *trans-trans*, a *cis-cis*, and a *trans-cis* form. Two products (**II-A** and **II-B**) were isolated from the reaction that correspond to Structure **II** in Scheme 1. They differ by the relative amounts of *cis* and *trans* structure present. The initial product (**II-A**) was precipitated by addition of 150 mL of water to the reaction mixture, isolated by filtration, and washed with 2 : 1 EtOH– $\text{H}_2\text{O}$ . A second viscous, liquid product (impure **II-B**) was recovered from the filtrate by careful re-filtration and isolated by dissolving in  $\text{CH}_2\text{Cl}_2$  and final removal of solvent.

The initially isolated soft, solid product (**II-A**) (41% yield) is reasonably pure by IR, NMR, and carbon/hydrogen analysis (Table I). The viscous liquid product is contaminated with triphenylphosphine oxide, a byproduct from the reaction. By passing a solution of this material in toluene through an acidic  $\text{Al}_2\text{O}_3$  column, the triphenylphosphine ox-

**Table I** Properties of 1,3- and 1,4-Bis(3-Ethynylstyryl)Benzene

Properties	1,3-Isomers ( <i>cis-trans</i> Mixtures)		1,4-Isomer
	II-A Soft Solid	II-B Viscous Liquid	III Crystallized Solid
Isomer composition	High in <i>trans</i>	High in <i>cis</i>	All <i>trans</i>
Melting point	Cloudy melt $\approx 40^\circ\text{C}$ Clear liquid $\approx 120^\circ\text{C}$	—	183–185°C
Carbon/Hydrogen analysis			
Carbon (%) (94.51) <sup>a</sup>	94.20	94.94	93.96
Hydrogen (%) (5.49) <sup>a</sup>	5.62	5.69	5.85
FTIR absorption <sup>d</sup> (cm <sup>-1</sup> )			
$\equiv\text{C}-\text{H}$	3296 (s) <sup>b</sup>	3292 (s) <sup>c</sup>	3294 (s) <sup>b</sup>
$-\text{C}\equiv\text{C}-$	2105 (w)	2106 (w)	2108 (vw)
<i>trans</i> —CH=CH	960 (s)	960 (m)	968 (s)
Proton NMR <sup>e</sup> (ppm)			
$\equiv\text{C}-\text{H}$	3.05, 2.98 (d)	3.05, 2.99 (d)	3.07 (s)
Ar—H, —CH=CH—	7.66–6.50 (m)	7.59–6.51 (m)	7.68–7.11 (m)

<sup>a</sup> Theoretical.<sup>b</sup> KBr dispersion.<sup>c</sup> Liquid film on KBr plate.<sup>d</sup> Relative intensity: s = strong, m = medium, w = weak, vw = very weak.<sup>e</sup> s = singlet, d = doublet, m = multiplet.

ide is completely removed and a yield of 40% of theory is obtained. The total yield of solid and liquid phases is 81%.

### Synthesis of 1,4-Bis(3-Ethynylstyryl)Benzene III

The procedure was essentially as described for the 1,3-isomer except that the bis-triphenylphosphonium salt of  $\alpha,\alpha$ -dibromo-*p*-xylene was used. Into a 1 L flask equipped with a magnetic stirrer, Claisen adaptor, pressure-equalizing dropping funnel, and nitrogen inlet, 6.00 g ( $4.61 \times 10^{-2}$  mol) of 3-ethynylbenzaldehyde, 18.18 g ( $2.31 \times 10^{-2}$  mol) of the dried phosphonium salt, and 30 mL of anhydrous ethyl alcohol were placed. Not all the materials dissolved and a slurry was formed. Another 250 mL of anhydrous ethyl alcohol was placed in the dropping funnel and 1.08 g ( $4.70 \times 10^{-2}$  mol) of Na were added over a 30 min period. Approximately 100 mL of the NaOEt—EtOH solution was added rapidly over 1–2 min to the stirred reaction mixture under a nitrogen atmosphere and then the remainder was added dropwise over about 15 min; little or no heat was produced during the addition. The reaction mixture was stirred at room temperature for 6 h during which time chunks of the salt had to be man-

ually broken up in the reaction flask. The reaction was terminated by addition of 200 mL water. The product (III) was isolated and purified by filtration of the refrigerated cooled solution, recrystallization from benzene, and vacuum drying at 50°C. Yield was 0.72 g (9.4%), and mp, 183–185°C. Only the all-*trans-trans* isomer was obtained in this preparation. We do not know why the overall yield is so low, but a repeat of this same procedure gave similar results. Attempts were not made to improve on the yield since, as will be more fully discussed later, the processing window (melting point vs. temperature of cure) is so narrow that the 1,4-isomer is not a practical material for melt polymerization technique. Table I summarizes the spectral properties and carbon/hydrogen analyses for the new materials (II-A, II-B, and III) described in this paper.

The 1,4-bis(3-ethynylstyryl)benzene was isolated in the pure *trans-trans* form as indicated by a reasonably sharp melting point and a very strong absorption at 968 cm<sup>-1</sup> in the IR.<sup>7</sup> The presence of a chemical shift at 7.11 ppm in the proton NMR appears to be indicative of a *trans* configuration, and the lack of any absorption between 7 and 6.5 ppm appears to be indicative of the absence of a *cis* configuration for this system.

Table II

Post-Processing Conditions <sup>a</sup>		II-B 1,3-Bis(3-ethynylstyryl)-benzene ( <i>cis</i> rich)		II-A 1,3-Bis(3-ethynylstyryl)-benzene ( <i>trans</i> rich)		III 1,4-Bis(3-ethynylstyryl)-benzene (all <i>trans</i> )		I (X = —C=CH, Y = H) N,N'-(1,4-Phenylene-dimethyldiynyl)bis(3-ethynylaniline) (all <i>trans</i> )	
Temp (°C)	Time (h)	% Wt loss	Cond (s/cm)	% Wt loss	Cond (s/cm)	% Wt loss	Cond (s/cm)	% Wt loss	Cond (s/cm)
400	100	3.49	<sup>b</sup>	3.50	<sup>b</sup>	7.87	<sup>b</sup>	5.51	$2.98 \times 10^{-9}$ <sup>c</sup>
500	100	9.09	<sup>b</sup>	11.37	<sup>b</sup>	14.26	<sup>b</sup>	10.81	$1.60 \times 10^{-5}$
600	100	12.08	$3.93 \times 10^{-2}$	16.18	$2.40 \times 10^{-1}$	18.75	$1.60 \times 10^{-1}$	13.73	$3.30 \times 10^0$
700	100	14.32	$1.46 \times 10^1$	19.09	$2.11 \times 10^1$	21.57	$1.72 \times 10^1$	14.10	$3.7 \times 10^1$
900	5			20.66	$9.30 \times 10^1$	24.89	$5.00 \times 10^1$	19.11	$7.98 \times 10^1$
1200	5			23.40	$1.76 \times 10^2$	31.85	$9.85 \times 10^1$	21.79	$1.87 \times 10^2$

<sup>a</sup> Heating and cooling rates were 0.5°C/min; argon atmosphere.

