Charles Vest, 723

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Interim Summary Report

for

High Thermal Conductivity Polymeric Materials for Spacecraft Use

(1 July 1966 to 1 June 1968)

Contract No.: NAS5-10260

Prepared by

Astropower Laboratory
Missile & Space Systems Division
Douglas Aircraft Company
McDonnell Douglas Corporation
Newport Beach, California

for

Goddard Space Flight Center

Greenbelt, Maryland

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R. K. Jenkins

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Contracting Officer: A. L. Essex
Technical Monitor: Charles Vest

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Project Manager: N. R. Byrd, Ph.D.

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ABSTRACT

This program was undertaken to investigate the possibility of preparing new classes of polymers, which through various structural geometries, and modifications would give rise to increased thermal conductivity.

The design goals recommended for the program were:

Electrical Resistivity	1×10^{10} ohm cm
Thermal Conductivity	0.05 cal/cm-sec-^{o}K
Working Temperature	-30^{o} to 200^{o}C
Working Pressure	Ambient to 10^{-12} torr

The program plan for the study of thermally conductive polymers involved an initial literature survey followed by analysis of available data. The results of the survey led to a program to determine the contribution of various parameters, such as (1) electron density, (2) crosslink density, and (3) crystallinity, to the thermal conductivity of a particular polymer structure.

The polymer system first evaluated for electronic contribution was the ring substituted polyphenylacetylenes having a conjugated polyene backbone structure. It was found that substituted phenylacetylenes such as p-formamido, p-nitro, and p-amino yielded approximately constant thermal conductivity values as a function of temperature. A value of about 5.5×10^{-4} cal/cm-sec-^{o}C indicated that, regardless of either the inductive and/or electromeric effect of the para substituted phenyl group, the polyene backbone was not sufficiently influenced so as to display increased or decreased thermal conductivity. It was concluded that the main polyene backbone was not sufficiently conjugated to promote an electronic contribution to thermal conductivity.

Some synthetic effort was put forth to enhance thermal conductivity of linear conjugated polymers through a lattice vibration approach by crosslinking. Unfortunately, results obtained in this phase of the program were negative. Regardless of the mole ratio of polymer to crosslinking agent employed, the thermal conductivity at intermediate temperatures was never greater than that of the polymer alone, i.e., about 6.0×10^{-4} cal/cm-sec-^{o}C.

A series of charge transfer polymers having pseudo crystallinity was investigated for thermal and electrical conductance as a function of synthesis parameters. The polymers were prepared by reacting various α, ω-alkanediamines in an excess of p-benzoquinone thereby forming a "redox" type polymer containing both the quinone and hydroquinone groups. During molding the quinone-hydroquinone groups in the chain appear to orientate so that a charge transfer complex was formed. The formation of this complex yielded a

polymer of high thermal conductivity in the 10^{-3} cal/cm-sec-°C range as a function of temperature, and an electrical resistivity of 10^{12} - 10^{15} ohm-cm.

The polymers displaying the optimum thermal conductivity-temperature results were prepared from the 1, 7 heptane and 1, 8-octane diamines and benzoquinone. At higher temperatures, the thermal conductivity values for these two polymers remain at about 1 x 10^{-3} cal/cm-sec-°C, while at lower temperatures the k values increase quite dramatically and in some cases approach 5 x 10^{-3} cal/cm-sec-°C. The flexibility of the polymers increases quite rapidly as the number of (CH_2) groups increase from 2 to 12. The polymer prepared from 1, 12-dodecanediamine and benzoquinone was quite strong and flexible whereas that prepared from 1, 2-ethanediamine was hard and brittle. The odd numbered diamines were generally more flexible than the next higher even numbered diamine.

It was found that the best system for obtaining enhanced thermal conductivity was that of the diamine/quinone (quinhydrone) polymers. The thermal conductivity was in the middle-to-low 10^{-3} cal/cm-sec-°C range, the electrical resistivity was 10^{12} to 10^{15} ohm-cm and they exhibited thermal stability to 200°C.

It is recommended that further effort be expended toward preparing a soluble system for use in coatings. In addition, it is recommended that the general reaction be extended from the use of diamines to other difunctional monomers, e.g., diols, dimercaptans and diacid halides, among others. Physical characterization of the polymers prepared should be undertaken with a view toward obtaining modulus data, cure studies, tensile and elongation.

CONTENTS

FIGURES

Section 1

INTRODUCTION AND SUMMARY

A major problem in the electronics industry is the unavailability of substances for coating electrical components to provide environmental protection electrical insulation, protection from heat and electrical charges, and heat dissipation from the component. A number of materials have been investigated for this purpose, with varying degrees of success. The materials have generally been in one of the following categories — epoxies, modified epoxies, silicones, polybutadiene or poly(butadiene/styrene) resins, parylenes (poly p-xylyenes), polyurethanes and phenolics, either filled or unfilled, depending on the ultimate end use.

The use of these polymeric systems, while solving the immediate mechanical and electrical problem, often present additional use limitation due to flammability in O_2 atmosphere and heat buildup in and around electronic components. This heat accumulation is caused by lack of an efficient thermally conducting medium that could dissipate the generated heat by allowing flow from the high temperature region to the ambient. The thermal conductivity of most unfilled electronic insulators is in the order of 3.0×10^{-4} cal/cm-sec-°C thus providing a highly efficient heat insulator rather than a conductor. This program was undertaken to investigate the possibility of preparing new classes of polymers, which through various structural geometries, and modifications, would give rise to increased thermal conductivity.

The design goals recommended for the program were:

Electrical Resistivity	1×10^{10} ohm cm
Thermal Conductivity	0.05 cal/cm-sec-°C
Working Temperature	-30° to 200°C
Working Pressure	Ambient to 10^{-12} torr

The properties of flexibility for absorbing mechanical shock, and electrical insulating capability are predicated upon having an almost totally saturated, inert, relatively elastic molecular structure; and the thermal conductivities of such systems would, in general, be relatively low. In fact, the ambient thermal conductivities of a number of representative polymers, such as poly(methyl methacrylate), polyethylene, rubber, and polystyrene have been found to be in the region of $2\text{-}8 \times 10^{-4}$ cal/cm-sec-°C (Ref. 1), which is about as low as can be found among most organic substances.

The initial program plan in the study of thermally conductive polymers involved a thorough literature survey followed by an evaluation of available data. The results of the survey suggested a program that was undertaken to determine the contribution of various parameters; e.g., crystallinity, electron density, flexibility, and crosslink density; to the thermal conductivity of a particular polymer structure. The polymer evaluated was the ring substituted polyphenylacetylenes having a conjugated polyene backbone. However, the approach was finally abandoned due to the adverse physical properties of these polymers, e.g., low molecular weight, intractability, poor solubility, marginal electrical resistivity, and generally poor thermal conduction. It was concluded that the backbone of the substituted phenylacetylenes was not coplanar and thus could not promote increased electronic mobility (Ref. 2). Secondly, the stereoregularity of these polymers initially thought to be trans-aligned were in most cases transunaligned, thus preventing orientation of the polymer.

The second, and current phase, of this program is the evaluation of various charge transfer complexes. The complexes are formed by electron transfer of the donor, D, to the electron deficient acceptor, A. Either, the donor or acceptor, or both, may be polymeric and may be synthesized as part of the main chain or as an appendage. The initial results in the investigation of this new area, utilizing acceptors such as tetracyanoquinonedimethane, tetracyanoethylene and chloranil, were somewhat disappointing in that the thermal conductivity of the systems advanced in small increments while the electrical resistivity decreased in large increments into the range of semiconductors.

However, a new series of polymers was prepared using an inter- and intramolecular charge transfer complexing mechanism which promotes high thermal conductivities as a function of temperature while maintaining good electrical resistivity (Ref. 3). The polymers, prepared by reacting an excess of benzoquinone with various alkanediamines, have properties ranging from hard brittle substances to flexible rubbery materials, depending on the length of the alkane chain of the diamine. They have good electrical resistivities (10^{12} to 10^{15} ohm-cm) and thermal conductivities in the mid to low 10^{-3} cal/cm-sec-°C range.

Section 2

ACCOMPLISHMENTS

2.1 THEORETICAL BACKGROUND

2.1.1 Thermal Conductivity of Saturated Polymers

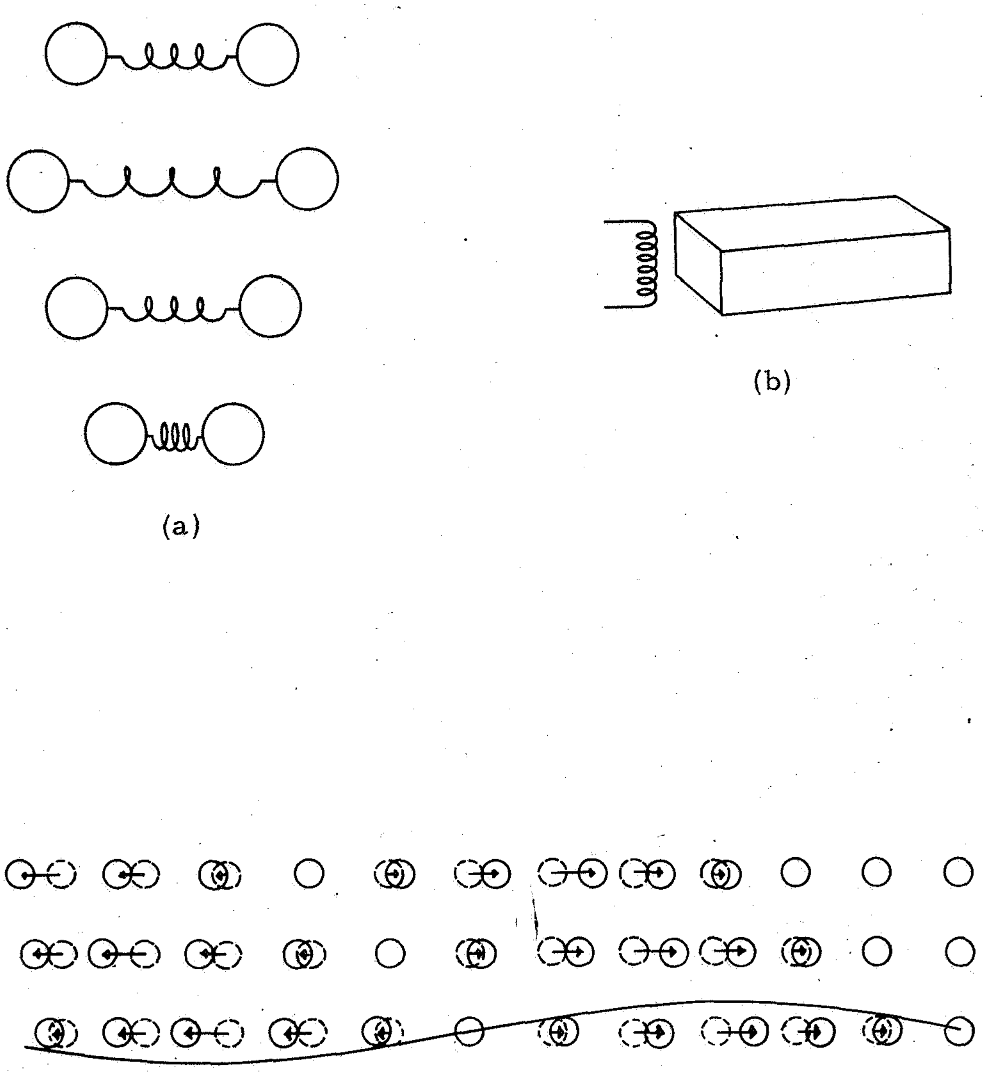
The transfer of energy in a solid may be accomplished by coupling of the lattic vibrations (phonon) or by the electronic movement and collision with atoms. In ordered crystal structures at low temperature, the phonon process of energy transfer is adequately described by:

$$k = 1/3\, C \bar{\upsilon} \lambda \qquad (1)$$

where k is the thermal conductivity, C the specific heat, $\bar{\upsilon}$ the average velocity of waves and λ the mean free path of phonons.

The concept of wave motion is best represented by considering energy introduced at one end of a solid which, in turn, causes the atoms in the lattice to increase the displacement of their normal vibrational amplitude. Successive displacements in the lattice create a traveling wave whose energy is proportional to the frequency of the wave. The energy and momentum carried by the waves in the solid are quantized, and exist in energy units called phonons (see Figure 1).

