

# An Environmentally Stable, Electrical Conducting Polymer Prepared from a Conjugated, Processable Acetylenic Monomer

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## Synopsis

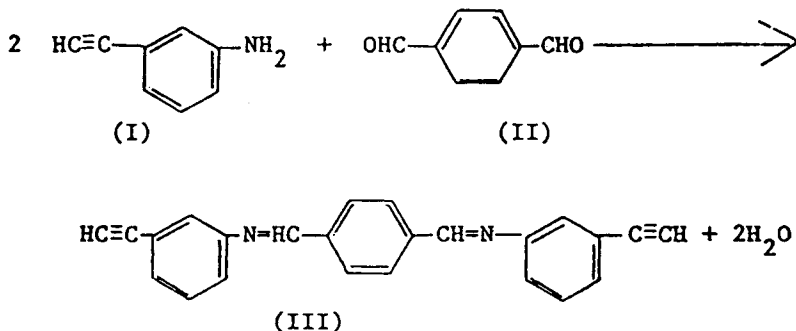
The synthesis, properties, and polymerization of an acetylene terminated monomer are described. The monomer melts and is thermally polymerized at 150°C and then at 300°C in an air environment. From the liquid stage, the monomer can be fabricated into moldings, castings, and prepregs. As initially cured, the polymer is an insulator. By further thermal processing at elevated temperatures in an inert atmosphere, conductivity can be controllably introduced into the polymer; for example, at 600°C a conductivity of  $3.3 (\Omega\text{-cm})^{-1}$  is obtained. Exposure of these conductive polymers to either boiling water for 1000 h or temperatures 100°C below their maximum process temperature (400–500°C) for 500–800 h did not produce any significant change in conductivity.

## INTRODUCTION

In an earlier paper<sup>1</sup> we reported the syntheses and properties of stable, electrical conducting polymers prepared from conjugated bis-phthalonitrile monomers. The basic approach was to design a monomer having a completely conjugated or aromatic structure between reactive end groups, e.g., the ortho-dinitrile groups. The end groups would be capable of chain extending and cross-linking through reactions that could form additional conjugated or aromatic connecting structures. The expectation of this approach was that an extended conjugated polymeric network, which should exhibit high thermal stability and perhaps an intrinsic conductivity, would be formed. Furthermore, if reactive dopants would not be required to introduce conductivity, the materials might be stable to much more aggressive environments than has been observed with doped conductive polymers. Finally, because the monomer passes through a liquid state during polymerization, the materials are also expected to be processable. Indeed, with the bis-phthalonitriles,<sup>1</sup> we found that thermally stable moldings and castings could be made with a stable electrical conductivity that could be varied from that of an insulator to a semimetal.

This paper reports a similar study of a monomer that is end-capped with terminal ethynyl (acetylenic) groups. The polymerization of a monomer through ethynyl end groups is not new; References<sup>2-8</sup> are a series of papers providing background information on the synthesis, chemistry, polymerization, mechanisms, proposed product structures, and earlier attempts to prepare conductive polymers.

The monomer described in this paper is *N,N'*-(1,4-phenylenedimethyldi-nyne)bis-(3-ethynylaniline) (III), which is readily synthesized in high yield by the reaction of 2 mol of 3-aminophenylacetylene (I) with 1 mol of terephthalaldehyde (II):



The monomer melts at about 139°C and, on continued heating at 150°C for a few hours, slowly solidifies into a hard, dark solid. The strength and conductivity of the polymer are increased by postcuring at elevated temperatures.

### SYNTHESIS

The 3-aminophenylacetylene was initially obtained from Gulf Research (but now is available only from National Starch and Chemical Corporation) and was used as received. The terephthalaldehyde can be obtained from a number of sources and was recrystallized from toluene before use. Two typical procedures for the monomer synthesis are described below.

(1) A solution of terephthalaldehyde (13.4 g, 0.10 mol) in toluene (300 mL) was added dropwise over a 1-h period to a stirred, refluxing solution of 3-aminophenylacetylene (24.6 g, 0.21 mol) in toluene (200 mL). A slight excess of the 3-aminophenylacetylene was used to ensure reaction of both aldehyde groups. After 26 h, 3.5 mL of water (theory, 3.6 mL) had been isolated from the reaction. Further refluxing did not produce more water. The hot mixture was filtered, and the filtrate volume reduced to 100 mL. On cooling, 30.4 g (91.6% yield) of crude III was obtained. Recrystallization from absolute ethyl alcohol (95% recovery) gave a product melting at 138.5–139.5°C.

