

Electrically Conducting Polymers From Conjugated Bis-Phthalonitrile Monomers

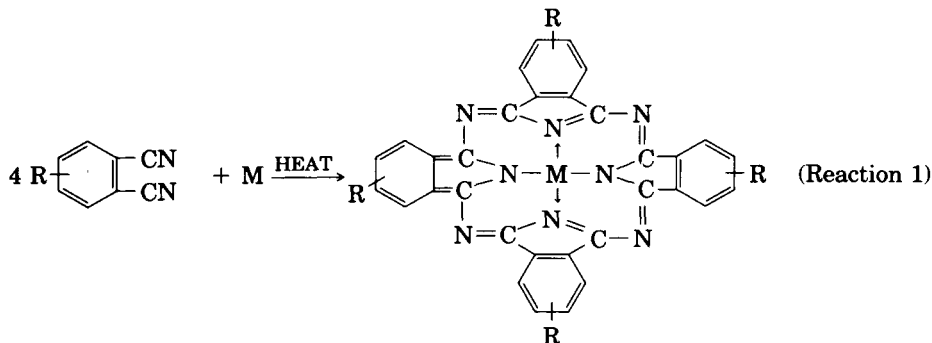
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Synopsis

Electrically conducting polymers have been synthesized from completely conjugated bis-phthalonitrile monomers. The monomers melt and are thermally polymerized at 260–300°C in air and then are converted into conductive materials by further processing at elevated temperatures in an inert atmosphere. Because the monomers remain in a liquid stage for 1–2 h, depending on the cure conditions, moldings, castings, and pre-pregs can be fabricated using conventional processing techniques. The conductivity can be varied from that of an insulator to approximately $10^{+2}(\Omega \text{ cm})^{-1}$. For example, after a 600°C treatment, the conductivity is approximately $1(\Omega \text{ cm})^{-1}$. Since reactive dopants are not used, the material and conductivity are stable in ambient as well as more aggressive environments, allowing them to function at 300°C and above. The monomers are well characterized, but the structure of the cured and postcured polymers are not yet well defined because of their high stability and intractability in the cured state.

INTRODUCTION

It is well known that under suitable reaction conditions, aromatic *o*-dinitriles can be converted into phthalocyanines¹:

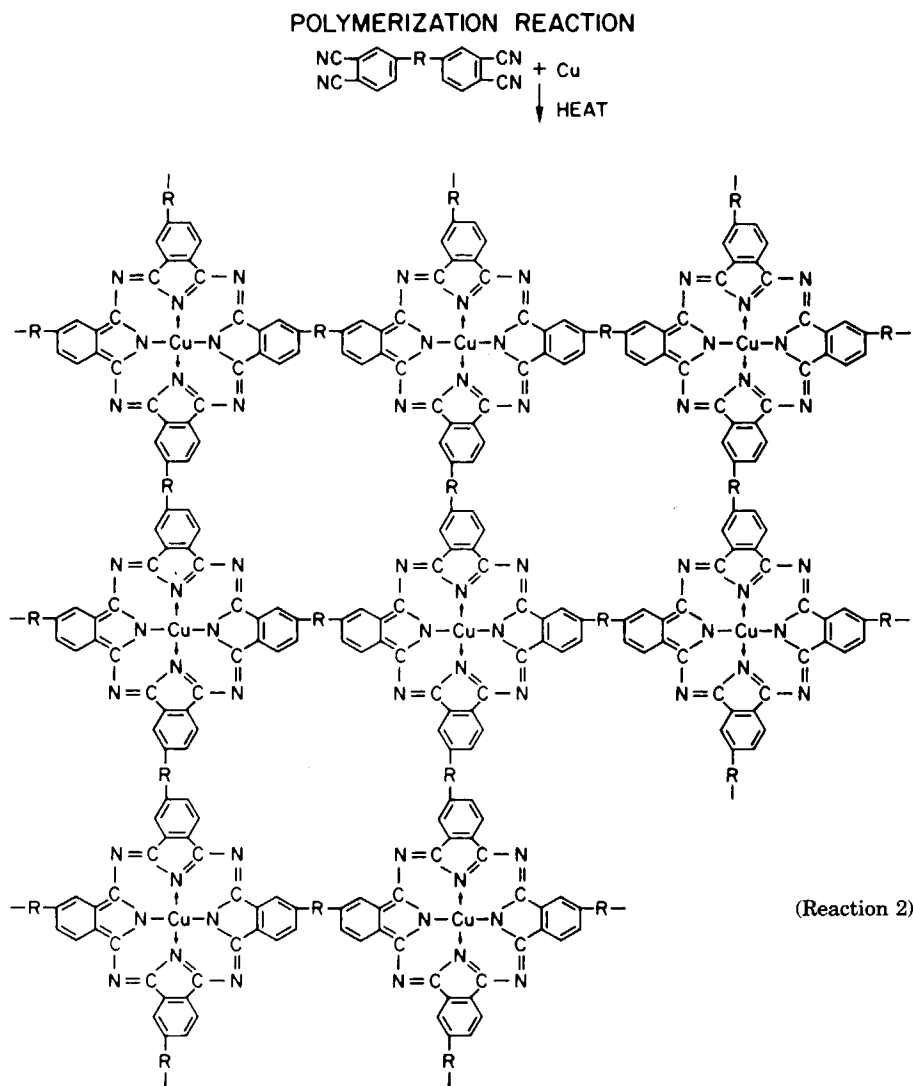


This can be a high yield reaction that produces thermally and chemically stable compounds. Furthermore, the reaction produces no volatile by-products. Thus, one can imagine this reaction to have synthetic utility in the preparation of stable, high molecular weight polymers; and indeed, over the last 30–35 years, intermittent efforts have been made in this direction.² Although 1,2,4,5-tetracyanobenzene has been converted into a polymer by reacting with Cu powder, the more successful and versatile approach has

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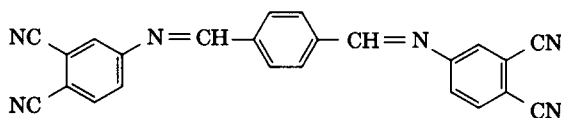
been to separate the bis-*o*-dinitrile groups by a spacer, as illustrated in Reaction 2.



The nature of the R group spacer greatly influences the processing characteristics of the monomer as well as the final properties of the polymer. Table I list several of these linking groups that this laboratory has investigated during the last few years. During the course of this work, we became interested in the possibility that polymers from certain of these structures might also exhibit electrical conductivity. Two of these materials are based on the monomers shown as structures 1a and 1b.