Thermal conductivity of crystalline material at low temperatures is simply the measurement of phonon flow. If the crystal lattice were perfect then phonons would flow unimpeded and the thermal conductivity would be infinite. However, phonons undergo interactions and collisions with themselves, crystal grain boundaries and defects thus reducing the phonon flow and consequently the thermal conductivity. The crystal lattice contribution to phonon flow may readily be observed by plotting thermal conductivity as a function of temperature for crystalline polymers (Ref. 4-6). Generally, the thermal conductivity of the crystalline phase follows a 1/T relationship up to the melting temperature of the polymer. The amporphous phase of the polymer also contributes to thermal conductivity and is generally 6.0×10^{-4} cal/cm-sec-^{o}C or less. The thermal conductivity of both phases are additive but appear to reach maximum values in the low 10^{-3} cal/cm-sec-^{o}C when measured at room temperature (see Figure 2). Polymers differ markedly from crystalline dielectric materials in many ways. Instead of a three-dimensional crystal, as in the dielectrics, there is basically a uni-dimensional system, viz., a linear chain with maximum forces along the chain due to bond energies between atoms. The bond energies between the chains are considerably weaker and are represented by such things as H-bonds, van der Waals forces and dipole interactions, among others. In addition, the chains are not in an



Atoms in a crystal lattice exert forces on one another that can be best represented by ordinary springs (a). When energy is introduced at one end of a solid, say by a heater (b), the first rank of atoms in the crystal lattice (c) experience an increase in vibrational amplitude, which they communicate to the neighboring atoms through the atomic forces represented by the springs. This creates a traveling wave along the rows of atoms.(1)

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Figure 1. Mechanism of Thermal Energy Transfer in a Solid(1)

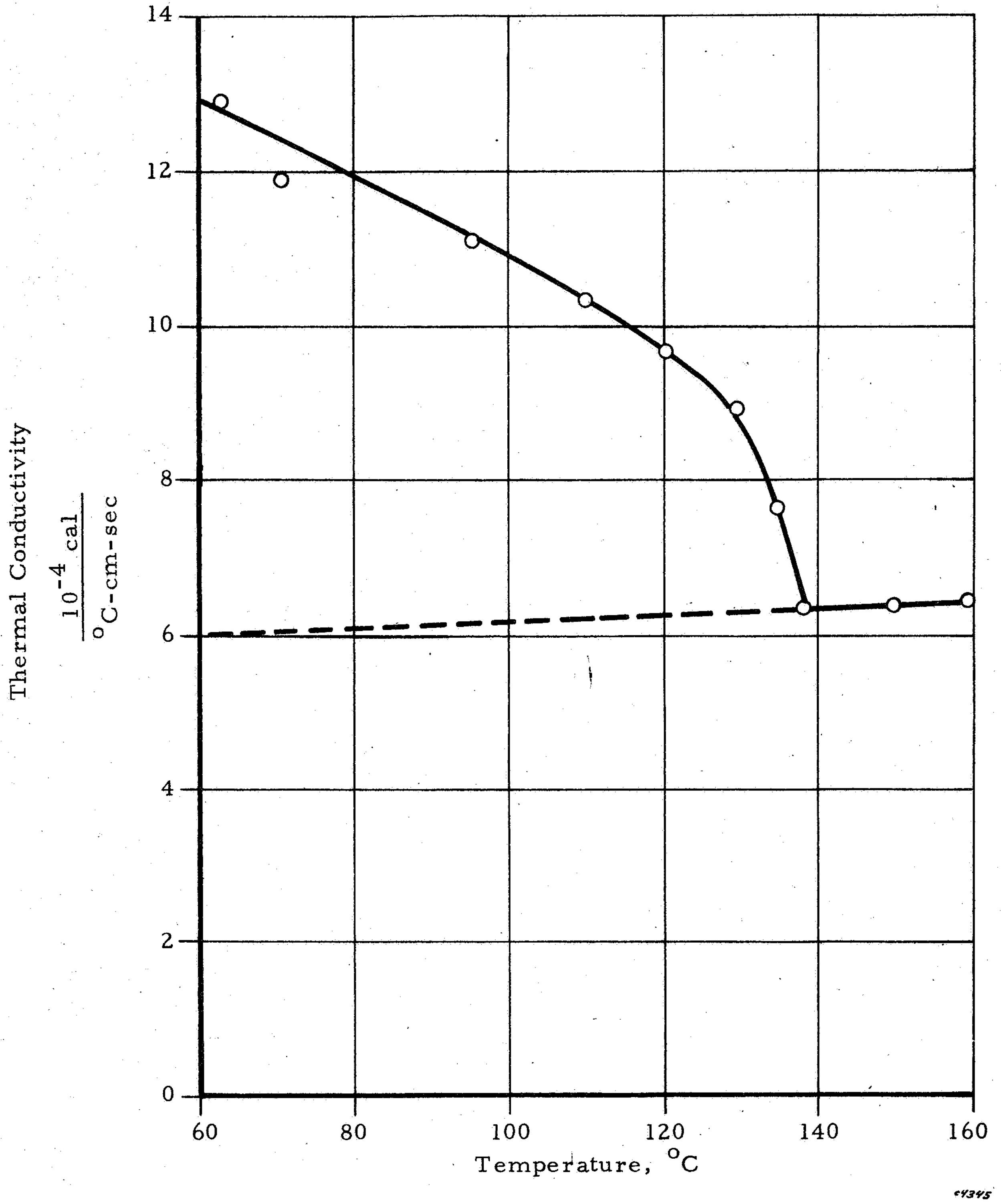

Figure 2. Thermal Conductivity of Linear Polyethylene as a Function of Temperature

idealized form of being totally extended, uniform in molecular weight, and stereochemically similar, but are of varying molecular weight, somewhat coiled in most instances, of varying degrees of tacticity, and directed in three dimensions. Furthermore, polymers exist in different states at different temperatures; e.g., above the glass transition temperature (Tg) the polymer is elastic; below the Tg, it is hard and glassy. However, the greatest changes usually occur at the glass transition temperature.

Eiermann (Ref. 4) has examined the change in thermal conductivity with respect to temperature for a number of substances. Figures 3 and 4 depict the changes in thermal conductivity of natural rubber and polyethylene, respectively, with temperature, and they show the effect of going through the glass transition temperature, i.e., for natural rubber (Figure 3) the thermal conductivity reaches a maximum at the Tg, and then drops off sharply; for polyethylene (Figure 4), the conductivity also approaches a maximum at the Tg, but then slowly increases to a room temperature value of about 6.0×10^{-4} cal/cm-sec-°C, as shown in Figure 2.

2.1.2 Thermal Conductivity of Semiconductors

Comparatively little data exist in the literature on the thermal conductivity characteristics of semiconductors. Where mention is made about the conductivity of semiconductors, it is primarily directed towards the electronic behavior of the systems with only a scant reference to the fact that both phonon and electron contributions would be found in the thermal conductivity of these materials. Furthermore, there are virtually no references to the thermal conductivity of organic semiconductors. In view of the fact that one of the proposed methods for obtaining thermally-conducting polymers was by means of a system containing conjugated double bonds, it is of importance that some comment be made regarding the behavior of semiconducting materials as heat transfer agents.

Organic semiconductors are capable of supporting electronic conduction by nature of the presence of linearly conjugated carbon-carbon double bonds. In fact, in the numerous papers devoted to organic semiconductors, it has been postulated that the band theory is applicable to the conduction mechanism of organic semiconductors. In view of this, with regard to electronic conduction, these systems are considered to be metallic in their conducting capability. By extrapolation, the thermal conductivities of these polymers should also be metallic in nature. The function of the conjugated main chain is to provide a low resistivity path for electrons and holes to migrate, thus providing both electronic and heat flow by the interaction of these electrons and holes with atoms and phonons.

2.1.3 Thermal Conductivity of Charge Transfer Complexes

Charge transfer complexes and hydrogen bonded complexes provide electrical and thermal coupling mechanisms between conjugated chains which allow a continuation of the free electrons and holes. Generally, the thermal conductivity of a mterial may be written as

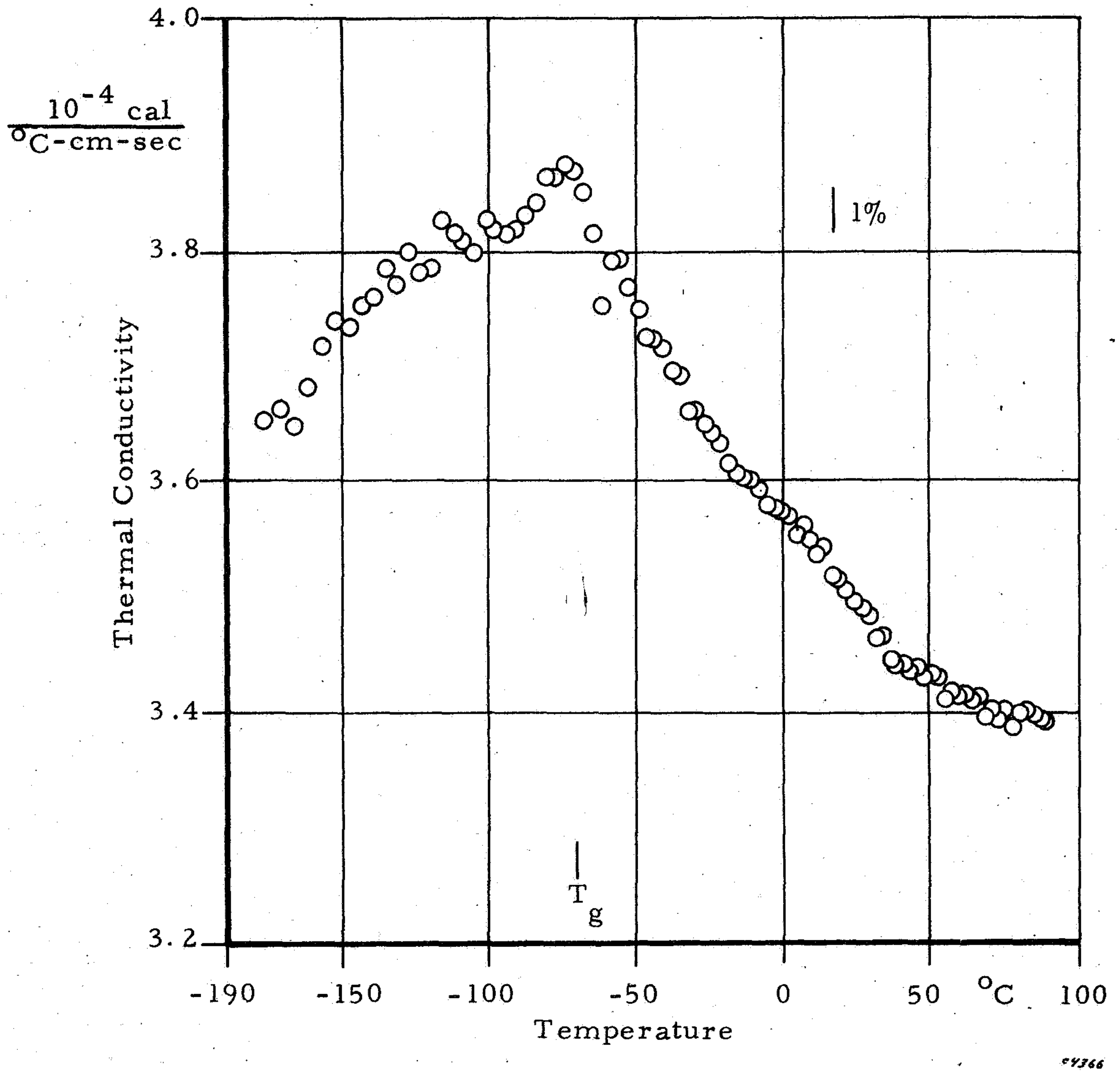

Figure 3. Thermal Conductivity of Natural Rubber (Ref. 4)

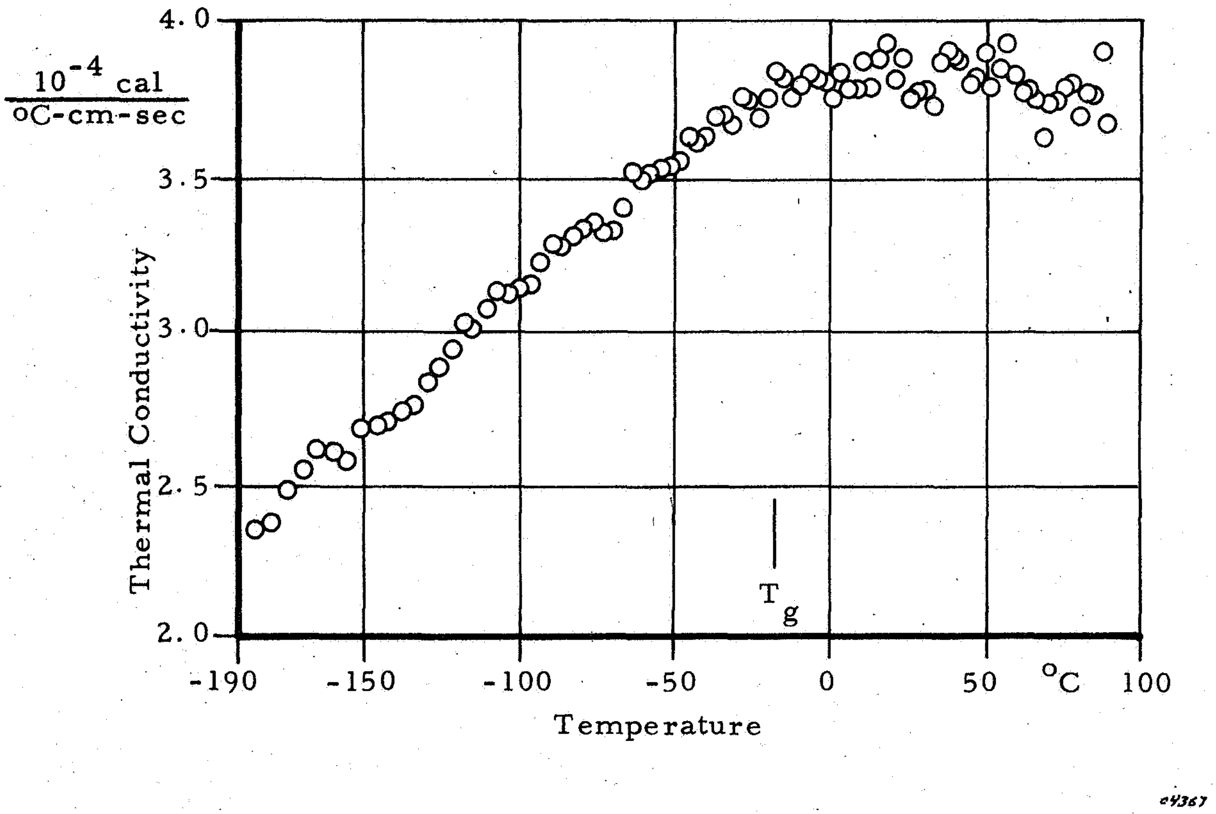

Figure 4. Thermal Conductivity of the Amorphous Phase of Polyethylene (Ref. 4)

$$k_t = k_p + k_e \qquad (2)$$

where k_t is the total thermal conductivity, k_p is the phonon contribution to thermal conductivity and k_e is the electronic contribution. In most organic polymers k_p may be further divided by considering the contribution of the crystalline and amorphous phase

$$k_p = \gamma k_c + (1 - \gamma) k_a \qquad (3)$$

γ = percent crystallinity

where k_a is of the order of 6×10^{-4} cal/cm-sec-°C, or lower, and k_c may reach values of about 1.5×10^{-3} cal/cm-sec-°C. The total thermal conductivity of a polymer may now be written as

$$k_t = \gamma k_c + (1 - \gamma) k_a + k_e \qquad (4)$$

The term k_e in most polymers may be approximated by using the Wiedemann-Franz Law

$$k_e/\sigma T = \delta_o \qquad (5)$$

Where k_e is the thermal conductivity (electronic contribution), σ the electrical conductivity, T the temperature, and δ_o a constant with a value of 5.84×10^{-9} ohm-cal/sec-°C. A few calculations using this equation indicates that σ must be quite high for even a minor contribution to k_t since $k_p \lesssim 10^{-3}$ cal/cm-sec-°C. However, for polymers that display semiconducting capabilities, the Wiedemann-Franz Law is modified to include the width of the energy gap (Ref. 7)

$$k/\sigma T \sim (k^2/e^2)\ (E_G/kT)^2 \qquad (6)$$

The term $(E_G/kT)^2$ may be of the order of many hundreds and if the number of electron-hole pairs produced are about equal it should make a large contribution to the thermal conduction without giving rise to electric current. Finally, one may write a general equation of heat flow that includes the parameters discussed.

$$k_t = \gamma k_c + (1 - \gamma) k_a + (\sigma T k^2/e^2)\ (E_G/kT)^2 \qquad (7)$$

2.1.4 Measurement of Thermal Conductivity "k"

There are three basic methods of heat transfer through a medium — conduction, convection and radiation. For solids, from low (0 - 200°K) to considerably above ambient temperatures (473°K), conduction makes the greatest contribution. Above this temperature radiation begins to show some effect, as well as the conduction mechanism. However, for the purpose of the present discussion, and conditions under which the materials in question will be operating, only conduction will be given any consideration.