<sup>b</sup> Conductivity too low to measure on four-point probe; minimum conductivity that can be measured with our setup is  $10^{-8}$ – $10^{-7}$  s/cm.

<sup>c</sup> Two-point method.

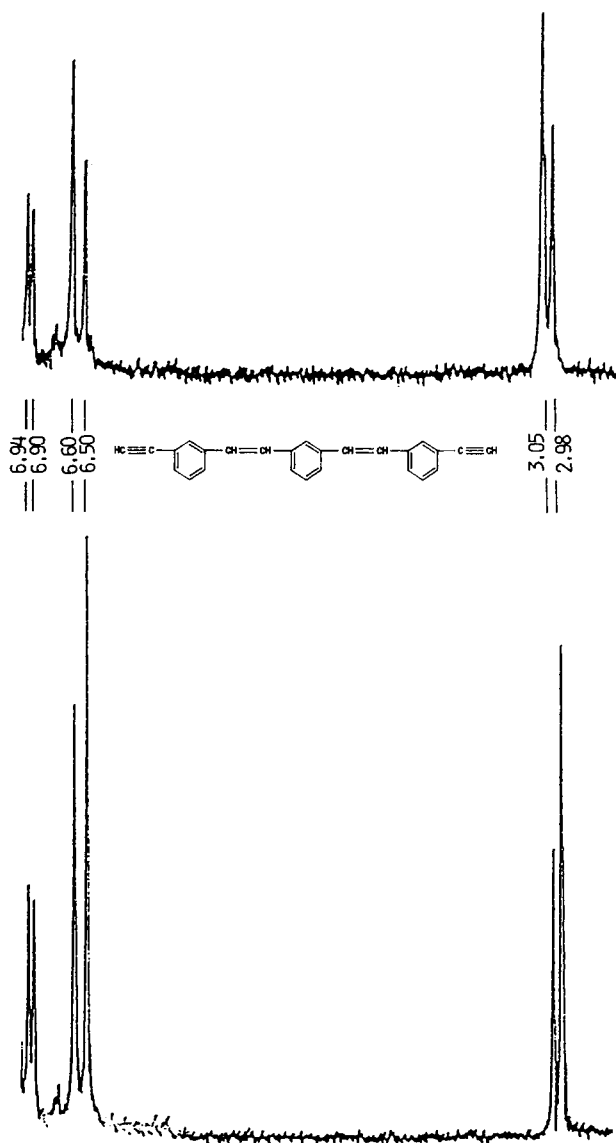
In the case of the 1,3-bis(3-ethynylstyryl)-benzene, pure single geometric isomers were not isolated. Two fractions were obtained: a soft solid (II-A) that is higher in *trans* configuration and a viscous liquid (II-B) that is higher in the *cis* configuration. Since there are two double bonds present, these mixtures may consist of the *trans-trans* and/or *trans-cis* and/or *cis-cis* structures. The IR absorption spectra are qualitatively the same for both mixtures (when both are run as liquid films), but some absorption intensities are different. For example, as might be expected, II-A has a stronger absorbance at  $960\text{ cm}^{-1}$  than does II-B. (Note that this *trans* absorption occurs at  $962\text{ cm}^{-1}$  in *trans*-stilbene and is completely absent in *cis*-stilbene.)

This paper will not attempt to resolve completely the question of the *cis-trans* isomer distribution present in each fraction (II-A and II-B). However, by using proton NMR spectra for *trans*- and *cis*-stilbene and phenylacetylene as models, and proton NMR results from our earlier work<sup>8</sup> on the all-*trans*-imine structures (Structure I), we believe that we observe some *cis-trans* correlation in the proton NMR region between the 7.1–6.5 ppm region and the 3.00 ppm region (Fig. 1). In the case of the proton NMR spectra of the all-*trans* (*trans-trans*)-imine acetylene-terminated prepolymers<sup>8</sup> and the *trans-trans*-1,4-bis(3-ethynylstyryl)benzene (this paper), we see only one singlet for the acetylenic hydrogen between 3.10 and 3.05 ppm. In the case of

the *trans/cis* mixtures, we see two peaks: one in the same region as above (3.05 ppm) and one at 2.98 ppm. The peak at 3.05 ppm is consistent for the acetylenic hydrogen in the *trans* environment, and the peak at 2.98 ppm, in the *cis* environment. Similarly, the peak at 6.60 ppm appears related to the *trans*-olefinic hydrogens in the all-*trans* or *trans-cis* environment, and the peak at 6.50 ppm, to the *cis*-hydrogen is the all-*cis* or *trans-cis* environment. We believe that the doublet at 6.94, 6.90 ppm is pure *cis* and the singlet at 7.10 ppm is pure *trans*. Integration of peak areas gives tentative values of a 65% *trans*; 35% *cis* distribution for the solid product, II-A; and 37% *trans*, 63% *cis* distribution for the liquid product, II-B. Although a definitive analysis should wait until the pure *trans-trans*, *cis-cis*, and *trans-cis* isomers can be isolated, it is believed that this tentative analysis might be useful.

### Thermal Analysis

Figure 2 shows the DSC thermogram for the all-*trans*-1,4-bis(3-ethynylstyryl)benzene (III). An exothermic transition beginning around 135°C (more obvious when the plotting scale is expanded) is caused by the thermal polymerization of the acetylene groups. At a slightly higher temperature, an endothermic melting transition occurs that initially overrides the ongoing exothermic cure. When the