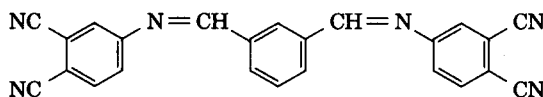
TABLE I
Some Previously Investigated Bis-Phthalonitriles

R group	Reference
$-\text{HNCO}(\text{CH}_2)_n \text{CONH}-$, $n = 2 - 36$	3
$-\text{HNCO}(\text{C}_6\text{H}_4\text{O})_n \text{C}_6\text{H}_4\text{CONH}-$	4
$-\text{O}(\text{C}_6\text{H}_4\text{O})_n \text{C}_6\text{H}_4\text{O}$	5
$-\text{OC}_6\text{H}_4-\text{X}-\text{C}_6\text{H}_4\text{O}-$, $\text{X} = \text{C}(\text{CH}_3)_2 \text{SO}_2$, CO	6



(Structure 1a).

N,N'-Terephthalylidene-bis(3,4-dicyanoaniline)
(*p*-dianil-bis-phthalonitrile)



(Structure 1b)

N,N'-Isophthalylidene-bis(3,4-dicyanoaniline)
(*m*-dianil-bis-phthalonitrile)

Both structures are completely conjugated (that is, alternating single/double bonds) and thus have the possibility of a continuous overlap of the *p*-orbitals in the Π -bonds from one end of the molecule to the other. Also, because of the 1,4-bonding in the central ring of structure 1a, extended resonance structures are possible in this system. Thus polymerization by means of the phthalocyanine reaction would in theory yield the highly conjugated, aromatic phthalocyanine rings interconnected by the conjugated R groups ($-\text{N} = \text{CHC}_6\text{H}_4\text{CH} = \text{N}-$), thus producing completely conjugated network polymers (Reaction 2).

Since charge carriers in organic molecules are readily generated by activation of Π -bonded electrons, one might expect an intramolecular conduction path of high mobility when the Π -bonded electrons are delocalized in these extended conjugated systems.⁷ The energy E_a , required to raise an electron from the ground state to the first excited state in a conjugated chain such as polyene ($-\text{CH} = \text{CH})_n$ and polymethinimine, ($-\text{CH} = \text{N})_n$ is given by the equation⁷

$$E_a \text{ (eV)} = 19 \frac{2n + 1}{2n^2}$$

Thus, for reasonable molecular weights of 13,000–14,000, n would equal approximately 500 and E_a becomes equal to kT at room temperature, which means that the excited levels become thermally populated and available for contribution to the conduction band and conductivity.

However, high conductivity along the polymer chain is no guarantee of high conductivity in the plastic made from that polymer. Polymer chains

are ordinarily quite short compared with the macroscopic dimensions of a plastic article. Held together principally by weak van der Waals forces and physical entanglement, the chains are widely separated on a molecular scale. To move from chain to chain, the conduction electrons rely on thermally activated hopping, which means that their mobility is low. Thus, the conductivity in most conjugated polymers, such as pure polyacetylene, is still low, $10^{-5}(\Omega \text{ cm})^{-1}$.

The conjugated structures discussed in this paper, however, have several features that favor their conversion into highly conductive materials. First, the monomer exhibits a functionality of 4 at each chain extension/cross-linking site, thus providing a multitude of alternate pathways for developing an extended conjugated network. Second, these materials have a high degree of thermal stability, which means that high temperature can be used to drive the reaction to complete the development of the conjugated network. Ideally, one would like to promote the continued reaction of the active end groups until the plastic part existed as a single macromolecule, that is, a true infinite polymer network. In such a single-molecule plastic, any discontinuity of the conduction path would be offset by a multitude of alternate pathways.

In practice, one cannot prepare infinite network polymers; that is, polymerize all of the monomer (prepolymer) into a single molecule. Side reactions and/or immobility terminates polymer growth such that the material is generally composed of a number of polymer molecules rather than one single molecule. Nevertheless, the amount of hopping would be greatly reduced, and increased conductivity would be expected as the polymer structure approached an infinite network. Thus, polymerization reactions that lead to high molecular weight network polymers are important requirements.

In our investigations with the other bis-phthalonitriles listed in Table I, we discovered that these monomers can be cured without the addition of a coreactant (a metal or metal salt) by simply heating them to 200°C, or above their melting point, whichever is higher. This method of cure has some advantages over the standard phthalocyanine synthesis (Reaction 1) in that (1) the difficulty of obtaining and holding a uniform dispersion of the finely powdered metal in the prepolymer melt during the cure does not have to be dealt with and (2) the metal-free cured polymers have shown greater thermal stability than the metal cured polymers.⁴

Although this metal-free thermal polymerization is a very convenient process that yields a high temperature stable material, it creates a new problem in trying to understand the mechanism of the polymerization and the structure of the polymer. Metal-free phthalocyanine is known, but it contains two hydrogens on two of the interior nitrogens in place of the metal.⁵ Since no hydrogen source is added (the only material present is the prepolymer), it is difficult to explain formation of phthalocyanine under these cure conditions. This structure problem will be further discussed in the body of the paper.

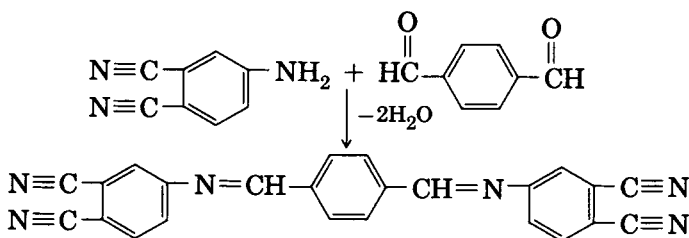
Because of the convenience and advantage of the metal-free cure as described above, we will limit the discussion in this paper to that system. The

uniqueness of this new material is that it has the potential to form a completely conjugated polymer network of high thermal stability from a prepolymer that passes through a liquid state and thus can be cast or molded using conventional polymer processing techniques. Furthermore, the conductivity of the polymer can be varied from that of an insulator to a semimetal by postcuring at higher temperatures.