The mathematical theory as well as the practical calculation of heat conduction is based upon a macroscopic interpretation. The basic equation for thermal conductivity, which serves to define that term is,

$$\frac{dQ}{d\tau} = -kA\frac{dT}{dx} \qquad (8)$$

where dQ is the amount of heat flowing normal to the area (A) in time ($d\tau$). The heat flow is proportional to the temperature gradient ($-dT/dx$), with the proportionality factor being a constant specific for each material, that is, the thermal conductivity k (Ref. 8).

Under steady-state conditions, the heat flux (q) and temperature at each point are independent of time. Integration of the equation

$$q = \frac{dQ}{d\tau} \qquad (9)$$

gives, for a flat slab, the heat flow as

$$q = -kA\frac{t_2 - t_1}{x_2 - x_1} \qquad (10)$$

Thus, for heat flow through a uniform wall, steady-state conduction is said to exist when the temperature at all locations in a substance is constant with time. Since $x_2 - x_1 = \ell$, the thermal conductivity coefficient (k) is given as

$$k = \frac{q/A}{(t_1 - t_2)/\ell} \qquad (11)$$

and has the dimensions cal/(sec)(cm)(^{o}C).

A comparative technique, described in ASTM C408-58 for thermal conductivity of ceramics, is employed. The apparatus consists of an evacuated chamber (capable of 10^{-6} torr), an electrical heater, water-cooled base plate and suitable radiation shields (see Figure 5). Thermal conductivity of the test sample is measured relative to that of copper bars. One-half inch diameter cylindrical copper thermodes have been employed. Iron-constantan thermocouples are permanently attached to the thermodes for temperature measurements.

The thermal conductivity values are computed as the simple inverse ratio of the temperature gradients from the following expression:

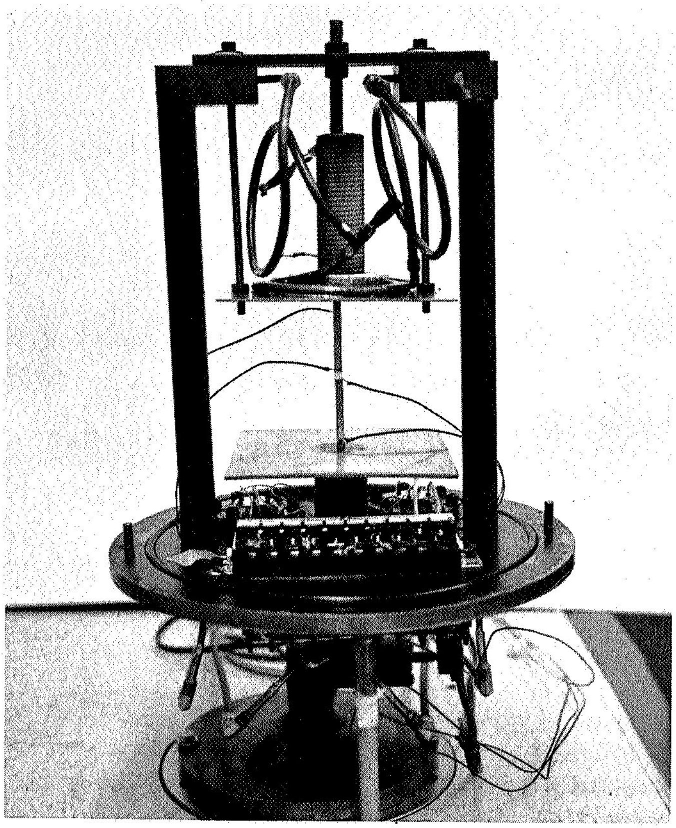

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Figure 5. Thermal Conductivity Apparatus

$$k_s = \frac{k_{Cu}\, t_{Cu}\, x_s}{t_s\, x_{Cu}} \tag{12}$$

where

k_s = thermal conductivity of sample

k_{Cu} = thermal conductivity of the copper thermode at the mean temperature of upper thermode

t_{Cu} = temperature difference between thermocouples on lower copper thermode

t_s = temperature difference across specimen

x_s = length of specimen

x_{Cu} = distance between thermocouples on lower copper thermode

To ensure good thermal contact between the organic polymer specimen and the copper thermodes thin foils in indium, 0.010 inch, are positioned between the copper thermodes and the organic polymer specimens, and a small compressive force is maintained by use of a compressed spring on the upper thermode.

2.1.5 Electrical Resistivity

Cylindrical discs were used to measure electrical resistivity of organic polymers. The volume resistivity is calculated from the expression

$$\rho = \frac{R \cdot A_e}{L_e} \tag{13}$$

where R is the measured value of resistance, ρ is the volume resistivity of organic membrane, L_e and A_e are effective length and area.

The technique for measuring the volume resistivity of insulating materials follows procedure outlined in ASTM D257-61. This requires the use of a third electrode to guard against surface effects.

2.2 POLYMER SYNTHESIS

This program has consisted of two areas of endeavor — synthesis and thermal conductivity measurements. Since the major intent has been to study methods of increasing the thermal conductivity of unfilled organics, this phase of the program is being discussed in the text of this report. The synthesis of various materials investigated for thermal conductivity will be found in Appendix I.

Section 3

RESULTS AND DISCUSSION

3.1 BASE POLYMERS

During the early phase of this program considerable effort was expended in investigating various substituted polyacetylenic derivatives with respect to crosslink density, crystallinity and electron density, and their effect on the polymer's thermal conductivity. It was found that some of the substituted poly(phenylacetylenes); such as the p-formamido, p-nitro, and p-amino yielded approximately constant thermal conductivity values as a function of temperature as shown in Figure 6. The average value of about 5.5×10^{-4} cal/cm-sec-°C indicates that regardless of the inductive or electromeric effects of the para substituent, the polyene backbone was not sufficiently influenced to obtain increased or decreased thermal conductivity. One contributing factor may be that the polyene backbone was not sufficiently conjugated to promote an electronic contribution to thermal conductivity. The incomplete main chain conjugation arises from a statistical removal of chlorine resulting in residual chlorine at the alpha position when the thermal dehydrohalogenation step is completed. In addition, the linearity of the thermal conductivity-temperature (k-T) curves indicates that these particular polymers are in an amorphous state rather than crystalline and therefore contain the trans-unaligned rather than trans-aligned configuration.

Figure 7 depicts the (k-T) plot of poly(phenylacetylene). Notice, that the thermal conductivity decreases rapidly as a function of temperature up to 60°. At this temperature the conductivity passes through a minimum followed by a steady increase as the temperature is raised. Poly(phenylacetylene) is much less sterically hindered than its para substituted derivatives thereby providing a greater driving tendency for the trans-aligned state and subsequent crystallinity. The positive slope of the (k-T) curve, above 60°, appears to indicate an electronic contribution to thermal conductivity due to the partial coplanarity of the conjugated backbone system.

In addition to a possible electronic contribution to thermal conductivity from a conjugated polyene structure, there is the contribution from hydrogen bonding. For this purpose, polystyrene derivatives were used. The (k-T) plots of two polystyrene derivatives are shown in Figure 8. Both the poly(α-chloro-p-aminostyrene) and poly(α-chloro-p-formamidostyrene) curves appear to indicate crystallinity as evidenced by the sharp decrease in the initial portion of their (k-T) curves; however, this effect is most likely introduced by strong hydrogen bonding between the chlorine and amino/formamido groups. This type of bonding provides a secondary path for heat flow somewhat related to a pseuo-electronic effect analogous to the transfer of electrical energy found in proteins. The curves differ from that of poly(phenylacetylene) in that, above the inflection temperature, the curves decrease as a function of temperature

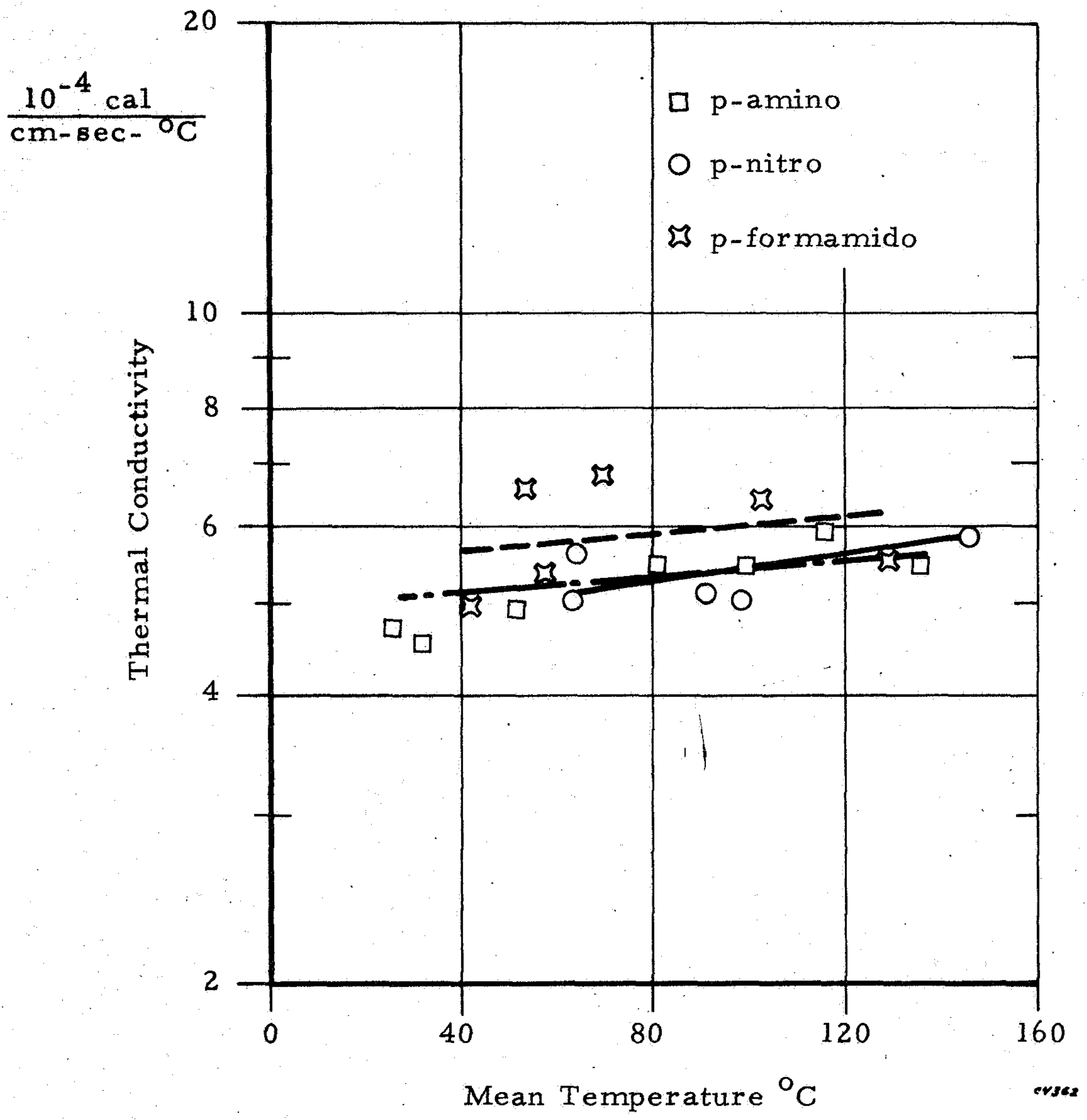

Figure 6. Thermal Conductivity-Temperature Plot of Some Para Substituted Poly(phenylacetylenes)

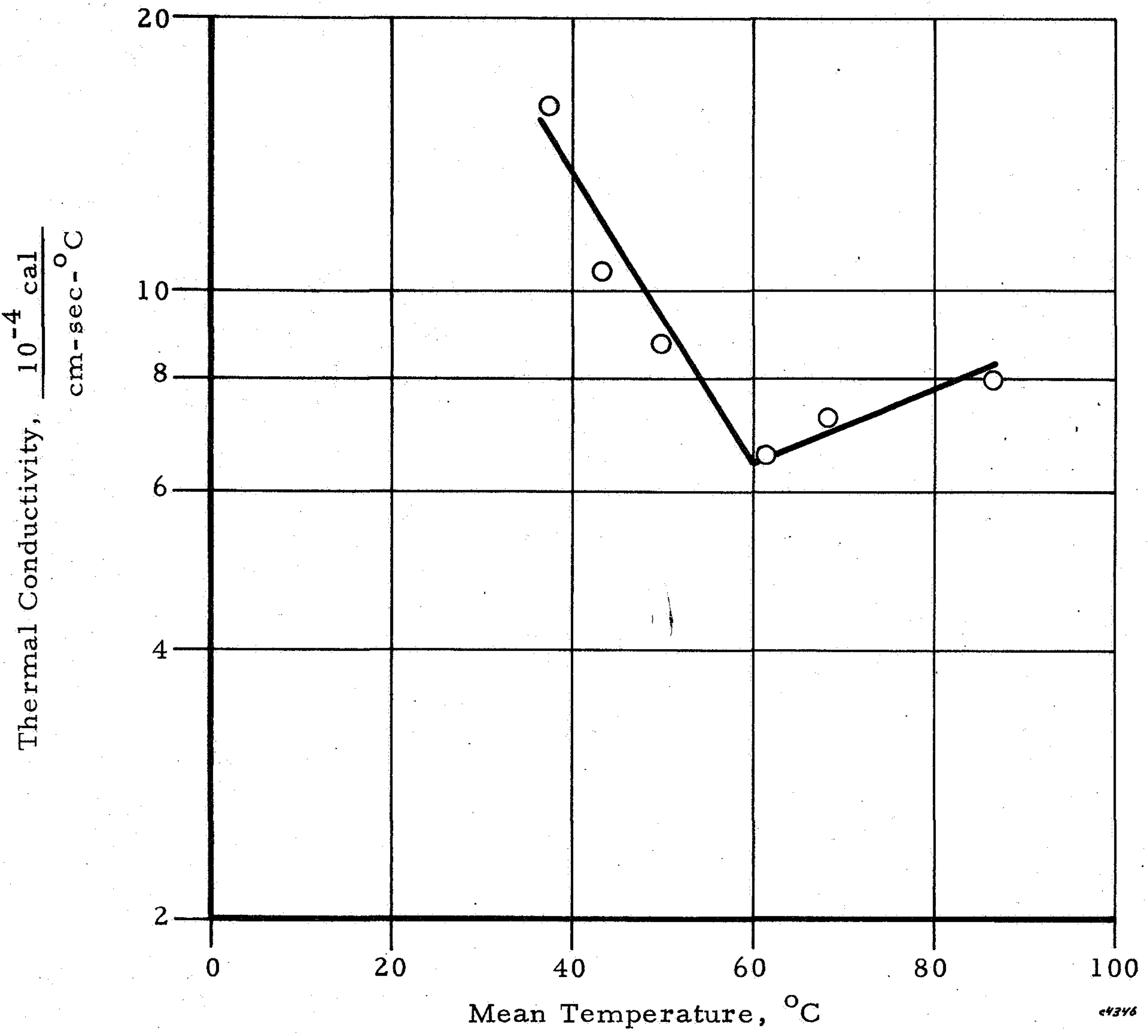

Figure 7. Thermal Conductivity, k, - Temperature Plot of Poly(phenylacetylene), Thermal $CuCl_2$ Preparation, Cu-In Spacers