(2) A solution of terephthalaldehyde (1.34 g, 0.01 mol) in dry acetonitrile (32 mL) was added at room temperature over a 10-min period to a stirred solution of 3-aminophenylacetylene (2.46 g, 0.021 mol) in dry acetonitrile (20 mL). Stirring was continued for 6 h, the solution filtered through a drying agent (anhydrous  $\text{Na}_2\text{SO}_4$ ) to remove the water formed during the reaction, and the solvent evaporated. Recrystallization (absolute ethyl alcohol) gave an overall yield of III comparable to the synthesis in toluene.

The infrared spectrum (KBr pressed pellet) of III showed a strong acetylenic hydrogen absorption at  $3278 \text{ cm}^{-1}$ , the  $-\text{C}\equiv\text{C}-$  at  $2110 \text{ cm}^{-1}$  (weak), and the absence of any NH or carbonyl absorption. The imine  $-\text{N}=\text{CH}-$  absorption was observed at  $1622 \text{ cm}^{-1}$ , consistent with values reported for extended conjugation.<sup>9</sup> The elemental analysis results were calculated as

C = 86.71%, H = 4.86%, and N = 8.43%, and were found to be C = 86.75%, H = 5.00%, and N = 8.24%.

We have observed a phenomenon with this material that is not completely understood at this time; a more detailed report will be made after more extensive studies are completed. Compound III appears to have more than one form, which may result from polymorphism, hydrogen bonding effects, and/or geometric structural effects. We have observed that substantial changes occur in the melting point and the infrared absorption spectrum when the monomer is recrystallized from toluene rather than absolute ethyl alcohol. The melting point for the toluene recrystallized product is 149–150°C compared with 138.5–139.5°C for the ethyl alcohol recrystallization. In the infrared, the strong  $\text{—C}\equiv\text{C—H}$  absorption has shifted from  $3278\text{ cm}^{-1}$  (ethyl alcohol) to  $3195\text{ cm}^{-1}$  (toluene) and the  $\text{—C}\equiv\text{C—}$  from  $2110\text{ cm}^{-1}$  (ethyl alcohol) to  $2100\text{ cm}^{-1}$  (toluene). The imine absorption at  $1622\text{ cm}^{-1}$  is essentially the same after recrystallization from either solvent. Other areas in the IR (see Fig. 1) are substantially effected by the recrystallization procedure. If the toluene recrystallization product is recrystallized from ethyl alcohol, the IR spectrum obtained for the initial alcohol recrystallized product is observed. However, the melting point does not always revert to the 138.5–139.5°C range observed for the pure material recrystallized from alcohol. Indeed, on observing the melting of some samples of the EtOH-toluene-EtOH recrystallized material, an initial melting is evident around 138°C, then resolidification occurs with further heating, and finally complete melting at approximately 148–150°C. This phenomenon can be seen during

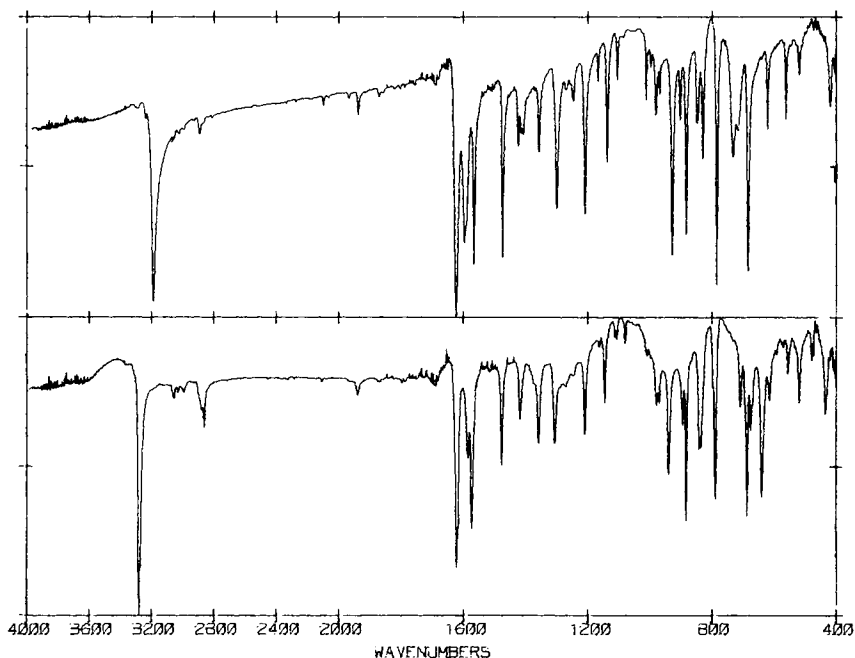


Fig. 1. FT-IR spectra of the two forms of compound III; bottom spectrum, recrystallized from absolute ethyl alcohol; top spectrum, recrystallized from toluene. Run as KBr pressed pellets.