SYNTHESIS

N,N'-Terephthalylidene-Bis(3,4-Dicyanoaniline)

The unpolymerized phthalonitrile monomer *N,N'*-terephthalylidenebis(3,4-dicyanoaniline) is prepared in high yield by the reaction of 2 mol of 4-aminophthalonitrile with 1 mol of terephthalaldehyde to give a Schiff's base or imine type structure:



A slight excess of the 4-aminophthalonitrile is used to ensure reaction of both aldehyde groups. The reaction can be followed by measuring the water evolved during the reaction. In a typical preparation, 12.1 g (0.0903 mol) of terephthalaldehyde recrystallized from toluene, 28.3 g (0.198 mol) of 4-aminophthalonitrile, and 1.42 L of toluene are charged into a 3-L r.b. flask fitted with a thermometer, a Dean Stark trap connected to a water cooled condenser, a heating mantle, and a magnetic stirrer. The reaction mixture is heated at reflux with stirring for approximately 24 h during which time 3.0 mL (theory 3.26 mL) of water collects in the Dean Stark trap.

At the end of the reaction, the mixture is allowed to cool to 100°C and the yellow precipitate collected by filtration and washed with 200 mL of hot toluene to give 30.8 g (theory 34.7 g) of crude product, mp 261–270°C. The crude product is purified by extracting twice with 200 mL of hot toluene and recrystallizing from acetonitrile with an overall yield of 71%, mp 270–272°C.

The IR spectrum (KBr pellet) showed absorption at 2235 cm^{-1} ($\text{C} \equiv \text{N}$ from nitrile), doublet at 1632 ($\text{C} = \text{N}$ aromatic imine and $\text{C} = \text{N}$ extended conjugated imine), and no absorption at 3380 cm^{-1} and 3480 cm^{-1} (NH_2) and 1685 cm^{-1} ($\text{C} = \text{O}$) showing absence of starting materials and half product for only one aldehyde group reacting $[(\text{NC})_2\text{C}_6\text{H}_3\text{N} = \text{CHC}_6\text{H}_4\text{CHO}]$.

ANAL. Calcd for $\text{C}_{24}\text{H}_{12}\text{N}_6$: C, 74.99%; H, 3.15%; N, 21.86%. Found: C, 74.90%; H, 3.33%; N, 21.67%.

***N,N'*-Isophthalylidene-Bis(3,4-Dicyanoaniline)**

The synthesis of *N,N'*-isophthalylidene-bis(3,4-dicyanoaniline) is identical to the preparation with terephthalaldehyde. The overall yield of purified product is 60%, mp 255–257°C.

ANAL. Calcd for $C_{24}H_{12}N_6$: C, 74.99%, H, 3.15%; N, 21.86%. Found: C, 74.86%; H, 3.26%; N, 21.64%.

In the following, we will describe the properties, polymerization, and experimental techniques in some detail for the *N,N'*-terephthalylidene-bis(3,4-dicyanoaniline) monomer. The isophthalylidene monomer is quite similar in behavior.

PROPERTIES OF THE BIS-PHTHALONITRILE MONOMER

Because of the Schiff base (imine) linkage in the structure, the monomer has a tendency to hydrolyze on exposure to the atmosphere. After several days, the hydrolysis is evidenced by the characteristic terephthaldehyde odor and by a lowering and broadening of the melting point, but no change in the infrared spectrum is observable. Even after a month, the infrared shows only a small change in the 3300–3500 cm^{-1} region (NH_2). Thus, the reaction of the monomer with air environment is sufficiently slow that there is no major problem in processing the material in an open environment. However, the material should be stored in a sealed jar or desiccator. Once the monomer is cured, the polymer is completely stable in air. This stability may result from the added resonant energy in the extended conjugated system, but most important is the fact that the highly electronegative CN groups that are responsible for the water sensitivity in the monomer are consumed in the polymerization.

POLYMERIZATION OF THE BIS-PHTHALONITRILE MONOMER

The monomer is cured by heating it above its melting point (270–272°C), typically at 300°C for 50 h. Gelation occurs in 1–2 h. During the liquid stage, the material readily flows and thus can be molded into various shapes. Some weight loss (3–4%) occurs during the early stages of polymerization because of a tendency for the material to volatilize. Evidence that the weight loss during the cure was due to loss of the monomer was obtained from collecting the lost material on a cold cover plate and obtaining a material balance between the weight loss from the monomer and weight gain on the cold cover plate. IR also indicated collected material to be pure resin. When cured in this manner, the material is dark brown in color, whereas the other bis-phthalonitriles listed in Table I form bright green polymers. The dark brown color may be a consequence of the extended conjugation in the cured polymer. If monomer is cured in the presence of Cu powder, a dark olive green color is initially obtained; in addition, the monomer cures much faster, gelation occurring within 15 or 20 min. Although strength measurements have not been made on the pure polymer, measurements on a copolymer of this material with a bis-phthalonitrile where the R spacer is the C_{10} diamide group ($-HNCO(CH_2)_8CONH-$) indicate it should have a high shear modulus and be rather brittle.

The IR spectrum of the initially cured material (KBr) indicates the presence of a small amount of CN. The remaining absorptions are somewhat broad and not very helpful for structural analysis, with absorptions bands near 1590, 1490, 1350, and 830 cm^{-1} . The carbon, hydrogen, and nitrogen analysis for monomer 1a cured at 300°C for 50 h was: C, 74.91%; H, 3.32%; N, 21.67%; total 99.90%. These values are essentially identical for the analysis of the monomer (see Synthesis section) and indicate no structural decomposition or oxidation during the 300°C cure for 50 h in air.

CONDUCTIVITY MEASUREMENTS

The structure of these monomers suggest that the polymers prepared from them should exhibit both thermal stability and electrical conductivity. However, after the initial cure in air at 300°C, the polymers are electrical insulators, reflecting the fact that molecular discontinuities are numerous. It was apparent that the polymers would have to be postcured to promote the continued growth of the conjugated system. The ability to introduce conductivity at higher postcure temperatures is a consequence of the thermal stability of the polymer that allows higher temperatures to be used without massive decomposition.

Samples for study were prepared by melting the crystalline monomer in a 2.5-cm diameter aluminum planchet and curing at 300°C in air for 25 h or longer. The solid disk was removed from the planchet and its faces polished smooth on 600-grit paper to a thickness of about 2–3 mm. The samples were postcured either (1) sealed in an evacuated tube after 3–4 flushings with nitrogen or argon or (2) kept in a stream of nitrogen or argon gas. The heat up and cool down of the samples were usually at a rate of 0.5°/min to minimize thermal stresses and cracks. After each heat treatment, measurements were made of sample weight, thickness, and resistivity.

Measurement of dc resistivity was done in either of two ways. For specimens of high resistance ($> 100\Omega$), the standard two-electrode technique was employed using a Keithley 610C electrometer. Gold electrodes, usually 1.9 cm in diameter, were vapor-deposited on each face of the specimens. They were housed in a well-shielded oven and cycled between 22 and 155°C. A continuous trace of resistance and temperature was made on a Houston Omnigraphic 3000 strip chart recorder. The volume resistivity was computed as:

$$\rho = (A/dR)$$

where ρ is in Ω cm, d is the sample thickness (cm), A is the area (cm^2) of an electrode (assuming the electrodes are of equal size), and R is the measured resistance (Ω).