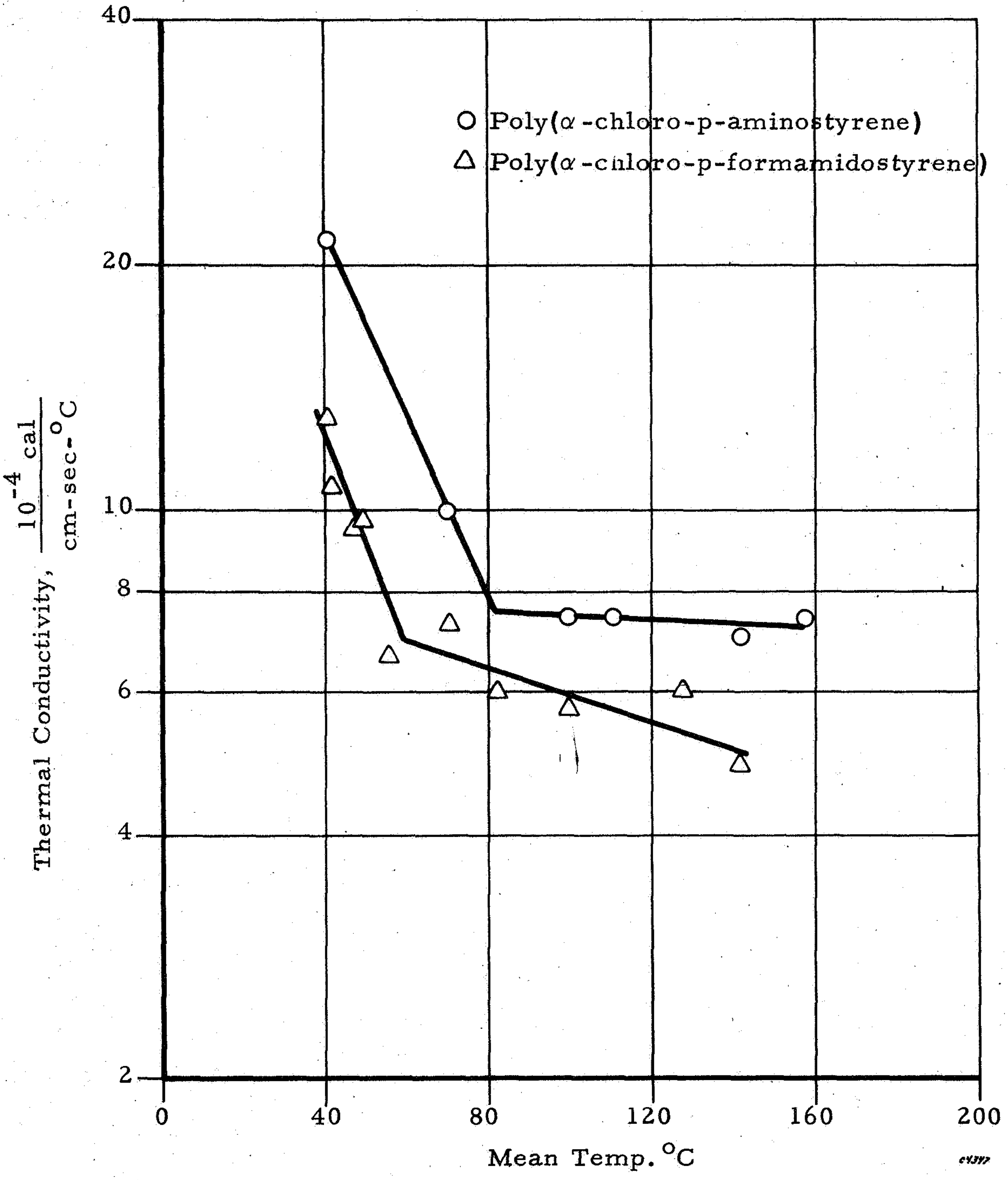

Figure 8. Thermal Conductivity - Temperature Plot of Poly(α-chloro-p-aminostyrene) and Poly(α-chloro-p-formamidostyrene)

which is the result of a complete breaking of all the hydrogen bonds with the resultant contribution of a saturated main chain as compared to the conjugated backbone of the previously discussed polymers. Figure 9 depicts a (k-T) curve of poly(α-chlorostyrene) in which none of the possible properties which could enhance the thermal conductivity are operative. Specifically, the structure of the polymer prevents crystallinity and hydrogen bonding due to hindered rotation of the main chain by the bulky chlorine and phenyl groups.

The synthesis of polymers that are capable of efficient heat transfer is hindered by: (1) the incompleteness of the dehyrohalogenation reaction of the various alpha chlorinated styrenes thus preventing the formation of a higher molecular weight totally conjugated main chain, and (2) the large, bulky, para-substituted phenyl groups that prevent close chain packing required for crystal formation, and thereby affecting the coplanarity of the polyene chain preventing possible electronic contribution to thermal conductivity (Ref. 2). One solution to this specific synthesis problem was to prepare an unsubstituted polyacetylene polymer by polymerization of acetylene. This type of polymerization would remove the possibility of incomplete conjugation of the main chain and also the steric problems encountered with the various substituted phenyl groups. Cis-polyacetylene was prepared and a (k-T) plot obtained, the results of which are depicted in Figure 10. Evidence of crystallinity was observed in the low temperature region of the (k-T) plot. At higher temperatures, beyond the minimum, a positive (k-T) was observed, which could be related to electronic effects. Unfortunately, this polymer was insoluble in all solvents investigated and slowly converted to the trans configuration whose thermal conductivity was much less thanthe cis; the trans being about 5 x 10^{-4} cal/cm-sec-°C.

3.2 CROSSLINKED POLYMERS

Some synthetic effort was put forth to enhance the thermal conductivity of linear conjugated polymers through a lattice vibration approach. By means of crosslinking it was considered possible to increase the thermal conductivity of conjugated polyenes. Thus, a crosslinking agent holding together the conjugated polyenes can be visualized as springs connecting discrete masses. A vibration imparted to one of the masses is transferred by means of the spring to other masses. Similarly, thermal vibration at the hotter end of a solid body will spread to the cooler end, and the transfer mechansim is similar to the propagation of elastic waves in a spring mass system.

Unfortunately, results obtained in this program on crosslink density — thermal conductivity responses were negative. Regardless of the mole ratio of polymer to crosslinking agent employed, the thermal conductivity at intermediate temperatures was never greater than that of the polymer alone. Figure 11 depicts the k-T plot of several pyromellitic anhydride — poly(p-aminophenylacetylene) crosslinked polymers. Notice that the optimum ratio of amine to anhydride is at 4:1; greater or lesser ratios decreased the thermal conductivity-temperature curve to very low values. The low-temperature thermal conductivity values for this system were generally fairly high followed by a rather sharp decrease as the temperature was increased. This response

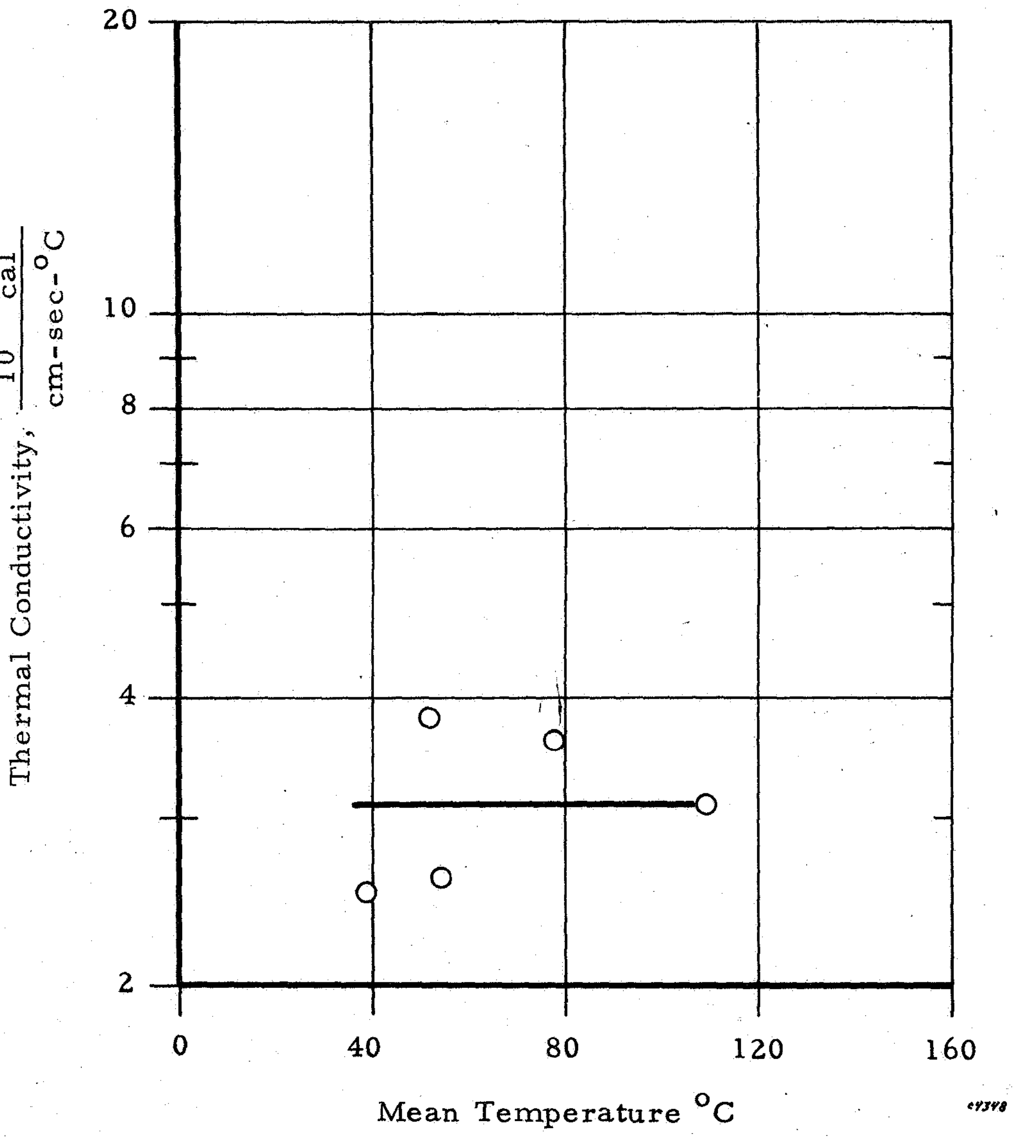

Figure 9. Thermal Conductivity-Temperature Plot of Poly(α-chlorostyrene)

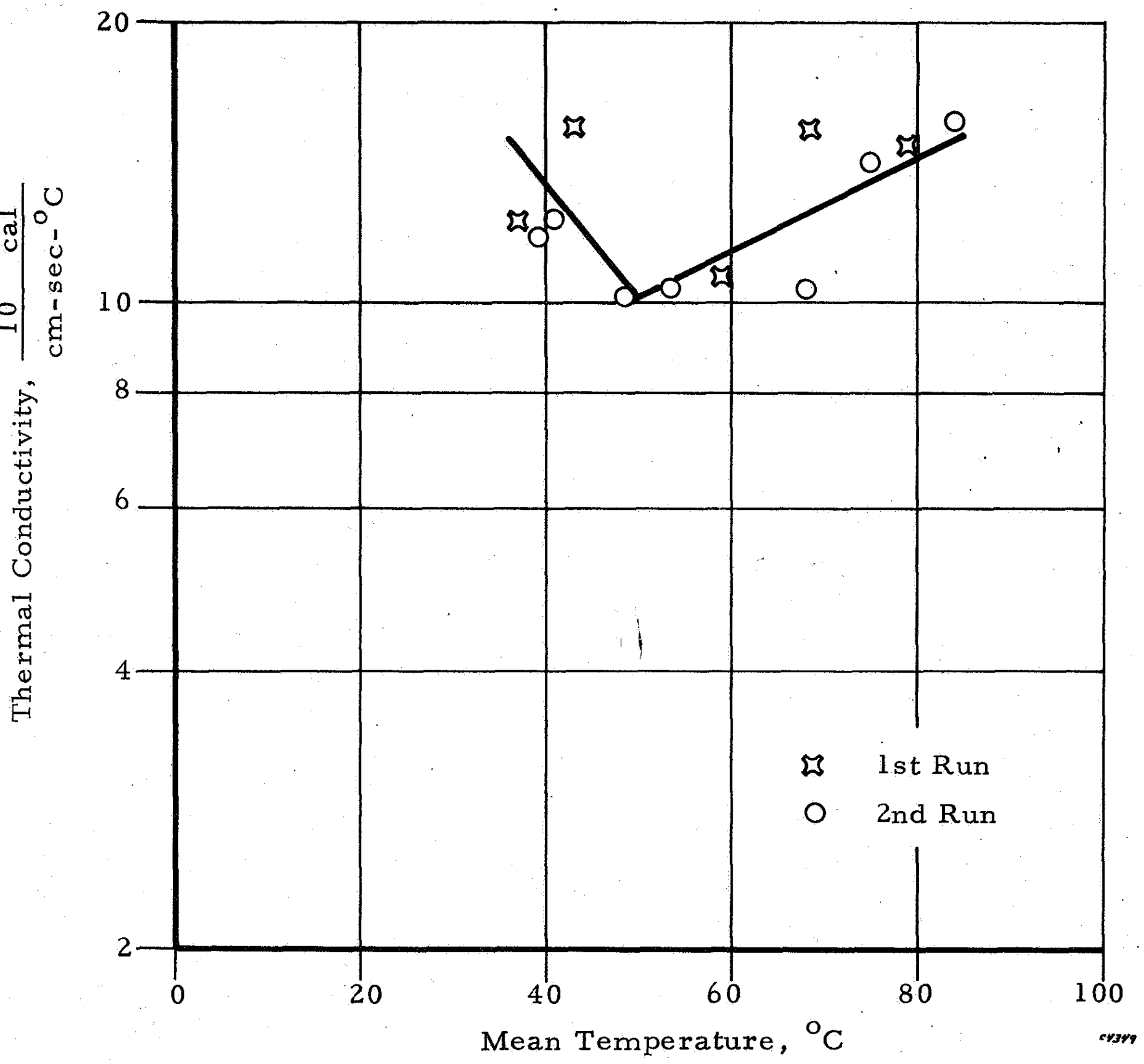

Figure 10. Thermal Conductivity - Temperature Plot of Cis Polyacetylene. Indium Spacers