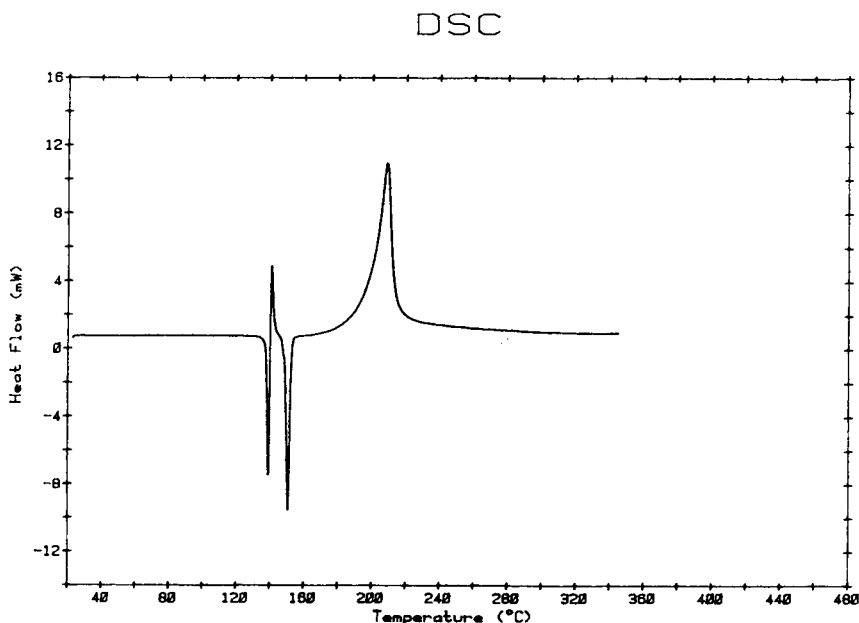


Fig. 2. DSC scan of III illustrating the first melting, resolidification, second complete melting, and, finally, the exothermic cure. (Heating rate,  $10^{\circ}\text{C}/\text{min}$ ; nitrogen atmosphere at  $80\text{ mL}/\text{min}$ .)

differential scanning calorimetry (DSC) experiments (Fig. 2). The initial endothermic melting at  $137^{\circ}\text{C}$ , the exothermic recrystallization at approximately  $140^{\circ}\text{C}$ , and the second melting at  $148^{\circ}\text{C}$  are readily observed. The large exothermic peak at  $209^{\circ}\text{C}$  is the heat of polymerization and will be discussed later.

For the form of this material with the acetylenic hydrogen absorption at  $3195\text{ cm}^{-1}$ , the higher melting point ( $149\text{--}150^{\circ}\text{C}$ ) is always observed. However, in cases in which the absorption is observed primarily at  $3278\text{ cm}^{-1}$ , we may observe the melting at  $139^{\circ}\text{C}$  in some instances, but in others, melting is primarily in the  $148\text{--}150^{\circ}\text{C}$  range. This latter observation may be a consequence of a trace or small amount of the higher melting form nucleating the recrystallization of the liquid melt of the lower melting form into the higher melting form. It has also been determined that the lower melting form can be regenerated from the higher melting form by cooling the melt. This procedure is more complex, however, since it is apparent from the DSC cure in Figure 2 that polymerization begins immediately on melting the higher melting material.

### POLYMERIZATION AND PROCESSING

Because III melts into a free-flowing, low-viscosity liquid, it can be cast or molded using conventional polymer processing techniques. At  $150^{\circ}\text{C}$ , the liquid melt slowly increased in viscosity and changed in color from a light yellow to brown-black. After approximately 1 h at  $150^{\circ}\text{C}$ , the material becomes a glassy solid. Our usual procedure is to melt process the material initially on a hot plate (in an aluminum planchet or mold) and then transfer without cooling to an oven that has been stabilized at  $150^{\circ}\text{C}$ . The cure is

continued for a total time of 2 h at 150°C, then 1 h at 200°C, 1 h at 250°C, and 50 h at 300°C. The cure is done in a furnace with no attempt to exclude air, and weight loss during cure is less than 0.1%.

It is important that the initial processing temperature not be allowed to get much higher than the 150°C during the first hour of cure. In fact, when the melted sample is placed in the furnace, we lower the temperature to 145°C and then increase it over 5–10 min to 150°C to prevent overheating. Although it is not totally apparent from Figure 2, the polymerization of both forms begins on melting. The heat of reaction is calculated from DSC to be approximately 761 J/g and represents a very energetic reaction. For samples in the 1–2 g range, allowing the furnace temperature to rise above 160°C caused a highly exothermic reaction accompanied by foaming, charring, smoke generation, and extensive decomposition.