The van der Pauw four-probe technique⁸ was used for low-resistance samples ($< 100\Omega$). Contact was made with small copper clips at the perimeter of one face of the specimen. A Keithley 164TT digital multimeter was used in the $m\Omega$ mode. The sample was allowed to equilibrate at various discrete temperatures between 22 and 172°C.

RESULTS AND DISCUSSION

The effect of the postcure temperature on the room temperature dc volume resistivity ρ is shown in Figure 1. Both meta and para isomers are included, the differences between them being insignificant. Of the 15 samples investigated, nine were held at the indicated temperature for 100 h, five for 60–90 h, and one, the 850°C sample, only for about 12 h. The dwell time at a given postcure temperature is also an important variable as will be described later. The purpose of this composite curve is to readily illustrate the range in resistivities that can be achieved by the thermal treatment.

The corresponding changes in activation energy E_a with postcure temperature are shown in Figure 2. The change in ρ was measured as the sample was cycled between room temperature and 172°C (155°C for the high-resistance samples) and E_a was computed from the Arrhenius relation:

$$\rho = \rho_0 e^{E_a/kT}$$

where ρ_0 is a constant, k is the Boltzmann constant, and T is the absolute temperature.

The activation energy is the parameter known to solid-state physicists as the band gap. In computing E_a for these polymers, the expression $\rho = \rho_0 \exp(E_a/kT)$ does not necessarily suggest any particular conduction model and is generally suitable for amorphous semiconductors.^{7,9} For an intrinsic

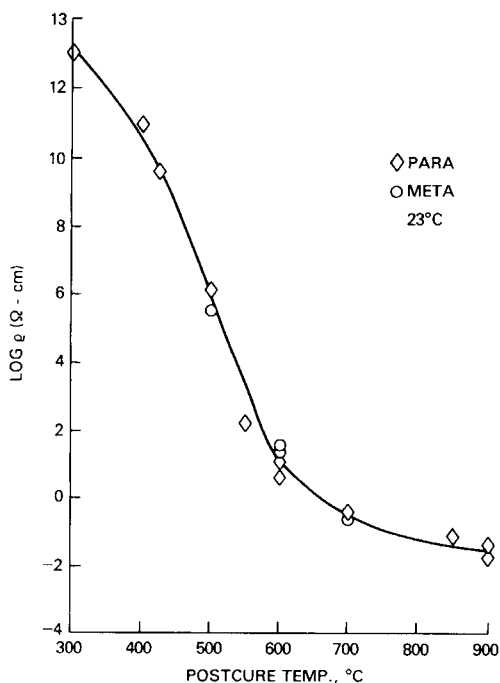


Fig. 1. The effect of postcure temperature on the electrical resistivity (measured at 23°C) of polymers prepared from the para (◇) and meta (○) dianil-bis-phthalonitrile.

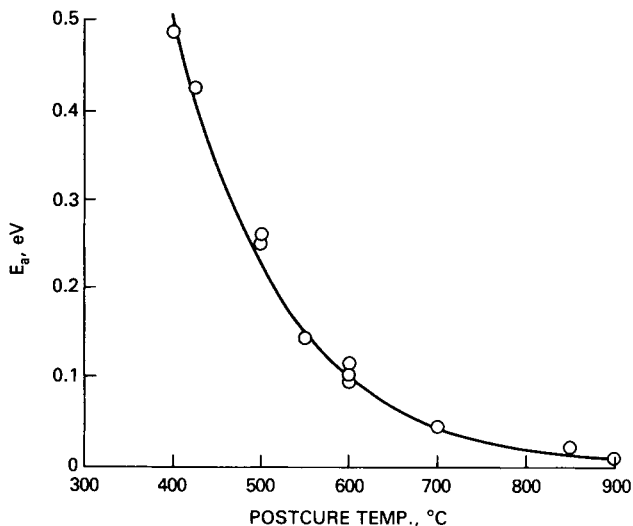


Fig. 2. The activation of conduction (energy gap) as a function of postcure temperature of the para dianil-bis-phthalonitrile polymer.

semiconductor, in which there is a hole carrier for every conduction electron, the relationship takes the form $\rho = \rho_0 \exp [(\epsilon/2kT)]$, wherein the factor of $\frac{1}{2}$ acknowledges that the current carriers are equally divided between electrons and holes. Some authors choose to characterize organic semiconductors by this latter expression.¹⁰ Our opinion, however, is that the *a priori* assumption of intrinsic conductivity, at least for the phthalonitrile polymers, is not justified, in particular because they are principally amorphous and also because the level of impurities in nearly all organic materials is much higher than in electronic-grade silicon or germanium.

A general scheme for classifying materials by the activation energy of conduction is the following¹¹:

	<u>Material</u>	<u>ϵ(eV)</u>
Insulators		3
Most of the useful semiconductors		1
Thermoelectric and infrared detectors		0.1
Semimetals		0

Keeping in mind that ϵ translates as $2E_a$, it is noteworthy that the activation energies shown in Figure 2 cover the entire range from useful semiconductors to semimetals. Thus, if one has an application that demanded a particular E_a , these polymers could be matched to the need simply by the appropriate postcure.

Figures 3–8 are plots of resistivity and temperature data representative of those which generated the curves in Figures 1 and 2 above. The resistance vs. temperature curve in Figure 3 is typical of the polymer postcured at 500°C. The same data are presented in an Arrhenius plot in Figure 4; the negative deviation from linearity at the lower temperatures should be noted for future reference. Figure 5 illustrates the rather dramatic drop in re-

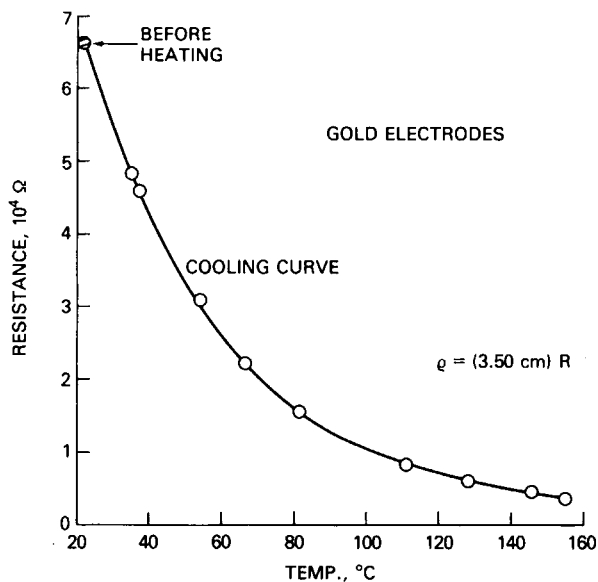


Fig. 3. A typical resistance vs. temperature curve for a meta dianil-bis-phthalonitrile polymer postcured at 500°C. Temperature as shown on the abscissa is the temperature of measurement.