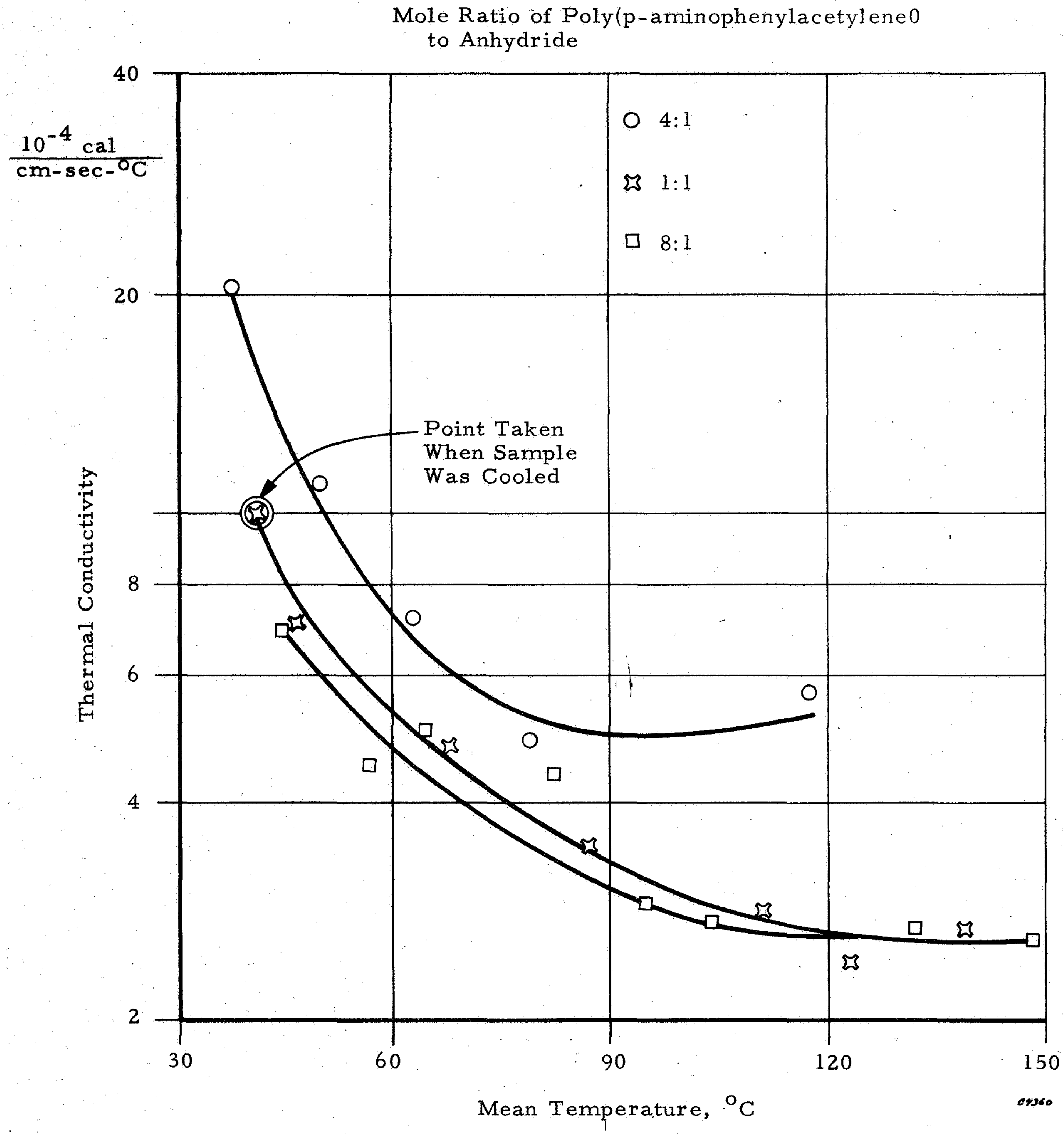

Figure 11. Thermal Conductivity-Temperature Plot of the Reaction Products of PAPA and Pyromellitic Anhydride

was initially attributed to a preferred orientation of the polymer by means of crosslinking. However, one would not expect a k-T decrease with increasing temperature but rather a constant k-T curve if the linkage were strong primary bonds. Later work in charge transfer complexes indicated that the initially high thermal conductivity values were due to the strong charge transfer complexes that exist between the amine donor and anhydride acceptor (Ref. 9). The reaction sequence would depend upon the solubility of the complex, the half imide and also on the total number of such groups present including the diimide. This hypothesis is somewhat substantiated by considering the results (Figure 12) obtained when poly(p-aminophenylacetylene) was reacted and crosslinked with toluene diisocyanate, as discussed below.

The value of 6×10^{-4} cal/cm-sec-°C obtained for the 100% TDI crosslinked PAPA is identical to that of the basic polymer PAPA. In addition, Figure 13 represents the optimum results obtained in the TDI work, in which variables such as mole ratios of TDI/PAPA, pellet pressing time, pressing temperature and various metallic plating of the pellet were investigated. The significant point is that TDI does not form a charge transfer complex of any type and therefore displays, in most cases, a flat k-T response. This is in direct contrast to the results obtained in the pyromellitic anhydride work utilizing known donor and acceptor compounds (see Figure 14).

Figure 15 displays the results obtained when PAPA was thermally crosslinked with chloranil. This represents a reaction product rather than a charge transfer complex, and further substantiates the reduction in thermal conductivity as a result of extensive crosslinking.

3.3 CHARGE TRANSFER COMPLEXES

Utilization of charge transfer complexes in polymeric systems to enhance thermal conductivity appears to be somewhat unique and not previously reported in the literature. The increased thermal conductivity is explained by the formation of either inter- or intra-molecular complexes which provide a low energy transfer gate for both electron and phonon flow. One may visualize charge transfer complexes to consist of graphitic-like stacks of alternating donor and acceptor groups which may or may not be attached to polymeric backbones. If attached to a flexible polymeric chain, the charge transfer complex would probably be the crystalline region in an amorphous or pseudocrystalline polymer. To prepare useful thermal conductivity materials, either the donor or acceptor (preferably both) must be attached to a polymeric backbone for vacuum and thermal stability considerations.

As energy (heat) is introduced into a polymeric charge transfer system, the efficiency of the complex gradually decreases due to increased molecular vibrations of the donor and acceptor thus reducing phonon flow. Continued increased excitation of the complex and polymeric chain finally prohibits any thermal conductive efficiency of the system as main chain rotation overcomes the positioning force of the CTC.

Figure 16 depicts representative (k-T) responses of a polymeric and salt-like charge transfer complex. The salt-like complex prepared from p-

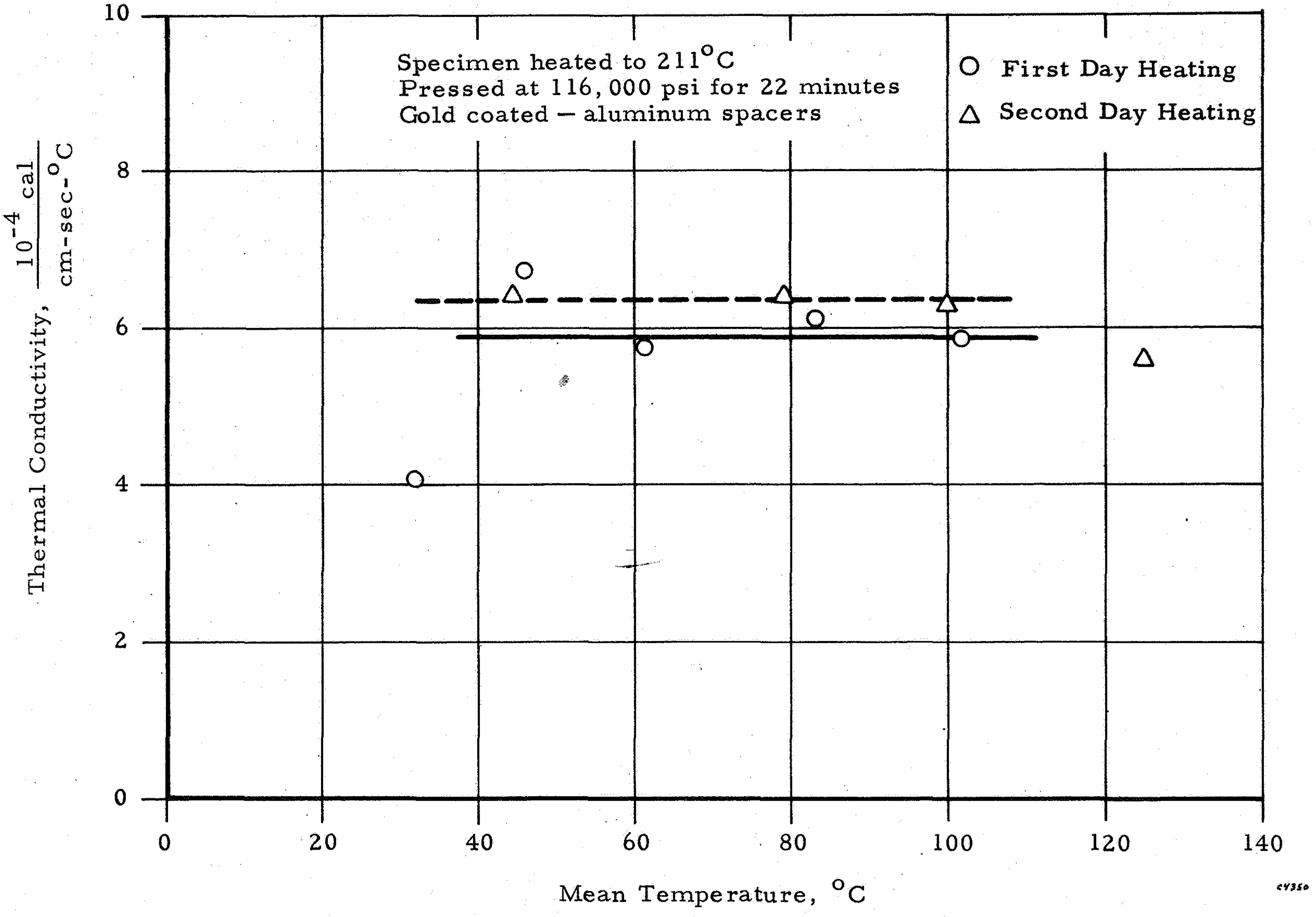

Figure 12. 100% TDI-Crosslinked Poly(p-aminophenylacetylene) (22 Minute Pressing)