**Figure 1** Proton NMR (ppm) of *trans*-rich (II-A) and *cis*-rich (II-B) isomers of structure II.

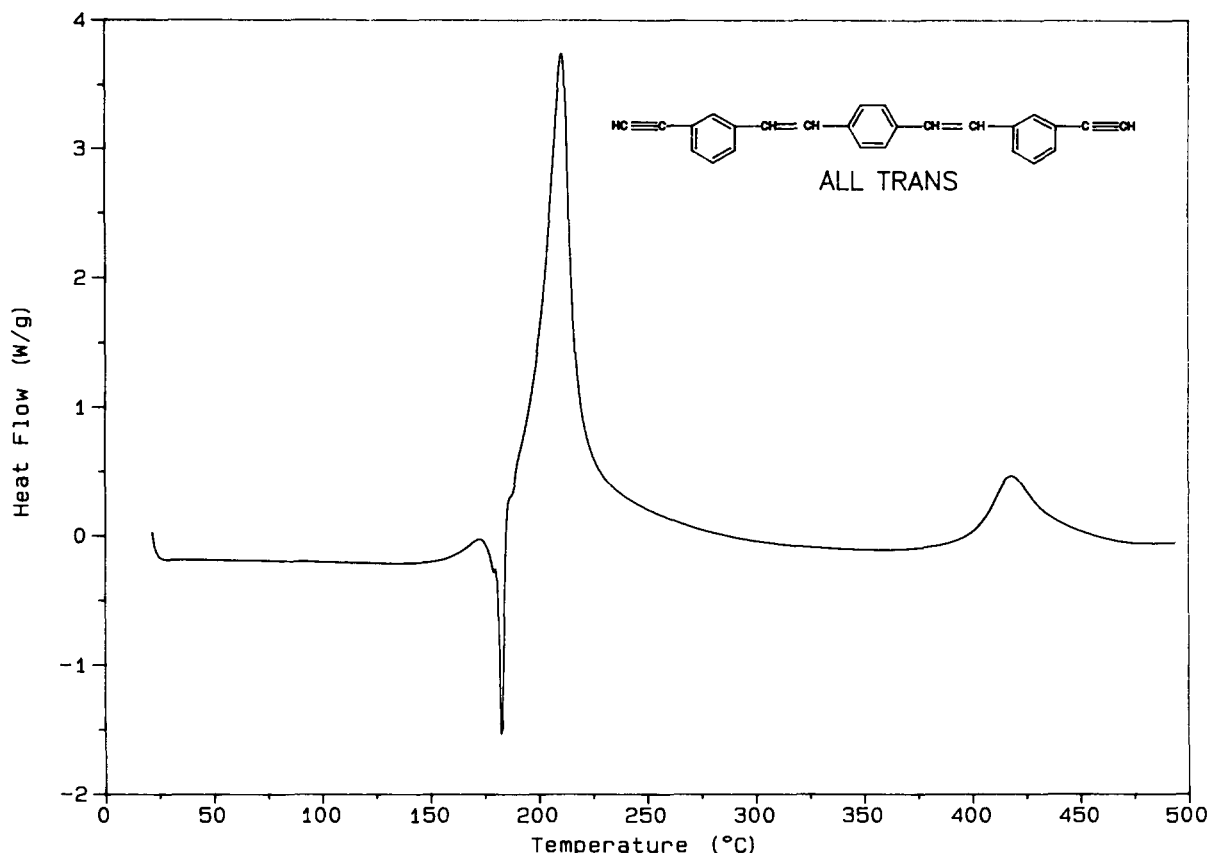
melting process is completed, the energetics of the polymerization dominate at higher temperature and the typical, strong exothermic peak for the acetylene polymerization is observed, with its maximum at 210°C. Because both the endothermic melting and exothermic polymerization are occurring at the same time, it is difficult to calculate an accurate heat of polymerization; it is probably more than 700 J/g (55.2 kcal/mol). These are extremely energetic reactions.

It is apparent from the DSC profile that this 1,4-isomer does not represent a very practical system for melt polymerization because the very rapid cure

at the melting point provides little or no time in the liquid phase for processing. Attempting to process large amounts of the resin could result in a "run-away" reaction. We have been able to prepare cured samples for further evaluation by rapidly heating small amounts of resin to 190–200°C. Even then, because of the high exotherm at these temperatures, the samples are of poor quality.

The DSC thermograms for the 1,3-bis(3-ethynylstyryl)benzene isomers are shown in Figures 3 and 4. The liquid *cis/trans* isomer mixture (II-B) does not show, of course, an endothermic melting. The soft (amorphous), solid, *cis/trans* isomer mixture (II-A) shows a minor endothermic transition at about 40°C and a broader transition that peaks at approximately 120°C. These transitions occur at the same temperatures for phase changes that are observed when a sample is heated on a melting-point block between glass covers; the sample becomes partially fluid but cloudy at about 40°C and forms a clear melt at 120°C. Because the 1,3-isomers are in a homogeneous liquid state at least 30° below the cure temperature, they have a good processing window, that is, the melts can be held at 120–125°C for several hours without a significant change in viscosity. The materials will gel in 1 h at 150°C. With quantitative and calibrated DSC, the heat of polymerization was shown to be 711 J/g (56.2 kcal/mol) for the *trans*-rich, amorphous solid isomer mixture (II-A) and 814 J/g (64.3 kcal/mol) for the *cis*-rich, viscous liquid isomer mixture (II-B). The approximate 12–13% difference between the heats of polymerization for the two isomer mixtures may be due to differences in the base-line selection for the area calculation in the two  $\Delta H$  curves. However, detailed analysis must wait until the development of procedures to isolate pure *cis* and *trans* isomers.

Figure 5 shows a DSC comparison between all-*trans*-1,4-bis(3-ethynylstyryl)benzene (III), the *cis*-rich 1,3-bis(3-ethynylstyryl)benzene (II-B), and the all-*trans*-*N,N'*-(1,3-phenylenedimethylydyne)bis(3-ethynylaniline) (Structure I, X =  $-\text{C}\equiv\text{CH}$  and Y = H, all-*meta* linkage). Except for the melting point endotherms, the transitions for the two all-*trans* isomers are very similar, while the mixed *cis-trans* isomer has a cure exotherm maximum that occurs approximately 12°C higher. This higher maximum is also observed for the other *cis/trans* mixture (II-A). All three materials show a similar, smaller exotherm around 425°C that represents secondary reactions in the temperature range where conductivity is beginning to develop. At present, we do not have a complete understanding of the



**Figure 2** DSC of all-*trans* 1,4-bis(3-ethynylstyryl)benzene (**III**); powder, nitrogen atmosphere; heating rate 10°C/min.