After this initial cure, the material is removed from the aluminum platchet or mold in which it was prepared. At this stage, the polymer is nonconductive, but by further processing at higher temperatures, conductivity can be introduced. Typically a cured sample approximately 1 inch in diameter and 0.1 inch thick is further heated under an inert atmosphere in a tube furnace or under vacuum in a sealed glass or quartz tube. If a sealed tube was used, it was evacuated and flushed with nitrogen or argon several times before being sealed. If the tube furnace was used, a stream of oxygen-free nitrogen or argon was passed through the 1-inch diameter furnace tube at a flow rate of 50 mL/min. The outlet of the tube furnace was restricted with a capillary tube to reduce back diffusion of air. The heating and cooling rates for the furnaces were approximately 0.5°C/min.

For comparative purposes, a standardized heating procedure was used in further processing the samples into conductive polymers. After the 300°C cure in air for 50 h, each sample was heated to 400°C for 100 h, 500°C for 100 h, 600°C for 100 h, and so on. At the end of each 100 h treatment, the samples were removed for measurements.

## RESULTS

Conductivities were determined by using a four-point probe technique<sup>10–13</sup> consisting of an Alessi four-point probe head, a Keithly 225 current source, and a 616 digital electrometer. Figure 3 shows a typical plot of the change in room temperature conductivity for samples processed to 700°C as outlined above and then further processed at 900°C (5 h) and then 1200°C (5 h). Since the 900 and 1200°C measurements were not based on the samples processed the full 100 h at these temperatures, those data points are not a true uniform extension of the 400–700°C cure and thus that portion of the curve is represented as a dashed line. Nevertheless, the maximum conductivity obtained for this system below carbonization temperature appears to be between  $10^{2+}$  and  $10^{3+}$  ( $\Omega\text{-cm}$ )<sup>-1</sup>. Thus, longer processing times in the 900–1200°C range would not produce significant changes in the conductivity but would have resulted in greater weight loss in the sample.

In Figure 4 is shown the corresponding average weight loss for samples processed as discussed for Figure 3. Again, the samples processed at 900 and 1200°C were only held at these temperatures for 5 h, rather than the 100 h used for the lower temperature, and that portion of the curve is again shown

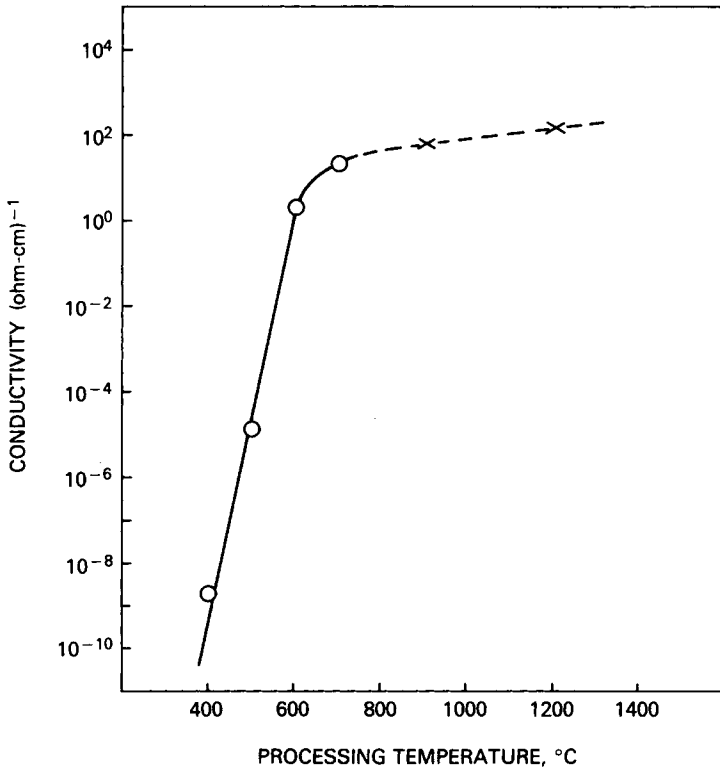


Fig. 3. Effect of postcure thermal treatment on the room temperature conductivity of III. (The values represented by  $\times$  were for the sample processed for 5 h at that temperature rather than 100 h.)

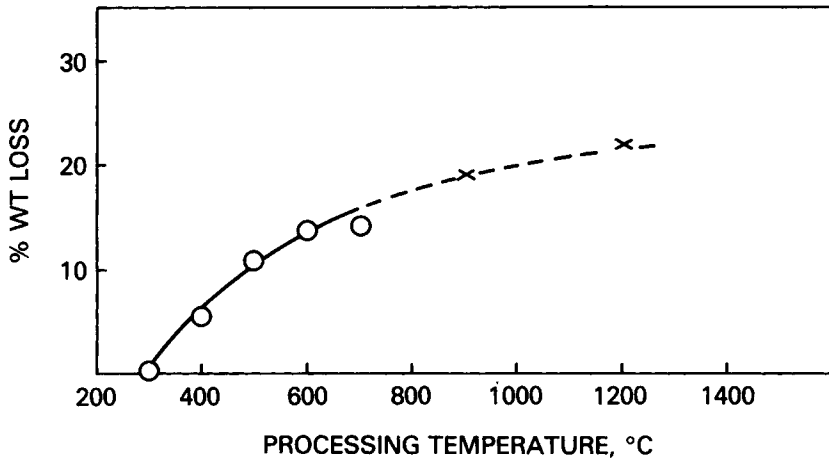


Fig. 4. Percentage weight loss (inert atmosphere) as a function of the processing temperature. Each point represents the accumulated weight loss after 100 h at each temperature, except the 900 and 1200°C values, which were for 5 h.