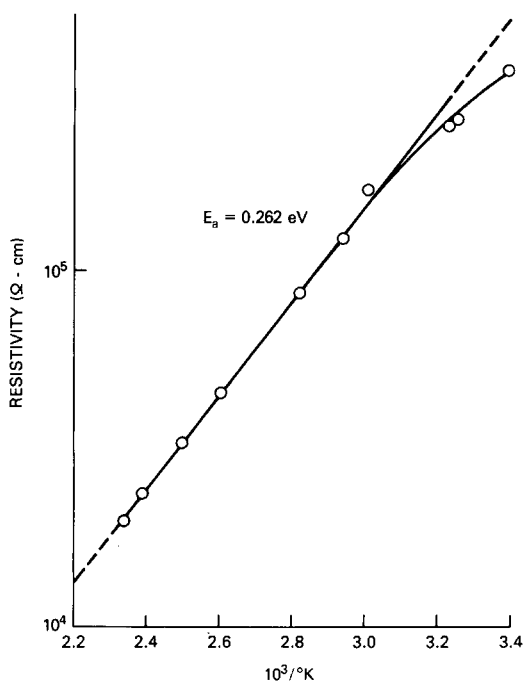


Fig. 4. Arrhenius plot of the data of the preceding Figure 3.

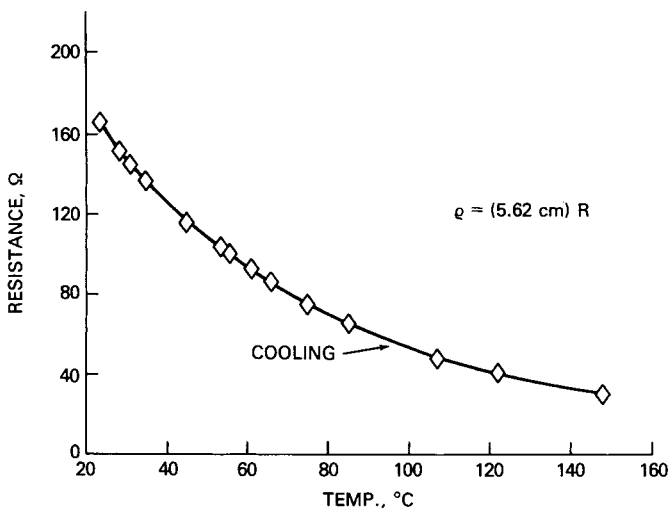


Fig. 5. A typical resistance vs. temperature curve for a para dianil-bis-phthalonitrile polymer postcured at 550°C.

sistivity that accompanies an increase in the postcure temperature of just 50°C.

Figure 6 portrays another hundredfold drop in resistivity following a further 50°C increase in postcure temperature to 600°C. When we have reached a 900°C postcure (Fig. 7), we are in the mΩ cm range and measure only a 12% decrease in ρ upon heating the specimen to 168°C, which corresponds to $E_a = 0.010$ eV. If, however, the range of measurement is extended down to cryogenic temperatures with liquid helium cooling, as in Figure 8, we see that the linearity of the Arrhenius plot is lost below -20°C. Indications of this negative deviation were just becoming manifest near room temperature in the earlier Arrhenius plot (Fig. 4).

In the previous examples, most of the resistivities were measured after the samples were postcured for 100 h at the recorded temperatures. How-

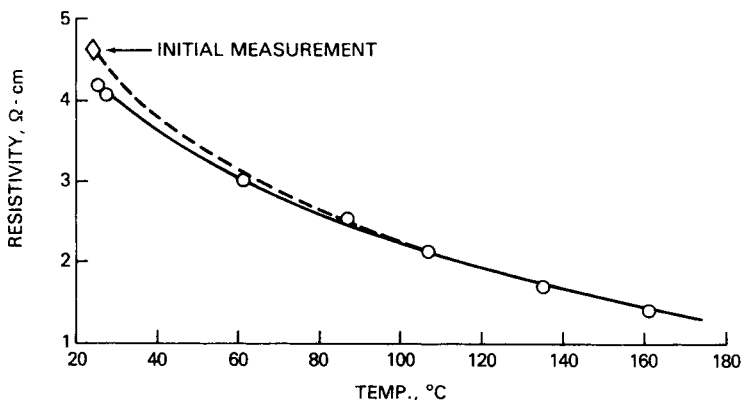


Fig. 6. Resistivity vs. temperature of measurement of a para dianil-bis-phthalonitrile polymer postcured at 600°C.

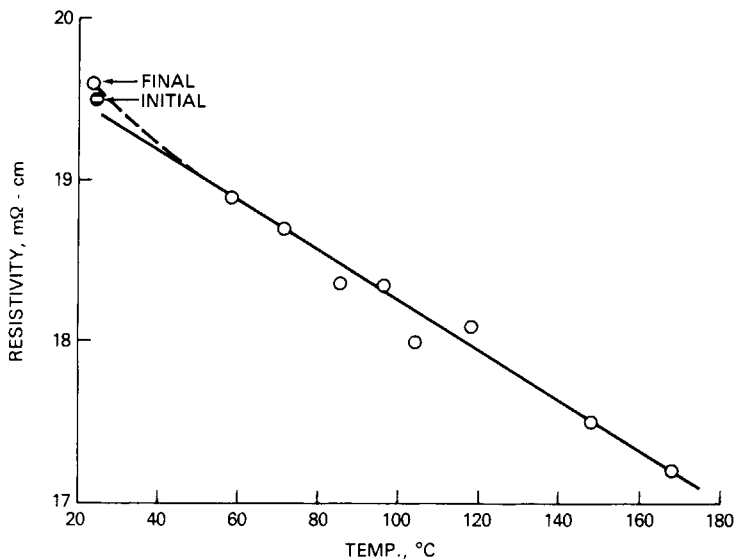


Fig. 7. Resistivity vs. temperature of measurement of a para dianil-bis-phthalonitrile polymer postcured at 900°C.

ever, as mentioned earlier, the length of time at a temperature is also important in controlling resistivity. Figure 9 shows the change in room temperature resistivity as a function of time at 500°C. This sample had previously been heated at 400°C for 230 h, and resistivity was still greater than $10^8 \Omega \text{ cm}$.