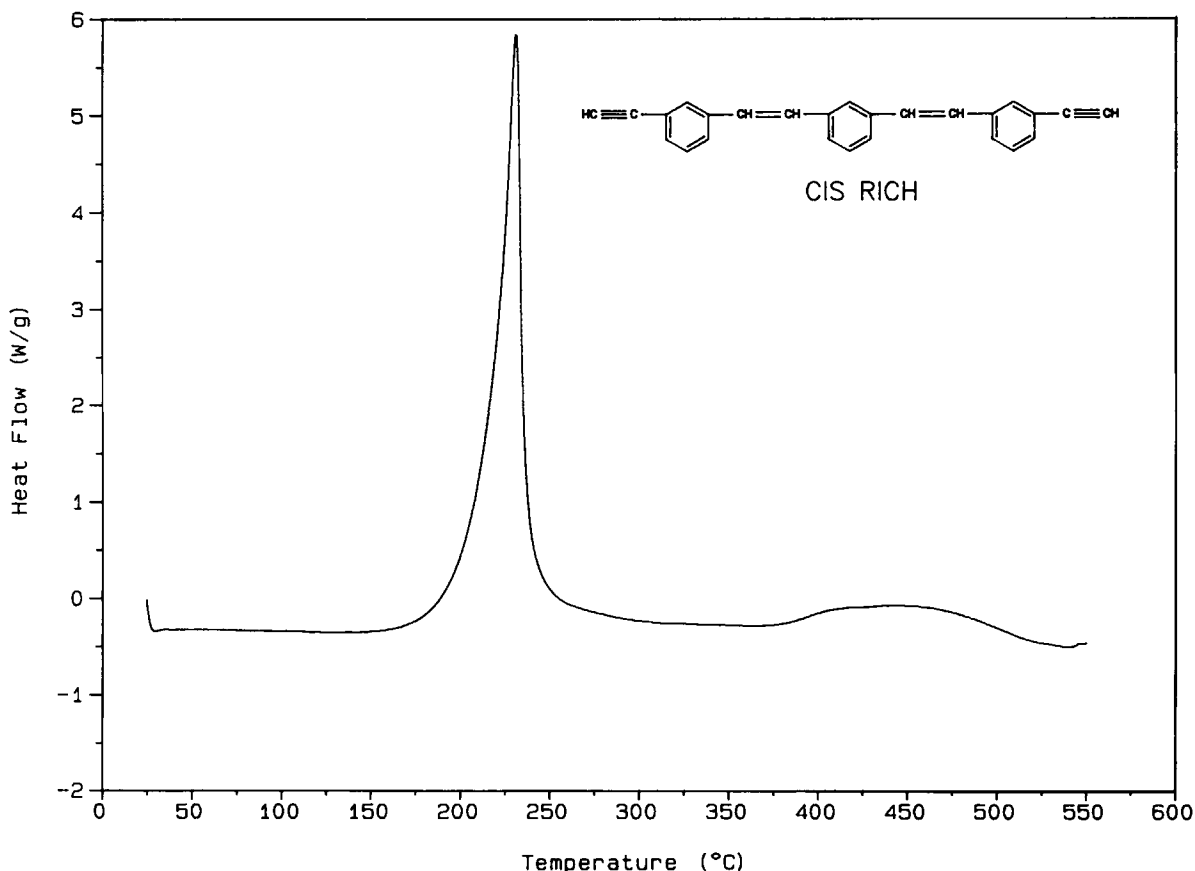
secondary reactions responsible for the development of conductivity; however, we believe that they involve the formation of aromatic and condensed aromatic ring systems from the polyene structures formed initially in the polymerization of the acetylene groups.

The TGAs for the *cis/trans*-1,3-isomer mixtures (**II-A** and **II-B**) are shown in Figure 6 and compared to the all-*meta*, all-*trans* system containing imine linkages  $-\text{N}=\text{CH}-$  in place of the  $-\text{CH}=\text{CH}-$  (Structure I, X =  $-\text{C}\equiv\text{CH}$  and Y = H, all-*meta* linkage). The samples were run as thin films (5–6 mg) cured in the TGA for 10 h at 300°C. The all-carbon/hydrogen systems show excellent TGA stability to 500°C and are very similar in their weight loss to about 600°C. Above 600°C, the *cis*-rich isomer (**II-B**) appears slightly more stable than the *trans*-rich isomer (**II-A**) but the difference is quite small, a little more than 1%.

Compared to the imine analog (Structure I, X =  $-\text{C}\equiv\text{CH}$ , Y = H, all-*meta* linkage), the all-carbon/hydrogen systems (**II-A** and **II-B**) show higher

thermal stability to 575°C, but above this temperature, they show poorer stability with higher weight loss. However, the difference in weight loss is only about 2% for all three materials at 900°C and is not sufficient to differentiate the relative performance of the three materials. This difference will become more evident in the long-term (100 h) exposures discussed later.

In Figure 7, we show the TGA oxidative (air) stability of the three materials after they were heated to 900°C in the previous TGA experiment (Fig. 6). Although these are drastic conditions for organic polymers, these materials show high thermal stability and thus might find application in carbon/carbon composites. As seen in Figure 6, after 900°C in nitrogen in the TGA, all three samples retained better than 80% of their weight, and weight loss was beginning to level off. In air (Fig. 7), these materials begin to show oxidative degradation around 475°C and, as might be expected, are completely consumed at the higher temperatures. Since oxidation will be diffusion-controlled and highly dependent on sample



**Figure 3** DSC of *cis*-rich fraction (II-B) of the *cis/trans* mixture of 1,3-bis(3-ethynylstyryl)benzene; liquid, nitrogen atmosphere; heating rate 10°C/min.

size, shape, and form (film, chip, powder), one should not attempt to make too much of the differences in time/temperature to zero weight once oxidation begins.