as a dashed line. Figure 4 illustrates the high stability to thermal degradation exhibited by this polymer. Even when no attempt was made to exclude air from the furnace used to initially cure these samples for 50 h at 300°C, the polymer showed essentially no weight loss. At higher temperatures in an inert atmosphere some weight loss occurs, but even after the extended thermal treatment to 600°C, the total weight loss was only 13.7%. During thermal processing the appearance of the material changes from a dark brown to black. The sample undergoes some shrinkage, approximately 12% at 600°C, but the shape of the 1 inch diameter disks is undistorted and is essentially a smaller replicate of the original sample. If the purity of the starting monomer is high, the sample does not become fragile (in fact, strength appears to increase with thermal treatment) or crack and a 0.1 inch thick sample withstands considerable hand-held flexing force without breaking.

Table I compares two alternative 700°C treatments with the standard procedure. Thus, faster processing times are possible than the one standardized for comparative purposes with other systems we have under development.<sup>1</sup> We believe that faster processing times are possible, but conditions have not been optimized.

Figure 5 shows the DSC curve for the polymer (as a powder) initially cured at 300°C for 50 h. As might be expected, the highly exothermic peak at approximately 210°C (Fig. 2) for the reaction of the acetylenic groups is no longer present. A very broad exotherm (352 J/g) now appears at approximately 230°C and ends at approximately 600°C. In Figure 2, this broad exotherm is not observed to 350°C; apparently the exothermic reactions in this region occurred during the highly energetic cure exotherm (peaking at approximately 212°C in Fig. 2), which resulted from the rapid DSC heating rate (10°C/min). Since in this experiment the sample was held at 150°C for 2 h before proceeding to a higher cure temperature, the cure exotherm was much milder and thus did not initiate higher temperature reactions during the initial cure. The DSC studies emphasize what actual sample preparation illustrated; an initial controlled cure at 150°C or lower is necessary to prevent

TABLE I  
Comparison of Alternative Thermal Treatments to 700°C  
on Sample Weight Loss and Conductivity

Processing condition <sup>a</sup>				Total % weight loss	Final conductivity ( $\Omega\text{-cm}^{-1}$ )
$T_i$	$T_f$	Rate	Hours at $T_f$		
Standard procedure					
RT	400	0.5	100		
RT	500	0.5	100		
RT	600	0.5	100		
RT	700	0.5	100	14.1	$3.60 \times 10^1$
Alternative Procedure					
RT	400	0.3	50		
400	600	0.3	50		
600	700	0.3	100	16.6	$3.80 \times 10^1$
Alternative procedure					
RT	700	0.3	100	15.4	$3.85 \times 10^1$

<sup>a</sup>Initial ( $T_i$ ) and final ( $T_f$ ) temperature in °C; rate in °C/min from  $T_i$  to  $T_f$ .

## DSC

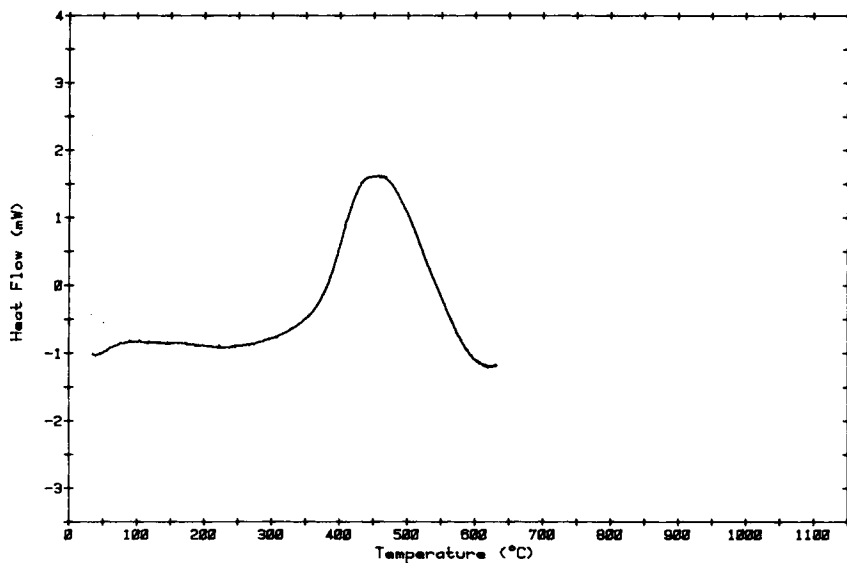


Fig. 5. DSC scan of III after initial cure at 300°C for 50 h (powder form, heating rate 10°C/min; nitrogen atmosphere at 80 mL/min.)