During the first 200 h at 500°C, very substantial changes in resistivity occur—a decrease of over 4 orders of magnitude. During the next 600 h, a much smaller change is observed, a decrease of approximately 1 order of magnitude. Even after 800 h at 500°C, a small decrease in resistivity is still occurring. In general, it would be more practical to proceed to higher tem-

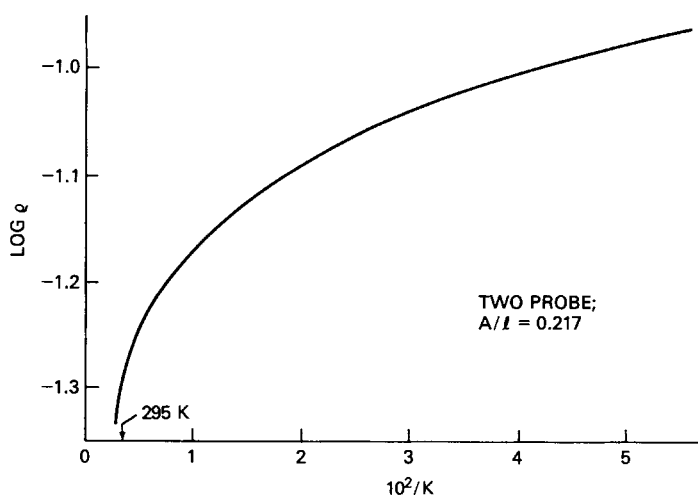


Fig. 8. Arrhenius plot of the resistivity data of a para dianil-bis-phthalonitrile polymer postcured at 900°C. The sample was cooled with liquid helium.

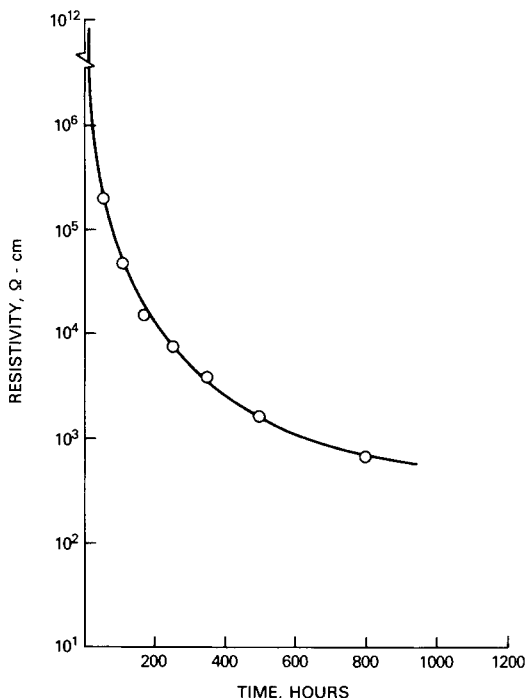


Fig. 9. The effect of the length of time at 500°C on the resistivity of a para dianil-bis-phthalonitrile polymer.

perature to obtain lower resistivity than to heat for times longer than 100 h at lower temperatures. However, in some applications it may be more appropriate to heat longer times at lower temperatures to obtain more precise control over a specific resistivity or to prevent thermal damage to other components in the system. Furthermore, although these lower temperatures (below 500°C) do not lead to rapid development of conductivity, we believe that they are important in developing the conductive polymer structure and in minimizing weight loss and the problem of sample cracking at the higher temperatures. Thus, proceeding directly to 600°C without some intermediate heating time at 400 and 500°C is undesirable.

THERMAL STABILITY

Figure 10 shows the TGA thermograms (DuPont 1090) for the *p*-dianil-bis-phthalonitrile after curing 50 h at 300°C in air. Samples were run both as a fine powder and as a single chip (approx. 27 mg). As a chip, the conditions are more closely related to the procedure used for the thermal (postcure) treatment of the polymer (a 2.54 cm diameter disk approximately 2–3 mm thick). A powder form is the usual condition for running a TGA on a solid material. In both thermograms, the samples were heated at 10°C/min under N_2 flow of 80 mL/min.

The initial weight loss of approximately 3% in both samples is absorbed water (by FTIR). The powder begins to show initial decomposition around 300°C and reaches 30 wt % at 700°C. The chip shows a weight loss of only

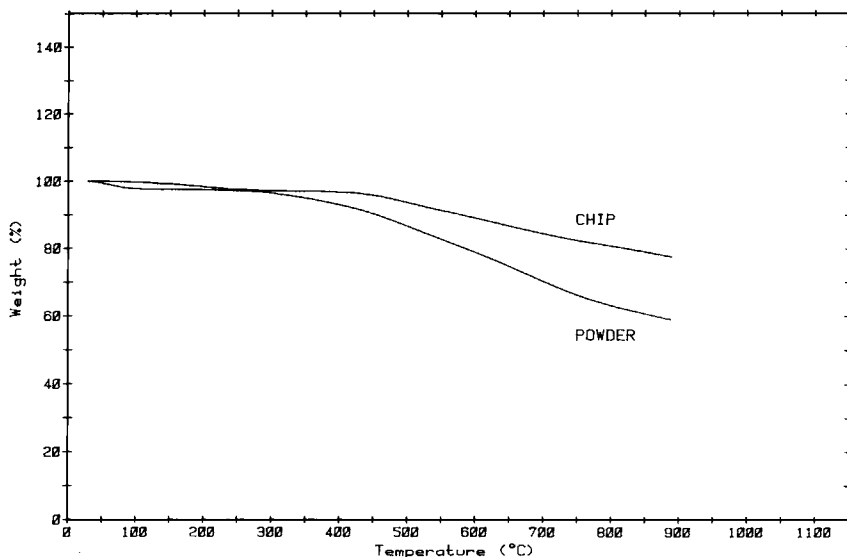


Fig. 10. TGA thermograms of the *p*-dianil-bis-phthalonitrile polymer after curing at 300°C for 50 h.

16% at 700°C. At 600°C, the chip shows a weight loss of 11% which occurs over a very short period of 57.5 min. This is indicative of the importance of using slow heat up and intermediate postcure temperatures for extended time periods to minimize weight loss during the postcure treatment that introduces conductivity into the samples. By first heating at 400°C for 100 h, then 500°C for 100 h, and finally 600°C for 100 h, the sample weight loss is only 9.0% over these long heating times.