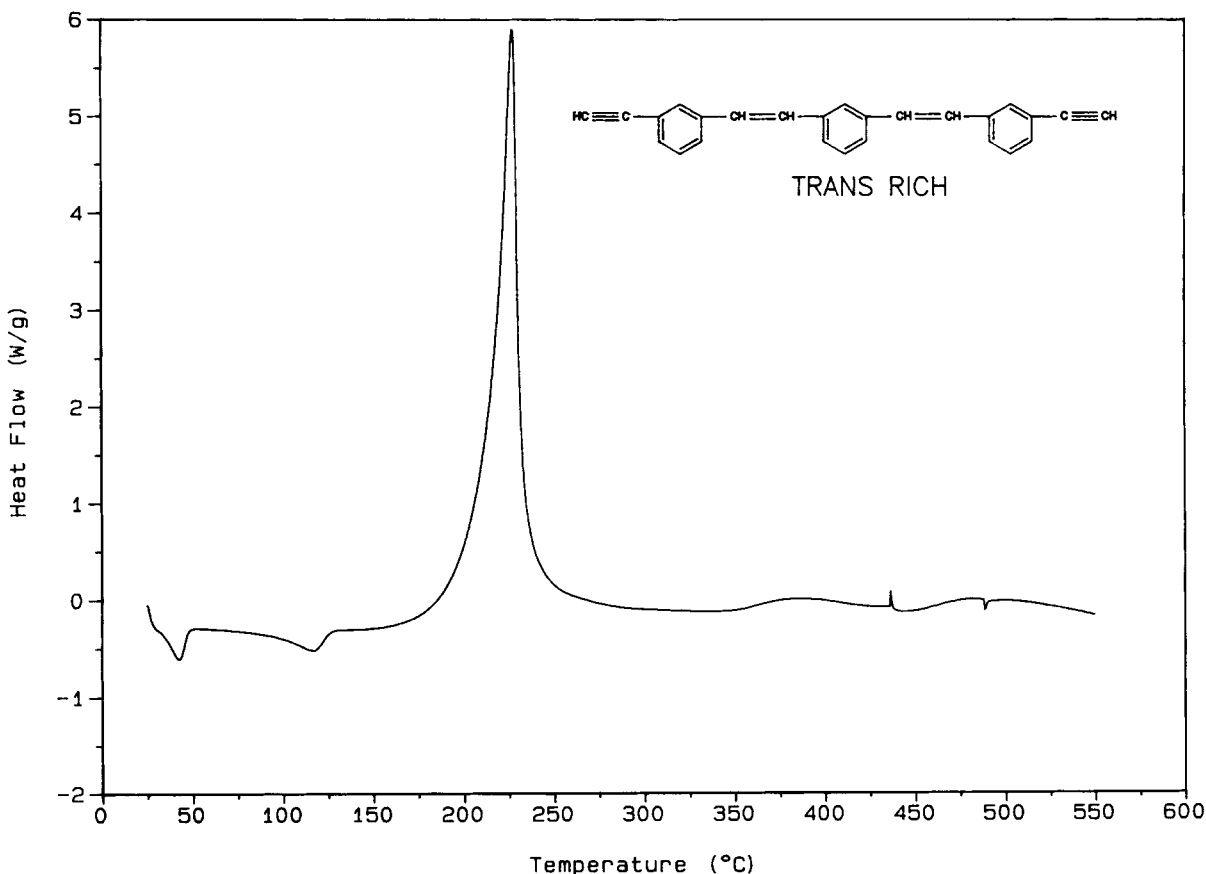
## PROCESSING/CONDUCTIVITY

The *cis/trans*-1,3-isomer mixtures (II-A and II-B) were initially cured in either a glass vial in an oil bath or in an aluminum planchet on a hot plate starting at 130°C. Over a period of 1.5 h, the temperature was gradually increased to 150°C and held there for 1 h. The gelled samples were then immediately transferred to a furnace preheated to 150°C and held there for 1 additional hour. The temperature was increased to 200°C for 1 h, then to 250°C for 1 h, and finally to 300°C for 50 h.

The all-*trans*-1,4-isomer (III) had to be cured by a different approach because it melts substantially

above the temperature where the cure is initiated. It was necessary to rapidly heat the powder sample to 190–200°C to melt it quickly before it cured into an infusible, powdery mass in the solid state. Although this procedure is necessary to obtain a cured material for evaluation, it has the problem that the reaction can become uncontrolled, resulting in substantial decomposition (and weight loss) because of the high energetic exotherm of the reacting acetylene groups at this temperature. Indeed, in our earlier papers,<sup>2,7</sup> we emphasized the importance of controlling the initial cure of these acetylene-terminated resins below 150–160°C. Obviously, with this 1,4-isomer, melt polymerization is not possible with the more gentle cure. By keeping the sample small (0.2 g vs. the usual 2.0 g), we were able to obtain a cured sample for evaluation. The sample was of poor quality in that it contained a number of pinpoint-head-size voids throughout. Indeed, the 1.5% weight loss observed during the cure of the sample (50 h at 300°C) indicated that the sample may have under-





**Figure 4** DSC of *trans*-rich fraction (**II-A**) of the *cis/trans* mixture of 1,3-bis(3-ethynylstyryl)benzene; amorphous powder, nitrogen atmosphere; heating rate 10°C/min.

gone some decomposition that is not observed (less than 0.5% loss) when the normal cure procedure can be followed.

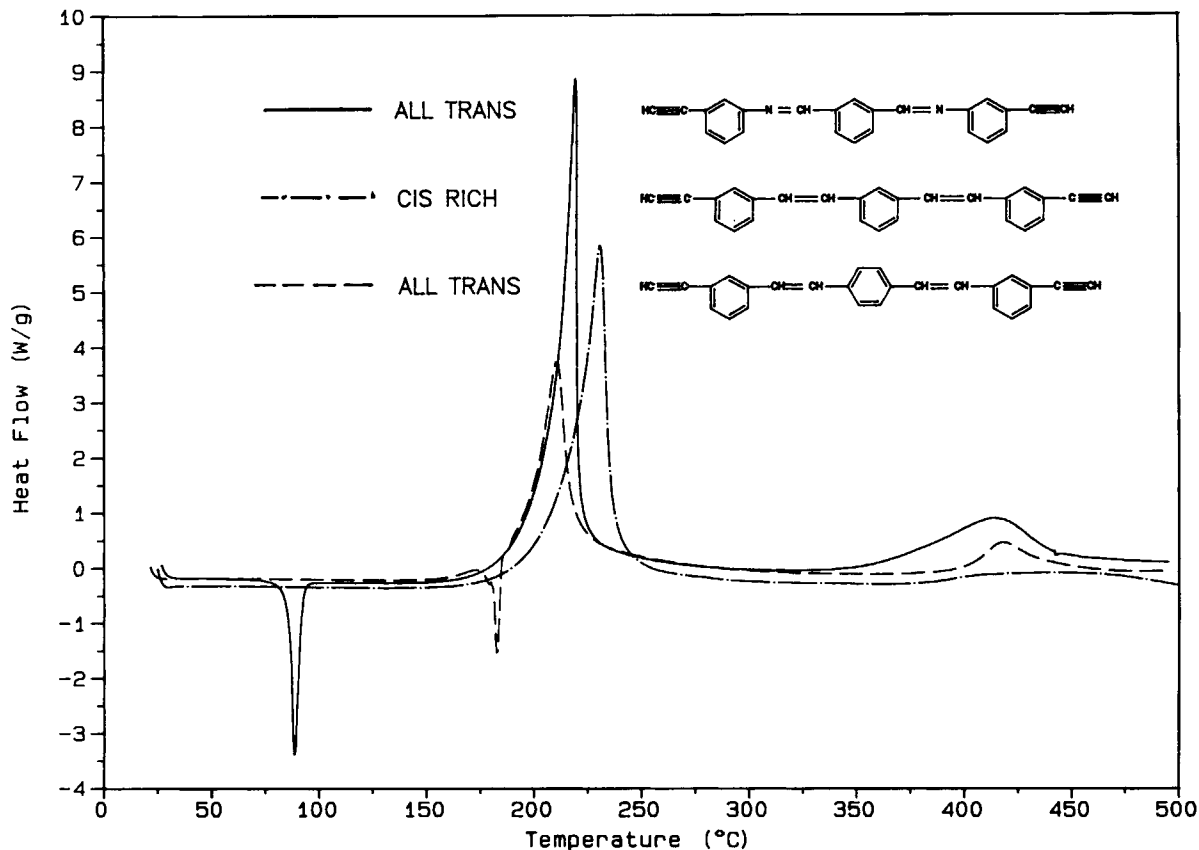
These acetylene-terminated resins do not require 50 h at 300°C to be completely cured. As we have discussed in earlier papers,<sup>1,3,8</sup> these materials are fully cured after 5 h at 300°C. The longer cures are used so comparison can be made with other systems under development that are much less reactive and require longer cure times.