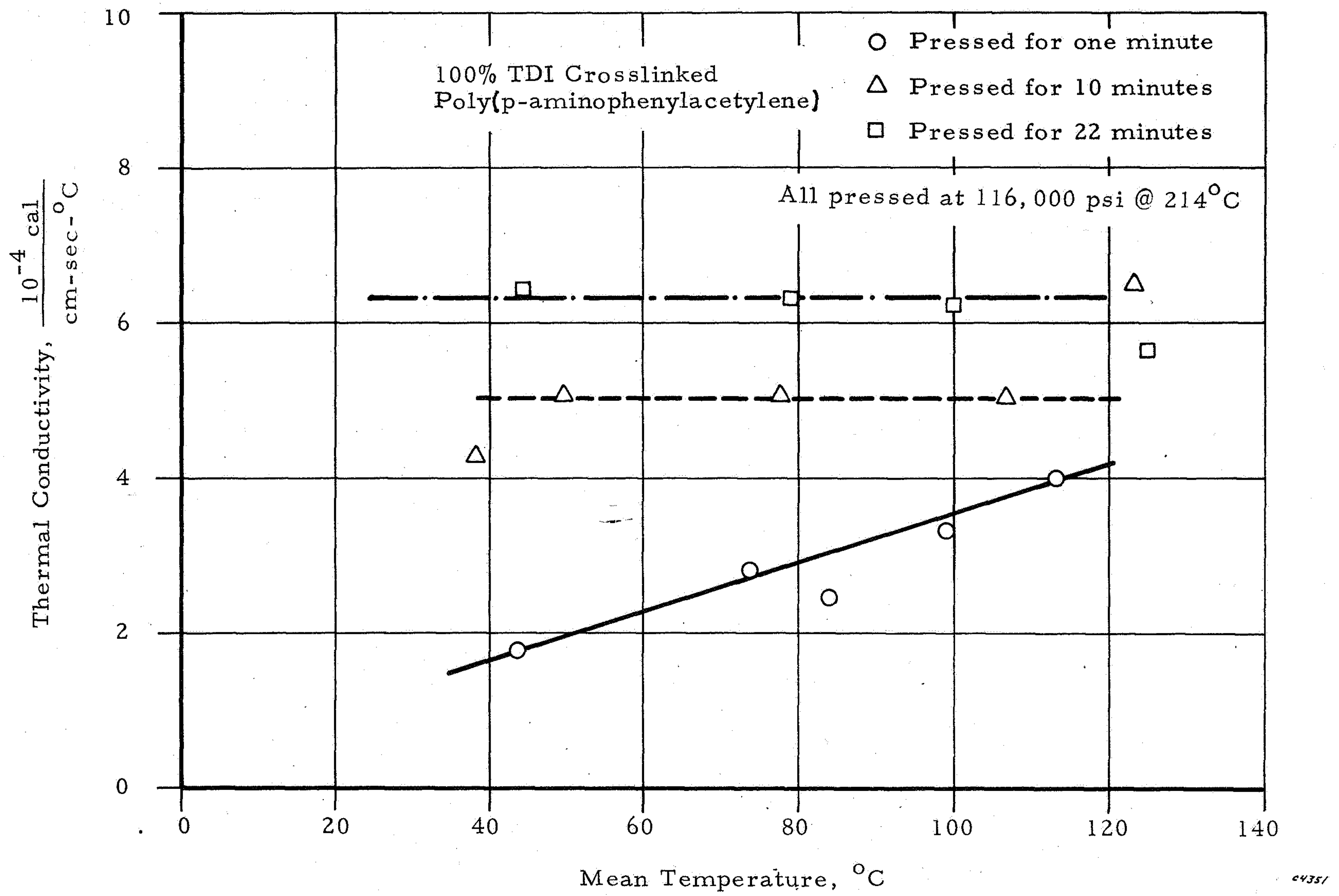

Figure 13. Comparison Plot of Effect of Pressing Time on Thermal Conductivity

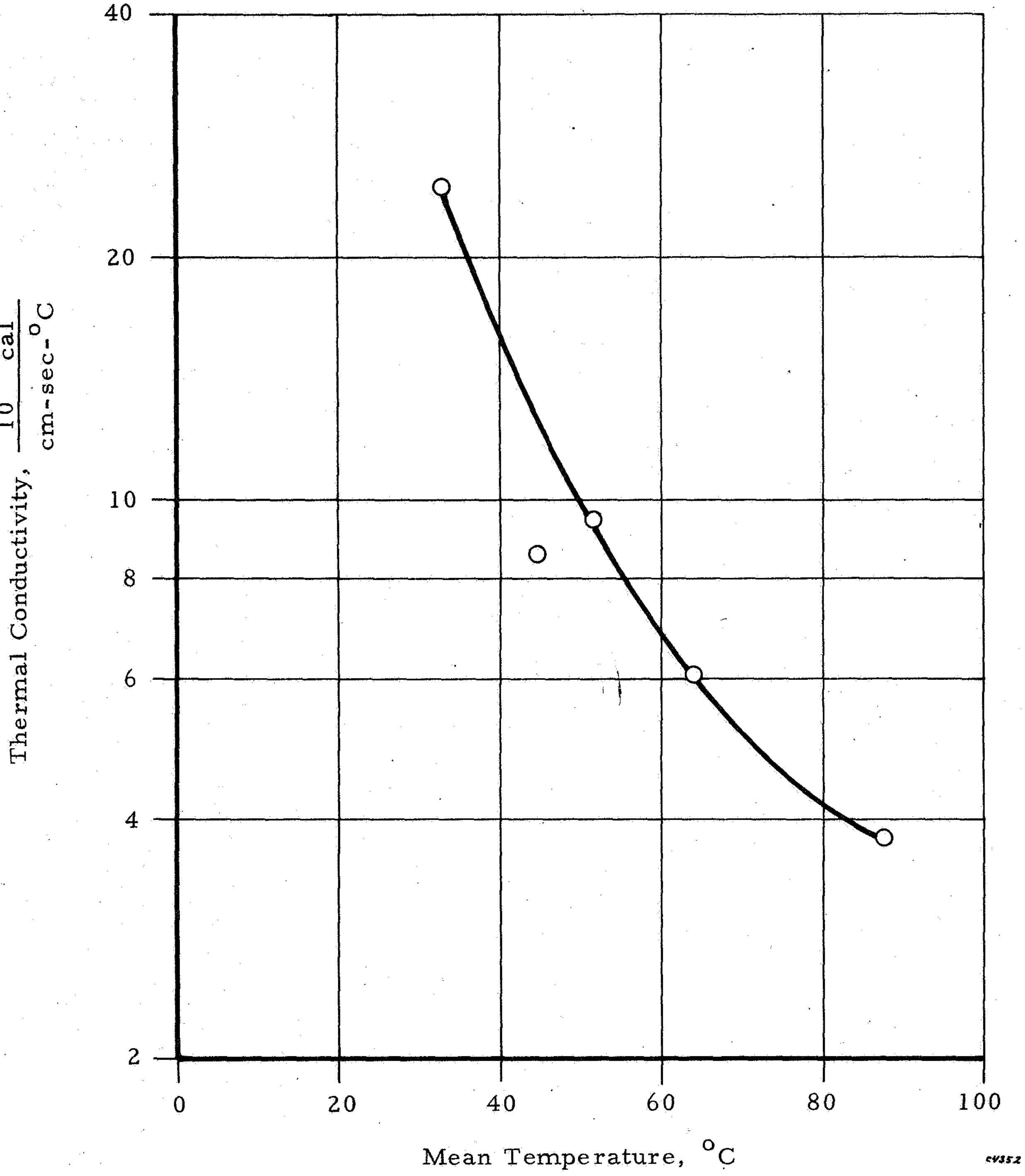

Figure 14. Thermal Conductivity – Temperature Plot of the Charge Transfer Complex of Poly(p-aminophenylacetylene) and Pyromelletic Dianhydride Prepared in CH_2Cl_2

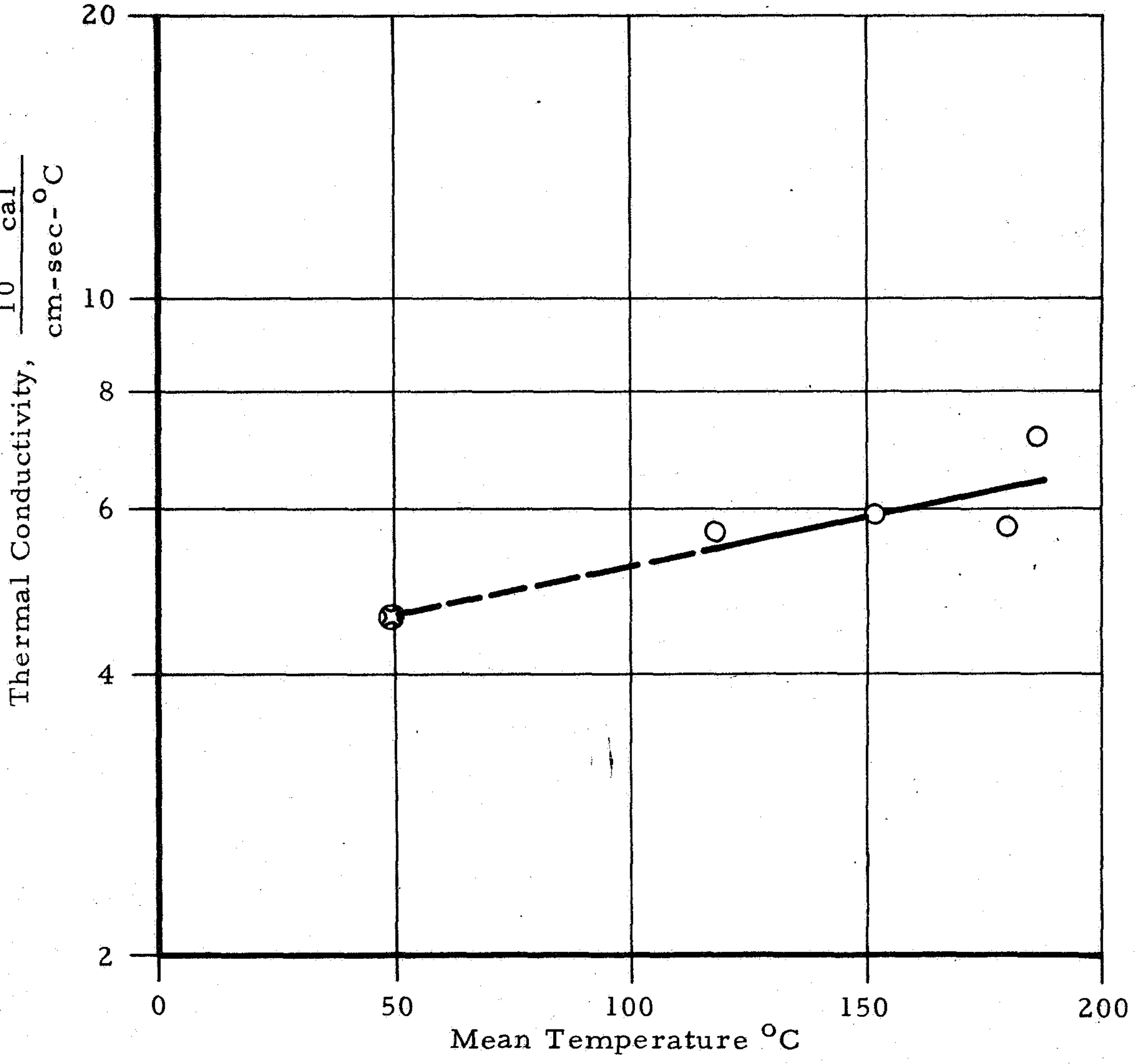

Figure 15. Thermal Conductivity — Temperature Plot of the Reaction Product from Poly(p-aminophenylacetylene) and Chloranil, 4:1 Mole Ratio

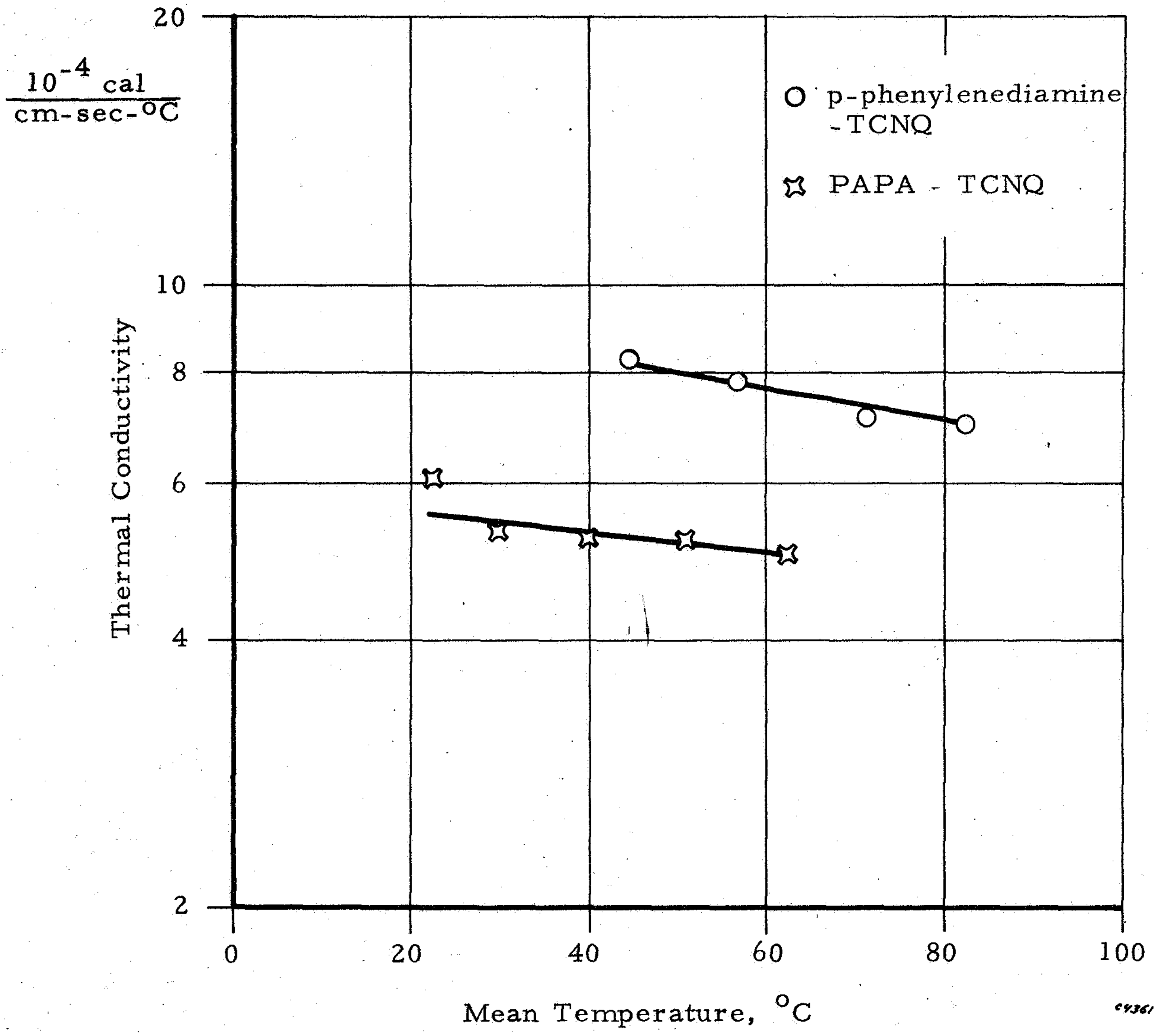

Figure 16. Thermal Conductivity-Temperature Plot of the Charge Transfer Complex from p-phenylenediamine and Tetracyanoquinodimethane and PAPA - TCNQ

phenylenediamine-TCNQ yielded a satisfactory (k-T) response indicating that a crystalline path for phonon conduction had been formed. The (k-T) response of the polymeric complex was not improved over that of the base polymer (PAPA) thus indicating a steric problem during the formation of the complex preventing the alignment of charge transfer donor and acceptor groups.

The reaction of poly(p-aminophenylacetylene) with chloranil in dimethylformamide yielded two products. The first product, an insoluble complex of PAPA-chloranil yielded a poor (k-T) response as evidenced by the curve shown in Figure 17. The soluble fraction yielded a high (k-T) response, maintaining a value of k greater than 10^{-3} cal/cm-sec-°C over the temperature range studied. In addition, the curve decreases initially, with temperature, up to about 65° and thereafter slowly increases. At present, the structure of the soluble fraction of the PAPA-chloranil complex is not known.

Table I lists some thermal conductivity and electrical resistivities of a number of polymers and complexes prepared and tested in this program.

Recently, a new series of charge transfer polymers has been investigated for thermal and electrical conductance as a function of synthesis parameters. The polymers, at optimum synthesis conditions, contain both electron donor and acceptor groups, are easily moldable to flexible products, and have both high electrical resistivity and thermal conductance. In those samples tested, the electrical resistivity has been in the 10^{12} to 10^{15} ohm-cm range.