In Figure 11 is plotted the weight losses as a function of postcure tem-

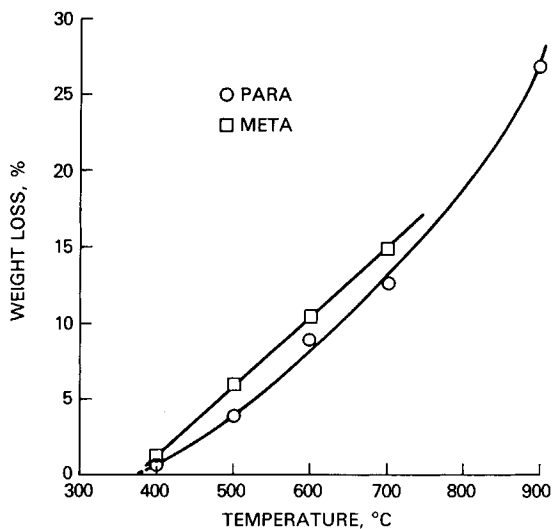


Fig. 11. Per cent weight loss of the para (○) and meta (□) dianil-bis-phthalonitrile polymers after curing for 50 h at 300°C (each point represents the weight loss after 100 h at the temperature).

perature for the para and meta dianil-bis-phthalonitrile polymers after the initial curing for 50 h at 300°C in air. These materials were heated at the indicated temperature for 100 h before measuring the weight loss and proceeding to the next higher temperature. The single point at 900°C for the para isomer had been arrived at by a somewhat different heating schedule which includes 90 h at 700°C, 60 h at 800°C, and 60 h at 900°C. Therefore, it should not be considered as a true point on the extension of the lower curve to 900°C.

Figure 12 shows the weight loss as a function of time of the para dianil-bis-phthalonitrile polymer heated at 500°C in a nitrogen atmosphere. (This material was previously cured 50 h at 300°C and postcured 230 h at 400°C, and the 5.1% weight loss during this treatment is included in the weight losses in Fig. 12.) After 800 h the weight loss appears to be leveling off at a maximum of 15%. As might be expected, shrinkage accompanies the weight loss during the postcure process. Figure 13 shows the increase in density that results from the weight loss on raising the postcure temperature to 900°C. Over this same temperature range there is a corresponding linear shrinkage of about 15%. However, the sample shape is undistorted and is essentially a slightly smaller replica of the original sample. In general, for samples prepared from well purified monomer, no macrocracks are observed for treatments below 700°C, but are occasionally noticed at 900°C. Although microcracks may be present, the samples do not become fragile and a 0.1-in. sample heated to 600°C can withstand considerable hand-held flexing force.

POLYMER STRUCTURE

As mentioned in the Introduction, there is a high degree of uncertainty in the structure of the initial polymer (300°C for 50 h) as well as the higher

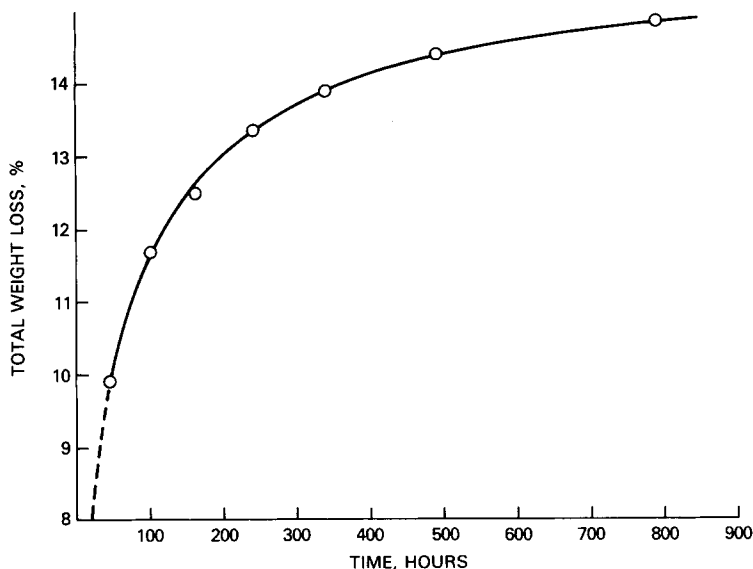


Fig. 12. Percent weight loss vs. time at 500°C for the *p*-dianil-bis-phthalonitrile polymer. (The 5.1% weight loss of the earlier treatment of 230 h at 400°C is included in the plot).

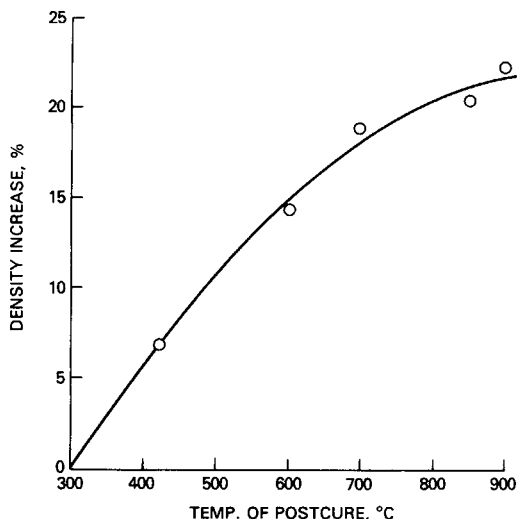


Fig. 13. The effect of the postcure temperature on the room temperature density of the para dianil-bis-phthalonitrile polymer. For the 300°C cured polymer, $D = 1.130 \text{ g/cm}^3$.

temperature postcured materials. Although our initial intentions were to convert these bis-phthalonitrile monomers into polyphthalocyanine by reacting with metals, our discovery that these materials could be polymerized by heat alone provided us with a much more convenient process procedure as discussed earlier. However, since no metal coreactant or specific hydrogen source is added for the polymerization, it is difficult to understand how the phthalocyanine structure might form since the cavity in the phthalocyanine ring contains either one metal atom (for +2 or higher valance states metals, for example, Mg^{++}), two metal atoms (for +1 valance state metals, for example, Na^+), or two hydrogen atoms for the metal-free phthalocyanine structure shown in Figure 14. The formation of a material called "dehydro" phthalocyanine, (Fig. 15) has been reported.¹² However, it was not isolated in a pure state, and its structure was not unequivocally defined. Although such a ring would be quite convenient to suggest for this new polymer, we have no data to support such an assignment. The theoretical hydrogen in