After the initial cure (50 h at 300°C in air), the materials are nonconducting, hard, black solids that assume the shape of the container in which they were cured. To make the materials conductive, their conjugated network must be extended by processing them to higher temperatures in an inert atmosphere. For comparative purposes, the processing conditions are the same as used in earlier papers. Heating and cooling rates were 0.5°C per minute, and samples were held at the specified temperature for 100 h. The weight loss and conductivity for the three ma-

terials described in this paper (**II-A**, **II-B**, and **III**) are summarized in Table II and compared to the all-*trans* isomer of *N,N'*-(1,4-phenylenedimethyldiylidene)-bis(3-ethynylaniline), i.e., the 1,4-isomer of Structure I where X = —C≡CH and Y = —H.<sup>1</sup>

The weight losses reported in Table II are for the cumulative weight loss from the initial cure. For example, the weight loss at 600°C includes the weight loss for 100 h at 600°C, 100 h at 500°C, and 100 h at 400°C. In general, the all-carbon/hydrogen systems (**II-A**, **II-B**, and **III**) show a lower conductivity than does the corresponding imine system (**I**, X = —C≡CH, Y = H, Table II). The difference at the higher processing temperatures (900° and 1200°C) is not as large, probably due to all the materials being eventually converted into very similar, highly aromatic, condensed ring structures.

The *trans*-rich isomer (**II-A**) shows higher conductivity than does the *cis*-rich isomer (**II-B**). The higher conductivity is attributed to the better-ordered packing of the molecules in the *trans* config-

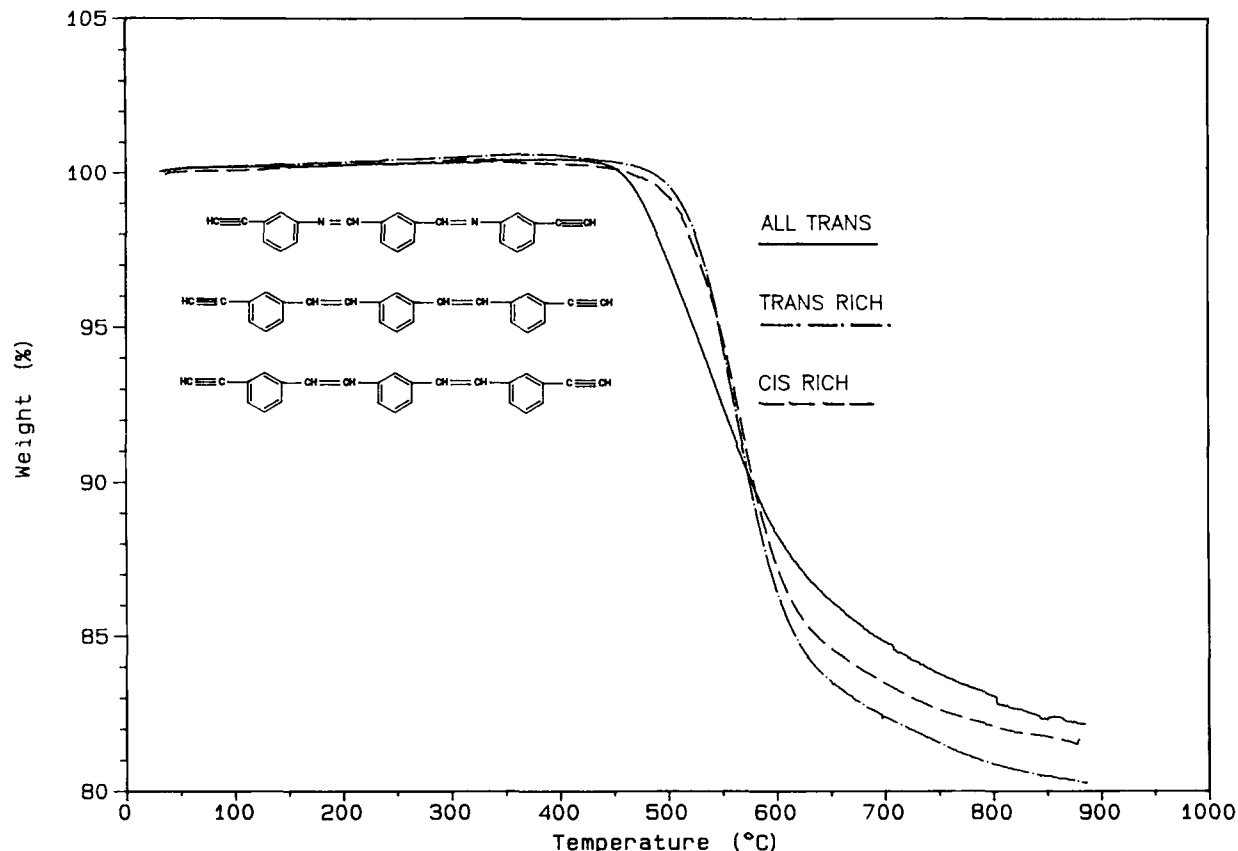


**Figure 5** DSC comparison between all-*trans*  $N,N'$ (1,3-phenylenedimethyldiynyl)bis(3-ethynylaniline) [I, where X =  $-\text{C}\equiv\text{CH}$  and Y =  $-\text{H}$  (—)]; *cis*-rich fraction of the *cis/trans* mixture of 1,3-bis(3-ethynylstyryl)benzene [II-B (- · - ·)]; and all-*trans* 1,4-bis(3-ethynylstyryl)benzene [III (- - -)]; nitrogen atmosphere; heating rate  $10^\circ\text{C}/\text{min}$ .

uration that allows the molecules to be planar with maximum overlap of  $\pi$  orbitals. The *cis* isomer cannot form a planar structure since the phenylacetylene group attached to the *cis* double bond is forced almost  $90^\circ$  out of the plane of the molecule. This interrupts the development of continuous overlap of the  $\pi$  orbitals in the extended conjugation and results in lower mobility of the electrons and thus lower conductivity. Indeed, the high conductivity of the imine-based materials (I) may result from less steric interaction in the *trans*-imine linkage ( $-\text{N}=\text{CH}$ ) compared to the *trans*-olefin linkage ( $-\text{CH}=\text{CH}-$ ) in which an extra hydrogen atom must be accommodated.