## TGA

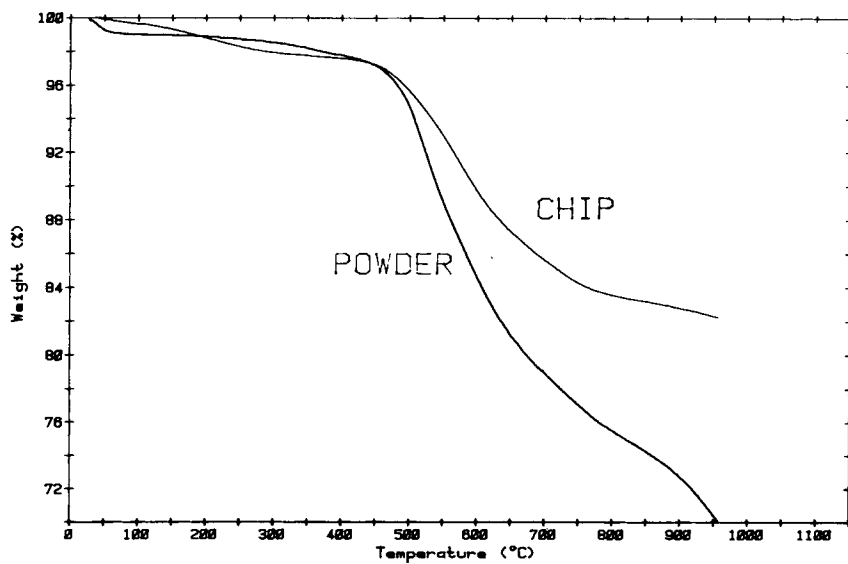


Fig. 6. TGA weight loss in nitrogen III after initial cure at 300°C for 50 h. (Heating rate, 10°C/min; nitrogen atmosphere at 80 mL/min.)



an uncontrolled reaction. Further, it is desirable to process slowly through the second exothermic range (Fig. 5) or hold the sample for a period of time at some temperature in the early part of this exotherm, e.g., 25 h at 420°C, to allow the reactions to occur in an orderly, constructive manner.

The thermogram of the weight loss in nitrogen for the polymer that was cured at 300°C (50 h) is shown to 950°C in Figure 6. The samples were run both as a single chip and as a powder to duplicate the behavior of the sample in the form used in processing it into a conductive polymer, and the conditions typically used for comparative thermogravimetric analysis (TGA). The initial weight loss (approximately 2.8%) observed to 450°C is believed to be mostly absorbed water. A sample of the 300°C cured polymer showed a 2.6% weight loss when heated in a vacuum oven at 120°C for several hours and regained this weight after being exposed to the normal laboratory environment for several weeks. (The reader should note that the percentage weight loss scale in Fig. 6 is from 70 to 100% compared with 0–100% in Fig. 7.)

Figure 7 reports the TGA weight loss in air. Again, the samples were run as a chip and as powder. The bulk form shows a gradual loss in weight (2–3%) to approximately 450°C and then more substantial weight loss as the oxidative environment takes effect. The powder form reveals a little more information; a slight weight gain is observed from approximately 250°C and indicates formation of preliminary oxidized species in the polymer structure. The weight increase reaches a maximum at about 400°C, where the polymer begins to undergo extensive oxidative decomposition. At about 675°C, the powder sample is completely consumed while the bulk sample, as would be expected, exhibits a slower oxidative weight loss and maintains approximately 80% of its original weight at this temperature.