The polymers are prepared by reacting various alkanediamines in an excess of p-benzoquinone thereby forming a "redox" type polymer containing both the quinone and hydroquinone groups. During molding, using pressure and temperature, the quinone-hydroquinone groups on the chain appear to orientate so that a quinhydrone charge transfer complex is formed. The formation of this complex yields a polymer of high thermal conductivity (in the 10^{-3} cal/cm-sec-°C range) as a function of temperature. The number of (CH_2) groups in the alkanediamine controls the flexibility of the polymer.

The reaction sequence, as shown in Figure 5 of Appendix I, depicts the formation of a linear diamino quinhydrone polymer showing alternating benzoquinone and hydroquinone groups. Actually, the polymer probably has random sequences of benzoquinone and hydroquinone groups. In the first step of the reaction, the amine adds to the benzoquinone causing a reduction of the benzoquinone to the hydroquinone. This aminohydroquinone is rapidly oxidized by the excess benzoquinone and undergoes a second addition reaction forming the diaminohydroquinone polymer. This hydroquinone polymer is partially oxidized in the presence of benzoquinone, but becomes insoluble prior to complete oxidation, thereby forming the aminohydroquinone-benzoquinone polymer. This polymer is capable of forming the quinhydrone complex either inter- or intra-molecularly by application of pressure and/or heat.

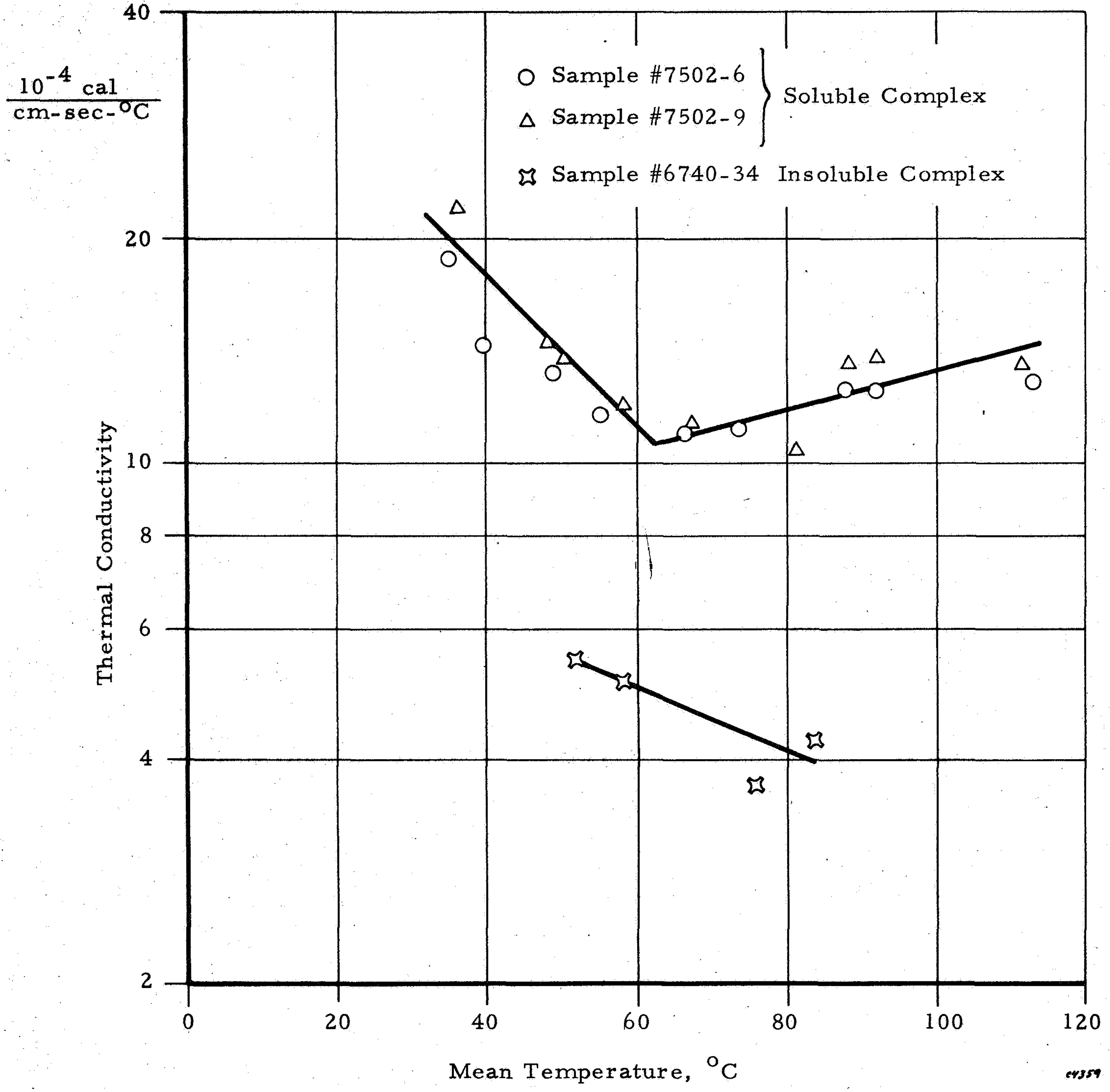

Figure 17. Thermal Conductivity – Temperature Plot of Chloranil and Poly(p-aminophenylacetylene) Complex

TABLE I

THERMAL AND ELECTRICAL PROPERTIES OF SOME POLYMERS AND COMPLEXES

Polymer	Thermal Conductivity, k, cal/cm-sec-°K, @ 50°C (mean pellet temperature)	Electrical Resistivity ohm-cm, 25°C
TCNQ(1) + 1, 4-PDA(2) (Purple)	8.0×10^{-4}	3.4×10^{5}
TCNQ + 1, 4-PDA (Orange)	7.2×10^{-4}	3.5×10^{5}
TCE(3) + 1, 4-PDA	5.9×10^{-4}	8.0×10^{13}
TCNQ + PAPA(4) (Red)	5.5×10^{-4}	1.0×10^{10}
TCNQ + PAPA (Black) (Filtrate)	9.0×10^{-4}	1.3×10^{12}
TCNQ + PAPA (Red-Orange)	5.5×10^{-4}	5.2×10^{13}
Chloranil + PAPA	1.0×10^{-3}	9.3×10^{10}
PPA(5) (Acetone Soluble)	5.5×10^{-4}	3.3×10^{15}
PAPA (Acetone Insoluble)	3.0×10^{-4}	8.0×10^{15}
PAPA + Iodine (Black)	5.2×10^{-4}	8.9×10^{6}
CPA(6) (Black)	8.0×10^{-4}	1.2×10^{15}
CPA + TCNQ (Black)	8.0×10^{-4}	1.3×10^{11}
Poly(p-nitrophenylacetylene)	4.0×10^{-4}	7.0×10^{11}
Trans-Polyacetylene	5.0×10^{-4}	6.0×10^{13}
Cis-Polyacetylene	1.5×10^{-3}	2.2×10^{8}
Graphite	3.5×10^{-2}	3.5×10^{2}
Chloranil + 1, 4-PDA (Black)	5.6×10^{-4}	5.0×10^{9}
TCE + 1, 4-PDA (Gold Flakes)	8.0×10^{-4}	4.1×10^{12}
PAPA - TCNQ Filtrate from #7470-7	8.0×10^{-4}	4.6×10^{9}

(1) TCNQ — Tetracyanoquinodimethane

(2) 1, 4-PDA — 1, 4- Phenylenediamine

(3) TCE — Tetracyanoethylene

(4) PAPA — Poly(p-aminophenylacetylene)

(5) PPA — Poly(phenylacetylene)

(6) CPA — Poly(β-chlorophenylacetylene)

Figures 18-26 depict the (k-T) response of the numerous polymers prepared by reacting the alkanediamines with benzoquinone in THF at a 1:3 mole ratio, respectively. It is apparent that the even numbered $(CH_2)_n$ $n = 2, 4, 6$ diamines such as ethane diamine, butanediamine and hexanediamine when reacted with benzoquinone yield an inferior polymer as evaluated by thermal conduction when compared to the odd numbered or the higher even numbered diamines.

The polymers displaying the best (k-T) results were prepared from 1, 7 heptane and 1, 8-octane diamines. At higher temperatures, the thermal conductivity values for these two polymers remain at about 1×10^{-3} cal/cm-sec-°C, at lower temperatures the k values increase quite dramatically and in some cases approach 5×10^{-3} cal/cm-sec-°C. The flexibility of the polymers increases quite rapidly as the number of (CH_2) groups increase from 2 to 12.

The polymer prepared from 1, 12-dodecanediamine is quite strong and flexible whereas that prepared from 1, 2-ethanediamine is hard and brittle. The odd numbered diamines are generally more flexible than the next higher even numbered diamine. All the polymers prepared were of various shades of red-brown; however, when pressed at 190°C the polymers changed to blue-black.

Figure 27 is the infra-red spectrum of the polymer prepared from 1, 6-hexanediamine-benzoquinone. Notice the amine absorption at 3280 cm^{-1}, the methylene at 2940 and 2880 cm^{-1}, quinhydrone at 1660 cm^{-1} and a major new band at 1580 cm^{-1} which may be the amine substituted quinone.

Figure 28 depicts the (k-T) curve of quinhydrone. It is quite remarkable that this complex is extremely similar to the amino-quinone polymers and leads one to speculate that perhaps the controlling factor in obtaining high thermally conducting polymers lies in the choice of polymerizable donor and acceptor charge transfer monomers.

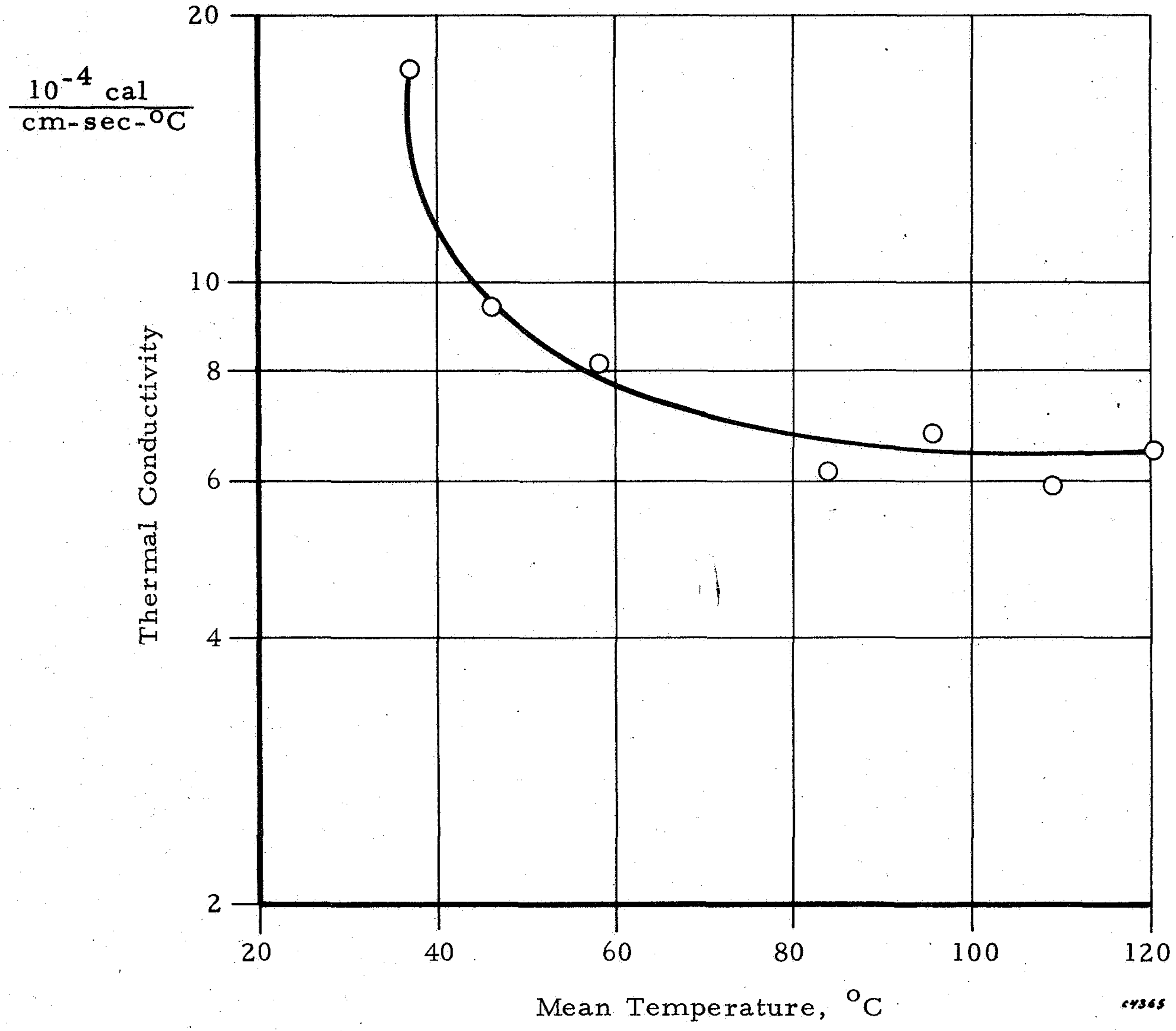

Figure 18. Thermal Conductivity-Temperature Plot of Ethylenediamine and p-Benzoquinone