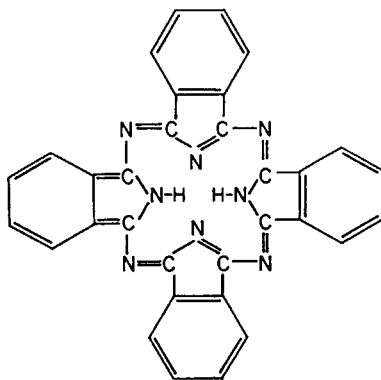


Fig. 14. Phthalocyanine

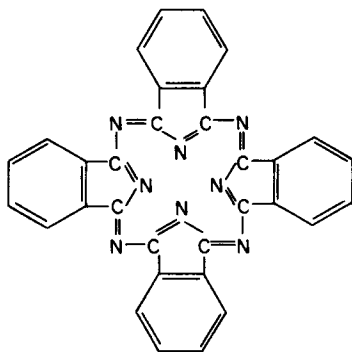


Fig. 15. "Dehydro" phthalocyanine.

the "hydro" phthalocyanine and the "dehydro" phthalocyanine polymer is 3.48% and 3.16%, respectively. The percent hydrogen found in our polymer is 3.33%, exactly splitting the two theoretical values.

It has not been possible to obtain good infrared spectra for structural interpretations due to the intense dark color of the cured material. The disappearance of the CN absorption at 2230 cm^{-1} can be easily followed, and after 50 h at 300°C most of the CN has disappeared, but not all; the remaining absorption are very broad and weak in intensity. Further postcuring eliminates the CN absorption.

The results of limited ESCA (Electron Spectroscopy Chemical Analysis) study provides some indication that a phthalocyanine type of structure may be at least partially formed during some stages of the postcure sequence. ESCA analysis of the 300°C cured polymers did not reveal the characteristic spectra of the phthalocyanine ring bonding energies for carbon and nitrogen electrons. But, after postcuring at 550°C , ESCA showed two types of nitrogens of almost equal concentration with distinct binding energy levels of approximately 398.4 and 399.8 eV, and a single type carbon with a binding energy of approximately 284.6 eV. These values agree with measurements made on the simple (nonpolymeric) metal-free phthalocyanine. Even at 900°C , ESCA still indicates the presence of organic structure; however, the "phthalocyanine ring" concentration appear to be 0.25–0.5 that observed for the material heated to 550°C . Thus some of the hydrogen that is lost (see below) during the postcure treatment may become available to complete the formation of some phthalocyanine.

A carbon–hydrogen–nitrogen analysis was not obtained on the 900°C sample, but at 550°C (5.8% wt loss) values are 81.35%, 2.08%, and 16.69%, respectively, compared to theoretical values of 74.99%, 3.15%, and 21.86%. These results show carbon enrichment, which would be a logical consequence of further aromatization of the structure. This indicates some deviation from the ideal structure based on phthalocyanine, but it is also possible that some decomposition is at unreacted endsites which would lead to little change in the basic polymer structure. At 900°C , where a 27% weight loss occurs, a definite change in the polymer structure is expected. However, this temperature is too low for graphite formation, and the X-ray diffraction pattern was not indicative of a graphite structure. The X-ray diffraction scans shown in Figure 16 were made using a General

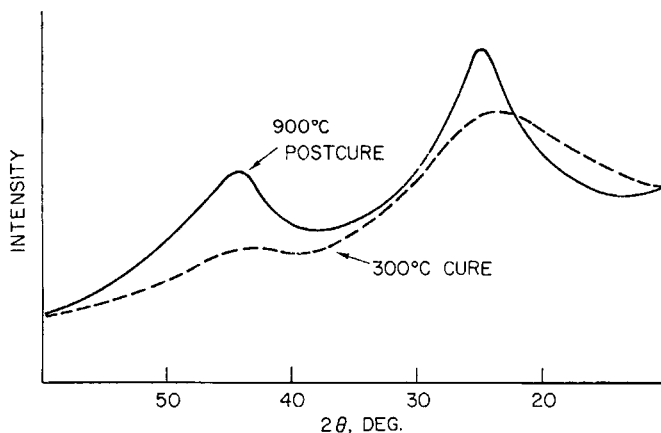


Fig. 16. X-ray diffraction scans (Ni-filtered Cu $K\alpha$ radiation) made on solid disks of the *p*-dianil-bis-phthalonitrile polymer.

Electric XRD-6 diffractometer with Ni-filtered Cu $K\alpha$ radiation. The broad peaks of the 300°C-cured specimen are typical of a semicrystalline polymer. The peaks grow progressively sharper with higher postcure temperatures, indicative of increasing structural order. The large peak at $2\theta = 25^\circ$ corresponds to a d -spacing of 3.56 Å (0.356 nm) which is approaching the 3.35 Å ($2\theta = 26.6^\circ$) spacing between the basal planes of graphite. This 25° peak, however, is much broader and much less intense than X-ray diffraction peaks from a high-grade graphite. In addition, the density of the 900°C samples (1.7 g/cm³) is far from that of graphite (2.25 g/cm³). Thus, the graphitic character of the postcured polymer is much too weak to account for their considerable electrical conductivity.

This limited information does not allow us to infer any specific structure to the polymer; however, our feeling is that the bulk of the conductivity results from a conjugated, condensed aromatic organic structure and not from the formation of carbon or graphite.

SUMMARY

We have reported the synthesis of two bis-phthalonitriles in which the two phthalonitriles are linked together through a conjugated para- or meta-dianil structure. These materials can be melt cured at 260–300°C and then further postcured to introduce conductivity. Although the cured materials are intractable, the prepolymers melt into free flowing liquids and remain fluid for 1–2 h depending on the cure temperature. Thus moldings, castings, and pre-pregs can be fabricated using conventional processing techniques.

The conductivity on these materials can be varied from that of an insulator to approximately $10^{+2} (\Omega \text{ cm})^{-1}$. The cured polymers have high thermal (only 9–10% weight loss after 100 h at 400, 500, and 600°C) and environmental stability. Since reactive dopants are not used, the conductivity is also stable in ambient as well as more aggressive environment. A material that has been postcured at 600°C would be able to survive extended

use at over 300°C with little or no change in conductivity and other properties.

However, since the polymerization processes are complex, and the cured polymers are stable and intractable (generally very desirable properties in a cured polymer), the exact structure of these materials is not known. Initially, we synthesized these bis-phthalonitriles to prepare polyphthalocyanines, and, indeed, under certain conditions, at least some phthalocyanine may form. However, it is difficult to understand how this could be the major structure formed under the condition we use for the polymerization. Work is being initiated to attempt to elucidate this structure, the chemistry of the polymerization, and the conductive mechanism.

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