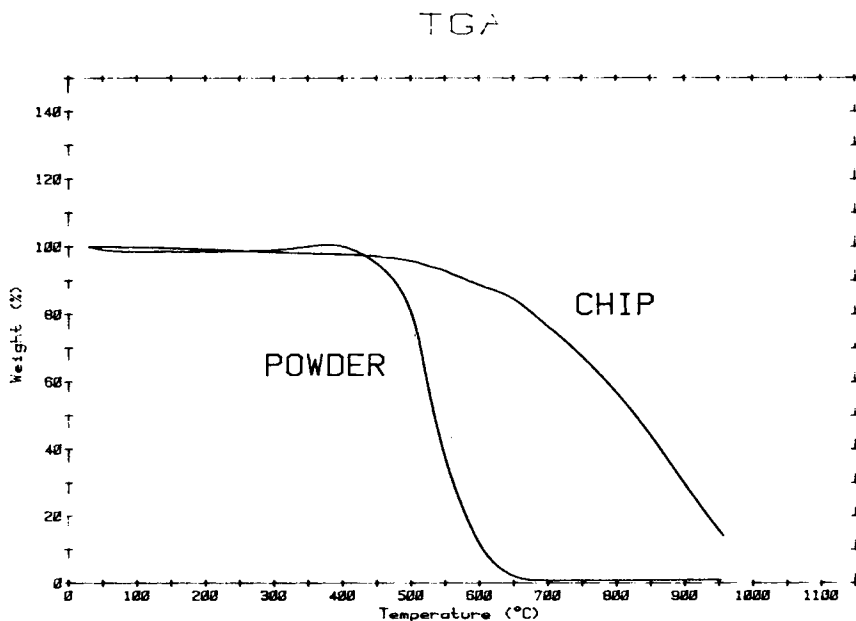


Fig. 7. TGA weight loss in air of III after initial cure at 300°C for 50 h. (Heating rate, 10°C/min; air atmosphere at 80 mL/min.)

These TGA studies, as well as the results from the long-term (100 h) thermal processing of the samples, illustrate the high thermal stability that this system possesses. Although we have not measured temperature effects on mechanical properties, the dynamic and isothermal weight loss studies indicate that the thermal stability of this material compares very favorably to the best of the thermally stable polymers previously reported.<sup>14</sup>

As discussed earlier, a main focus for this approach in developing conductive polymers is the expected stability in the conductivity. Figures 8 and 9 illustrate this high stability. Figure 8 compares the effect of boiling water on the conductivity of the polymer prepared from the acetylene-terminated monomer processed to 600°C and a polypyrrole containing a benzene-sulfonic acid salt derivative as the counterion (dopant). This latter material showed little or no change in conductivity over a year in a normal laboratory environment and thus represents one of the more stable doped conductive polymers. However, in the boiling water, its conductivity dropped almost 2 orders of magnitude in less than 24 h and could not be measured [less than  $10^{-8} (\Omega - \text{cm})^{-1}$ ] with the four-point probe after approximately 90 h. The

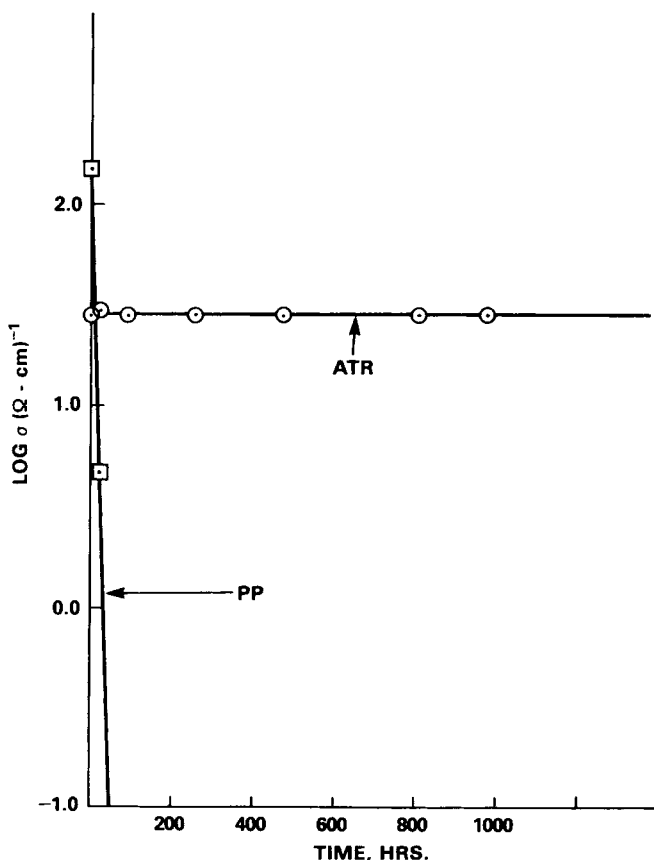


Fig. 8. Effect of boiling water on conductivity of the polymer from the acetylene-terminated resin (ATR) processed at 600°C and a doped polypyrrole (PP).