In addition to the TGA studies, the weight losses reported in Table II for the long processing times at the high temperatures are indicative of the overall thermal stability of these acetylene-terminated resins. The all-carbon/hydrogen, all-*trans*1,4-isomer (III, Table II) has the poorest thermal stability. We

attribute this poorer thermal stability to the initial high temperature needed to melt this material ( $190^\circ\text{C}$ ) and the violent, energetic reaction that occurs immediately at that temperature. This may lead to some decomposition in the initial polymer structure and thus compromise the polymer stability. Indeed, we had to make several attempts to prepare a material that showed properties as good as reported in Table II. The other three materials (II-A, II-B, and I) can be initially cured at lower temperatures,  $140^\circ\text{C}$  or less, to initiate a very gentle cure. Once the materials have gelled, or almost gelled, the energetic cure has been mostly completed, and one can proceed to higher temperatures without the violent reactions. If one attempts to initially cure these other isomers at  $190^\circ\text{C}$ , very poor quality materials are also obtained. Although the differences in weight loss may not be that significant, it is somewhat curious that the *cis*-rich isomer (II-B) shows the higher thermal stability.



**Figure 6** TGA comparison in nitrogen of three polymers prepared from all-*trans*  $N,N'$ (1,3-phenylenedimethyldiylne)bis(3-ethynylaniline) [**I**, where  $X = -C\equiv CH$  and  $Y = -H$  (—)]; *trans*-rich fraction of the *cis/trans* mixture of 1,3-bis(3-ethynylstyryl)benzene [**II-A** (- · - ·)]; and *cis*-rich fraction of the *cis/trans* mixture of 1,3-bis(3-ethynylstyryl)benzene [**II-B** (- - -)] after 10 h cure at 300°C. Nitrogen flow rate 75 mL/min; heating rate 10°C/min.

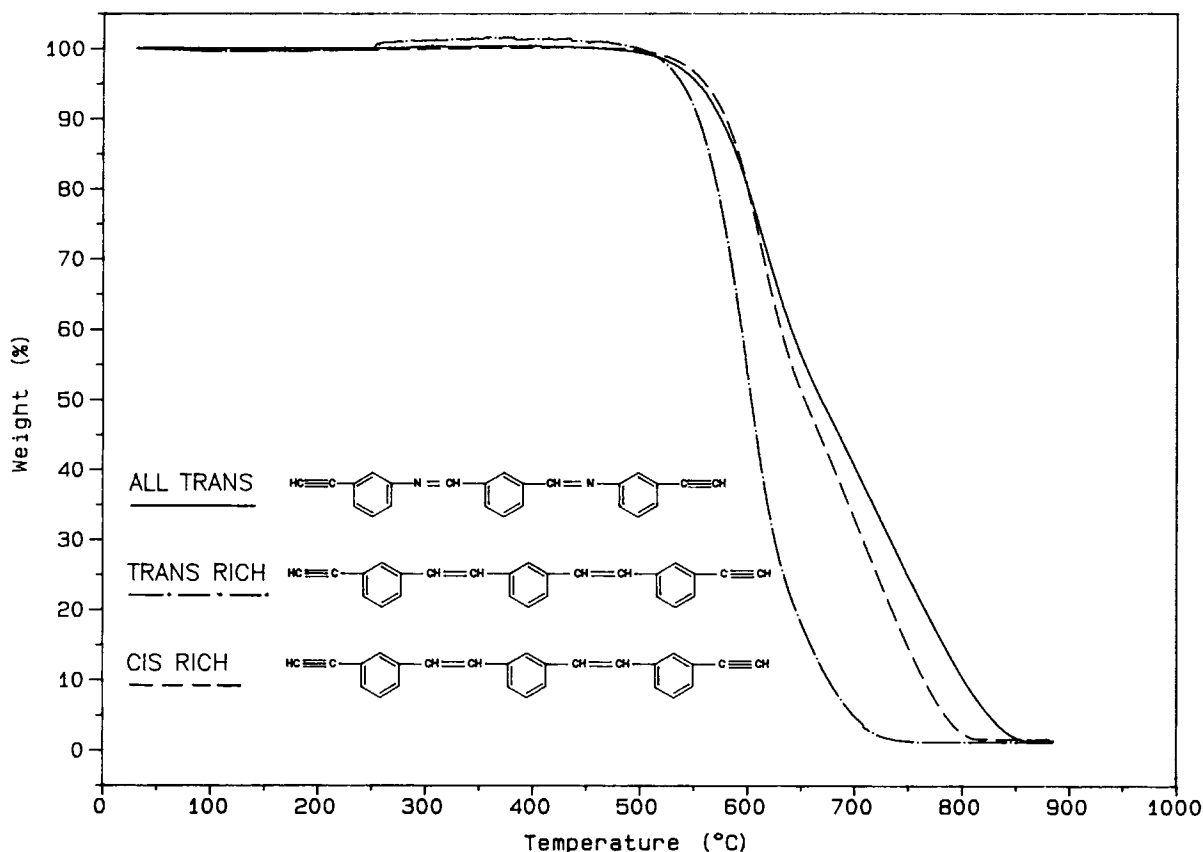
## ENVIRONMENTAL STABILITY

A major consideration for selecting the present approach to conductive polymers was that we expected the conductivity to show high stability to very aggressive environments, and earlier work<sup>3,8</sup> has verified this expectation. The new materials described in this paper also exhibit high environmental stability. Figure 8 shows the effect of boiling water on conductivity for the *cis*-rich, all-*meta* bis(ethynylstyryl)benzene (**II-B**). It is compared to an arylsulfonate-doped polypyrrole (one of the most stable doped conductive polymers) and to one of our earlier developed acetylene-terminated system based on  $N,N'$ -(1,4-phenylenedimethyldiylne)bis(3-ethynylaniline) (Structure **I**, where  $X = -C\equiv CH$ ,  $Y = H$  and the central linkage is 1, 4).

The two materials prepared from the acetylene-

terminated prepolymers (**II-B** and **I**, Table II) show no change in conductivity during the 1000 h in boiling water while the doped polypyrrole very rapidly loses its conductivity. After 100 h, the conductivity of the polypyrrole could no longer be measured by the four-point probe technique (conductivity less than  $10^{-8}$  s/cm).

The polymers described in this paper show a small drop in conductivity after removal from the processing furnace and storage in the ambient laboratory environment for a few days. When initially removed from the furnace, these materials are in a very anhydrous condition (500–700°C under dry argon for 100 h) and show maximum conductivity. After a few days in the laboratory environment, the conductivity drops slightly (2–3 s/cm for the more highly conductive materials,  $10^0$ – $10^{+2}$  s/cm) on absorption of 1–2% water from the atmosphere. After



**Figure 7** TGA comparison in air of three polymers in Figure 6 after heating in nitrogen to 900°C in TGA. All-*trans*-*N,N'*(1,3-phenylenedimethidyne)bis(3-ethynylaniline) [**I**, where X =  $-\text{C}\equiv\text{CH}$  and Y =  $-\text{H}$  (—)]; *trans*-rich fraction of the *cis/trans* mixture of 1,3-bis(3-ethynylstyryl)benzene [**II-A** (- · - ·)]; and *cis*-rich fraction of the *cis/trans* mixture of 1,3-bis(3-ethynylstyryl)benzene [**II-B** (---)]. Air-flow rate 75 mL/min; heating rate 10°C/min.

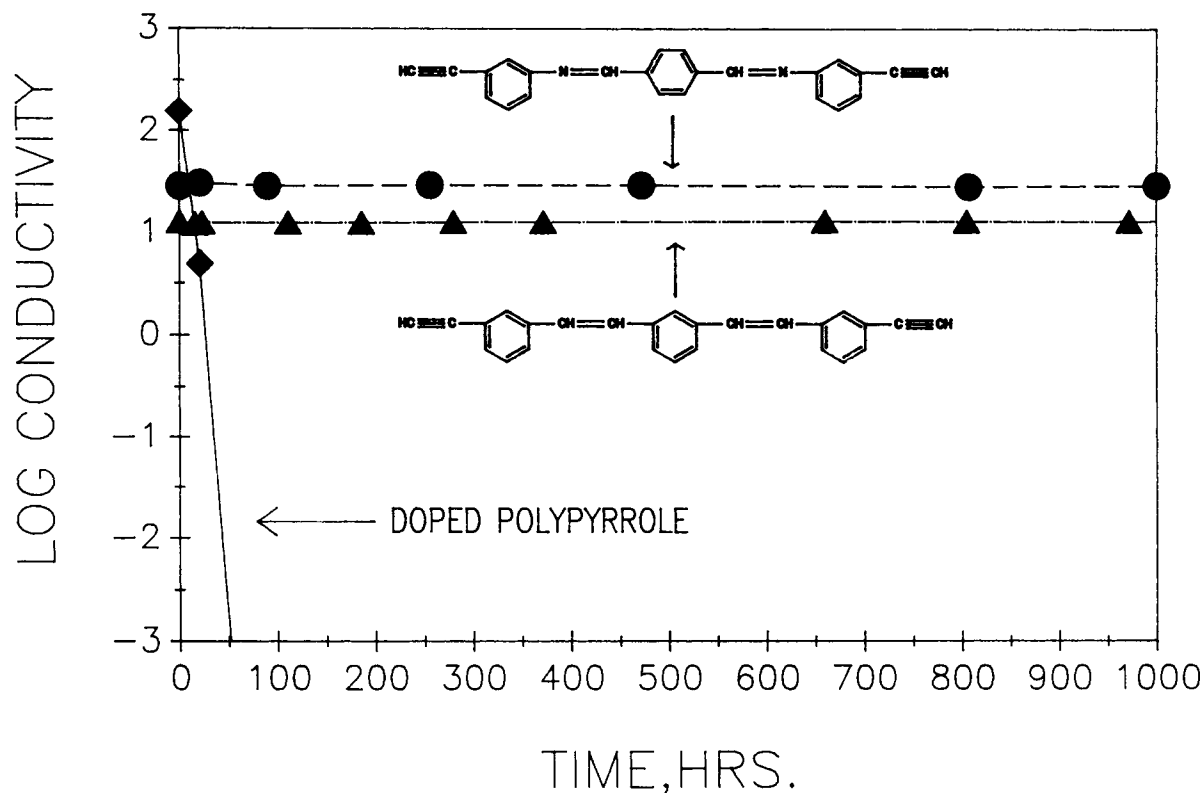
this initial drop, the conductivity remains constant. The original conductivity is restored if the materials are dried in a vacuum oven.

Finally, as might be expected, once these materials have been processed to a high temperature to introduce conductivity, they can be aged at lower temperatures without further change in the room temperature conductivity. For example, after samples prepared from the all-carbon-hydrogen 1,3-isomers (**II-A** and **II-B**) have been processed to 700°C for 100 h to give conductivities of 14 to 21 s/cm, no change in this room-temperature conductivity is observed when they are aged over 500 h at 500°C in an inert atmosphere; they also do not show any weight change. If the aging temperature were increased to 700°C or higher, the conductivity would increase rather than decrease. We know of no doped

organic polymer system that could withstand these aggressive environments.

## SUMMARY

Three new completely conjugated, all-carbon/hydrogen prepolymers have been synthesized and converted into conductive materials by simple thermal processing. The conductivity can be controlled from that of an insulator to  $10^2$  s/cm, and it is stable to aggressive environments such as boiling water and temperatures of 500°C and higher in an inert atmosphere. Two of the materials are readily processed since they can exist in the liquid state well below their cure temperature. The third material is much



**Figure 8** Comparison of the effect of boiling water on the conductivity of conductive polymers prepared from (1) polypyrrole doped with a benzenesulfonic acid derivative (—); (2) all-*trans* *N,N'*-(1,4-phenylenedimethyldiyl)bis(3-ethynylaniline) [I, where X =  $-\text{C}\equiv\text{CH}$  and Y =  $-\text{H}$  (---)] processed to 600°C for 100 h; and (3) *cis*-rich fraction of the *cis/trans* mixture of 1,3-bis(ethynylstyryl)benzene processed to 700°C for 100 h (-·-·-).

more difficult to process because it begins to polymerize before melting. Because these materials have high thermal stability, they may also find application in high-temperature polymers and carbon-carbon composites in addition to conductivity applications.

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