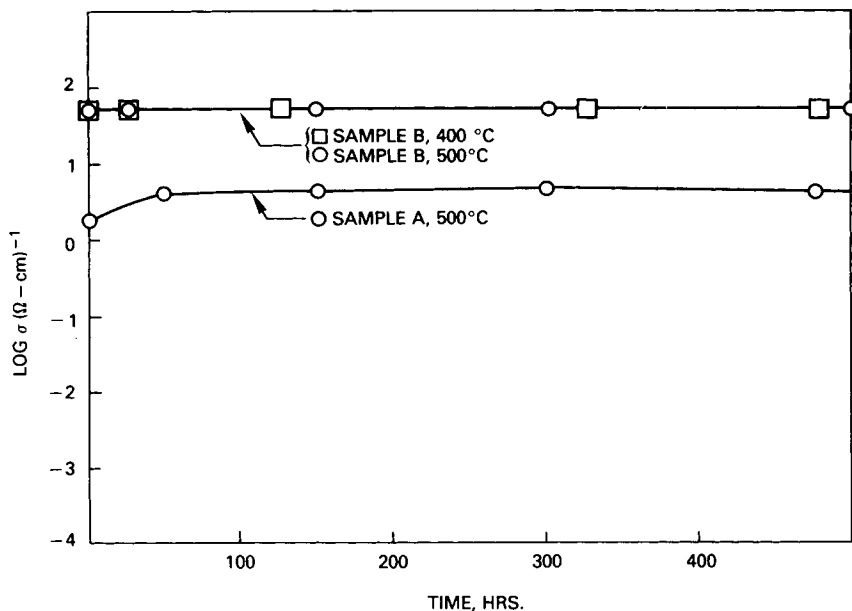


Fig. 9. Change in conductivity (RT) with time after heating the conductive polymers at 500°C (sample A processed at 600°C), and 400 and 500°C (sample B processed at 700°C).

conductive polymer from the acetylene-terminated monomer showed no change in conductivity during the 1000 h the experiment was conducted.

Figure 9 illustrates the stability of the conductivity after exposing the processed samples to elevated temperatures for 500 h or longer in an inert atmosphere. Sample A had been previously processed to 600°C to achieve the initial conductivity. Before beginning the long-term exposures, baseline conductivities were determined. After heating sample A for 100 h at 500°C, a small increase in conductivity [ $1.66$ – $3.94$  ( $\Omega\text{-cm})^{-1}$ ] was observed. Further heating at 500°C caused little further change in the conductivity. The initial change in conductivity is attributed to the removal of absorbed water. When this sample was allowed to stand for several weeks in the laboratory atmosphere after this experiment, a conductivity of 1.16 was obtained. After this sample was redried by heating in a vacuum oven for 22 h at 112°C, its conductivity was 4.43. Sample B was processed at 700°C and dried prior to determining baseline conductivity. This sample was first exposed at 400°C for 800 h with no change in conductivity and then exposed at 500°C for 500 h with little change in conductivity; thus the two plots fall on top of each other and the same line represents both conditions.

Rather than speculate on the minor role of the absorbed water in inhibiting conduction in this system, we believe that such a discussion should wait until more information is obtained on the conduction mechanism. However, we would point out that this observation may in part be related to the fact that the initial cure is carried out in an air environment at 300°C for 50 h. Although very little weight change occurs under these conditions, it was noted (see Fig. 7) in the TGA run of the powder material that a small weight increase began at approximately 250°C. This suggests that some stable, polar

oxidation species are formed and may influence the moisture absorption as well as conductivity.

Although it is perhaps not surprising that these materials exhibit high thermal stability at temperatures below their maximum processing temperature, it was important to establish that prolonged heating at high temperatures did not permanently alter the conductivity. It is also important to point out that the closer the thermal aging temperature approaches the maximum processing temperature, the more likely it is that a permanent change in conductivity will result. For the sample processed at 600°C and then thermally aged at 500°C, very few permanent changes in conductivity occurred. However, if the aging temperature was increased to 600°C, then this sample would exhibit significant and permanent changes in conductivity with time.

### SUMMARY

The high yield synthesis of a monomer terminated with phenylacetylene groups that are linked together through a completely conjugated interior is described. The monomer is converted through the terminal acetylenic groups into a conjugated polymer network by heating it in its molten state at 150°C for a few hours and finally at 300°C for 50 h. Further processing at higher temperatures in an inert atmosphere results in a significant increase in the electrical conductivity. The conductivity is controlled by the maximum processing temperature and length of time at that temperature. In this manner the conductivity can be varied from that of an insulator to approximately  $10^{+2} (\Omega\text{-cm})^{-1}$ . Weight losses during this processing are low (approximately 15% for samples aged for 100 h at 700°C) and appear to have a minimal effect on the integrity of the sample when a well-purified monomer is used.

Since the resin melts into a free-flowing liquid at 140–150°C and polymerizes at 150°C with no evolution of volatiles, it is processable using conventional molding techniques. The polymerization reaction is very energetic; therefore it is important to keep the initial cure temperature at 150°C or slightly lower. Once polymerized, the material possesses the inherent stability and solvent-resistant characteristics of a highly cross-linked polymer. Exposure of highly conductive samples to boiling water for 1000 h or to temperatures of 400–500°C in an inert atmosphere for 500–800 h does not alter the conductivity.

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