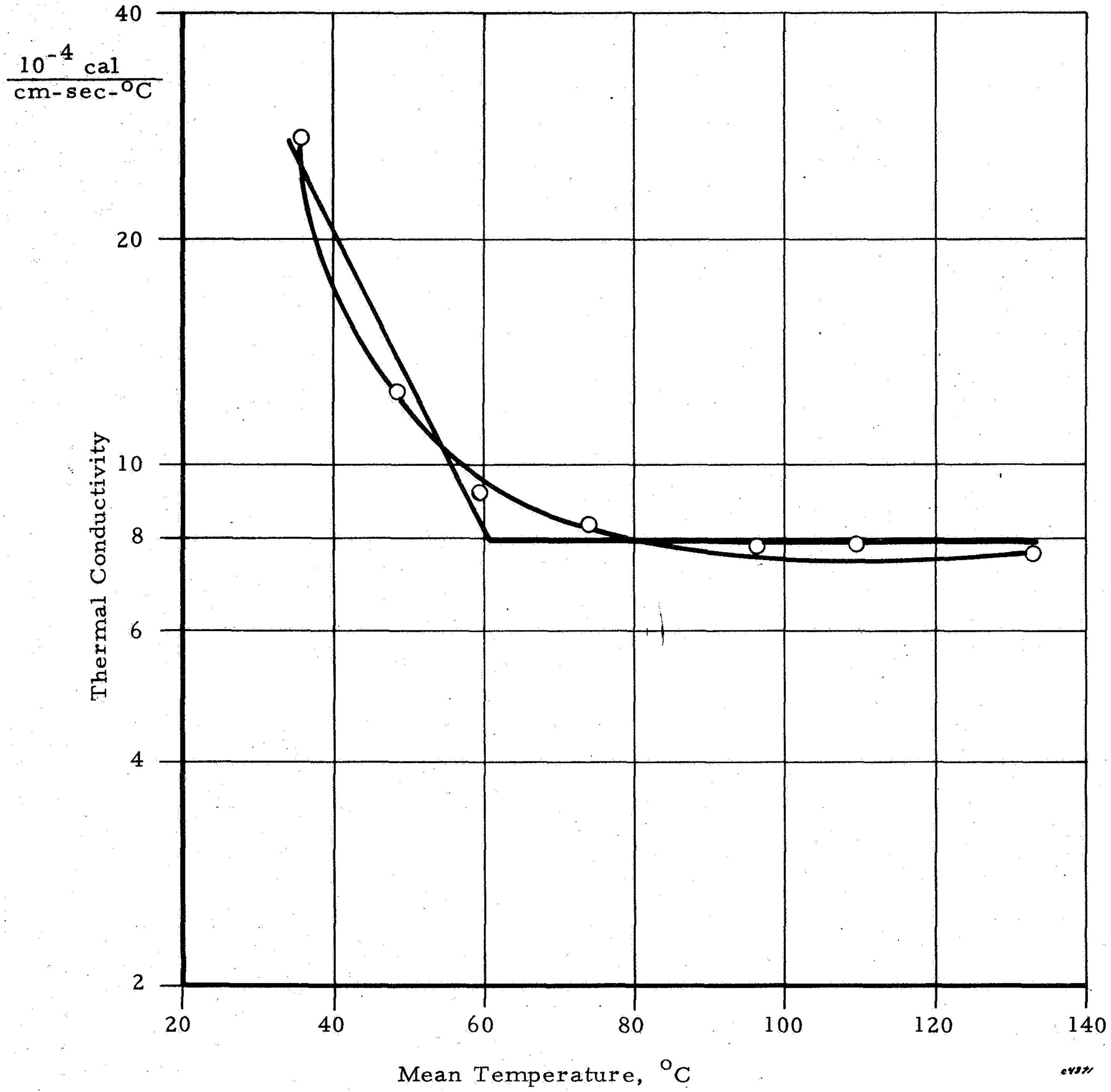

Figure 19. Thermal Conductivity-Temperature Plot of 1, 3-propanediamine and p-benzoquinone

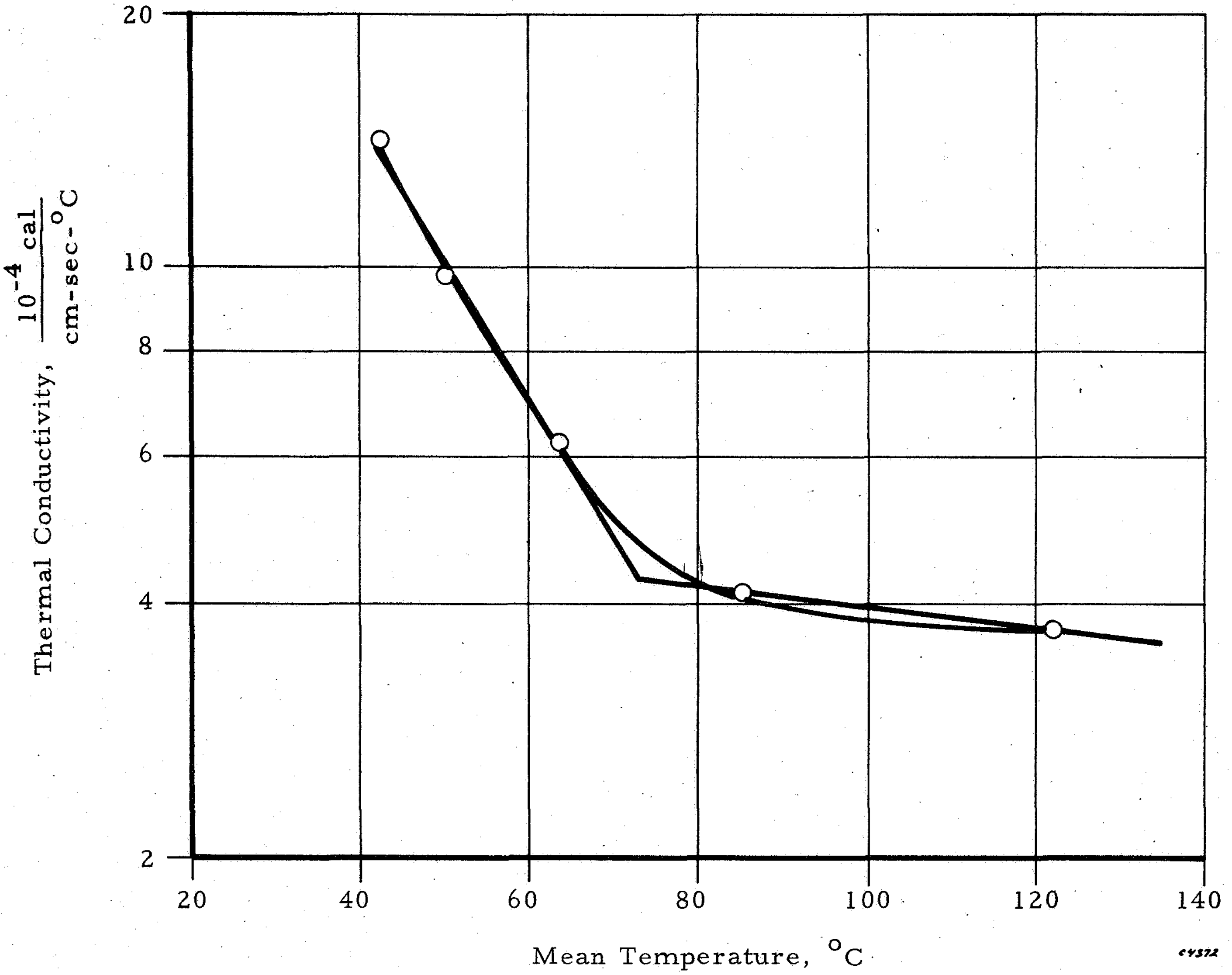

Figure 20. Thermal Conductivity - Temperature Plot of 1,4-Butanediamine and p-Benzoquinone

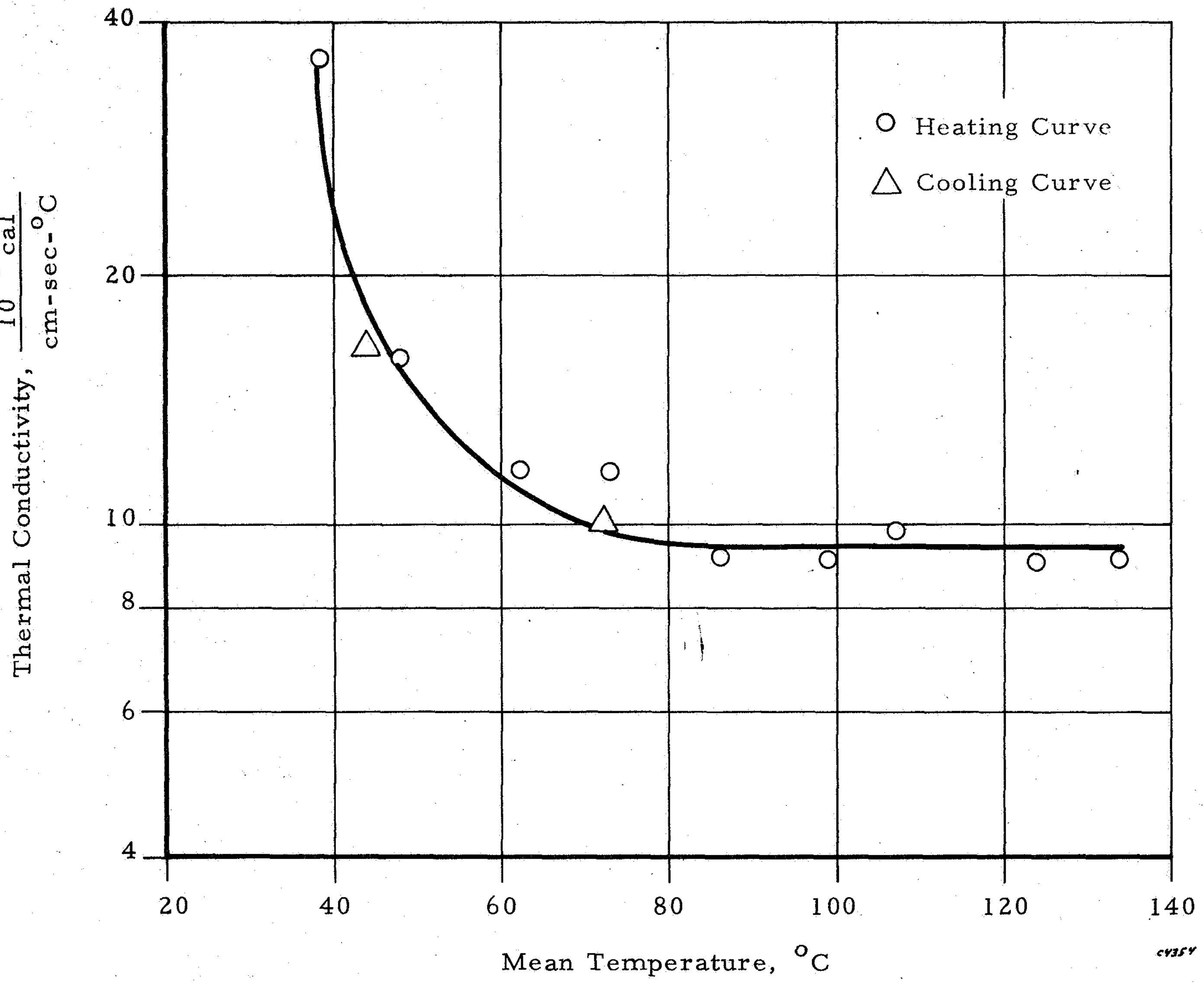

Figure 21. Thermal Conductivity-Temperature Plot of 1, 5-Pentanediamine and p-Benzoquinone

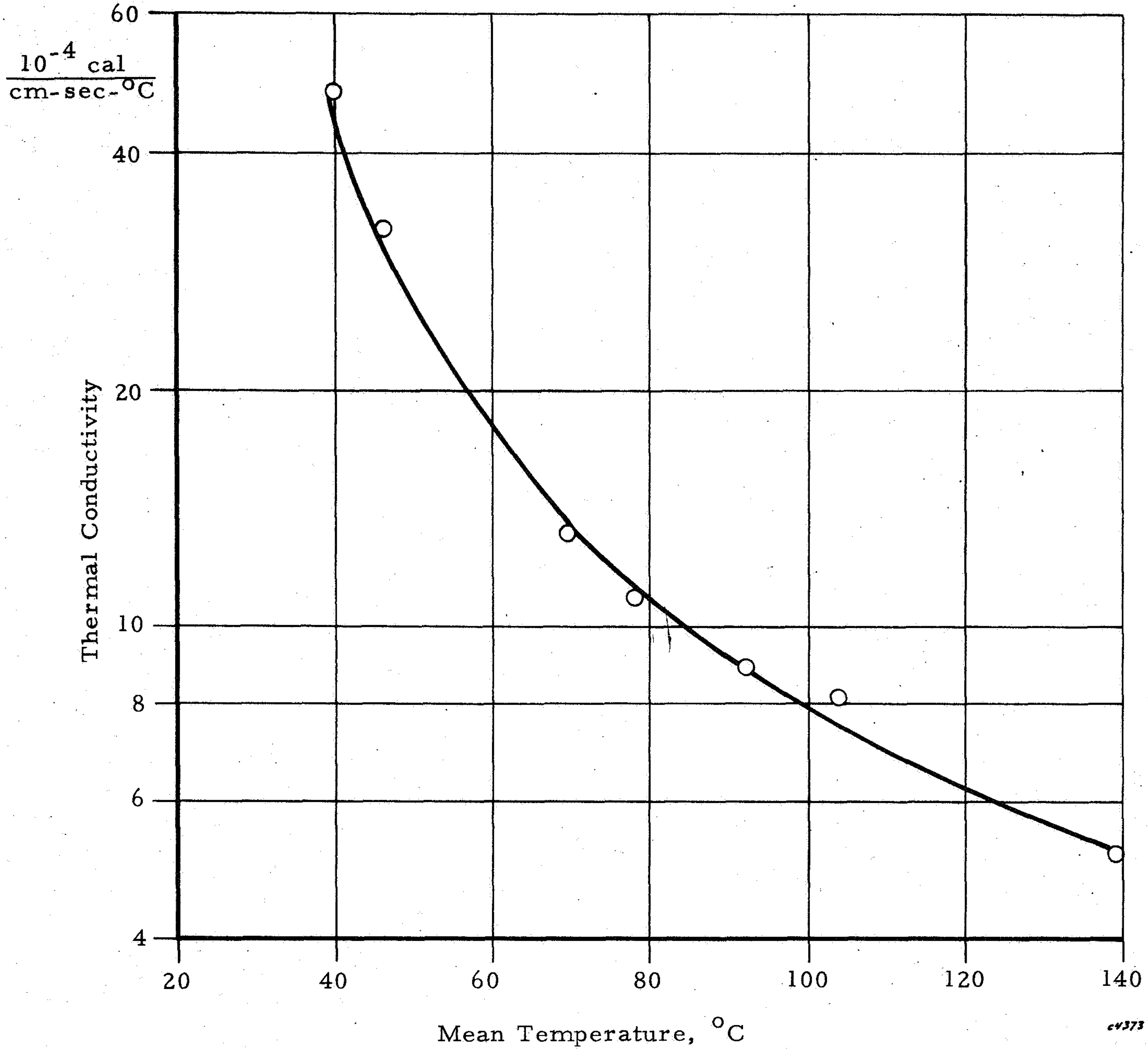

Figure 22. Thermal Conductivity-Temperature Plot of 1, 6-hexanediamine and p-benzoquinone

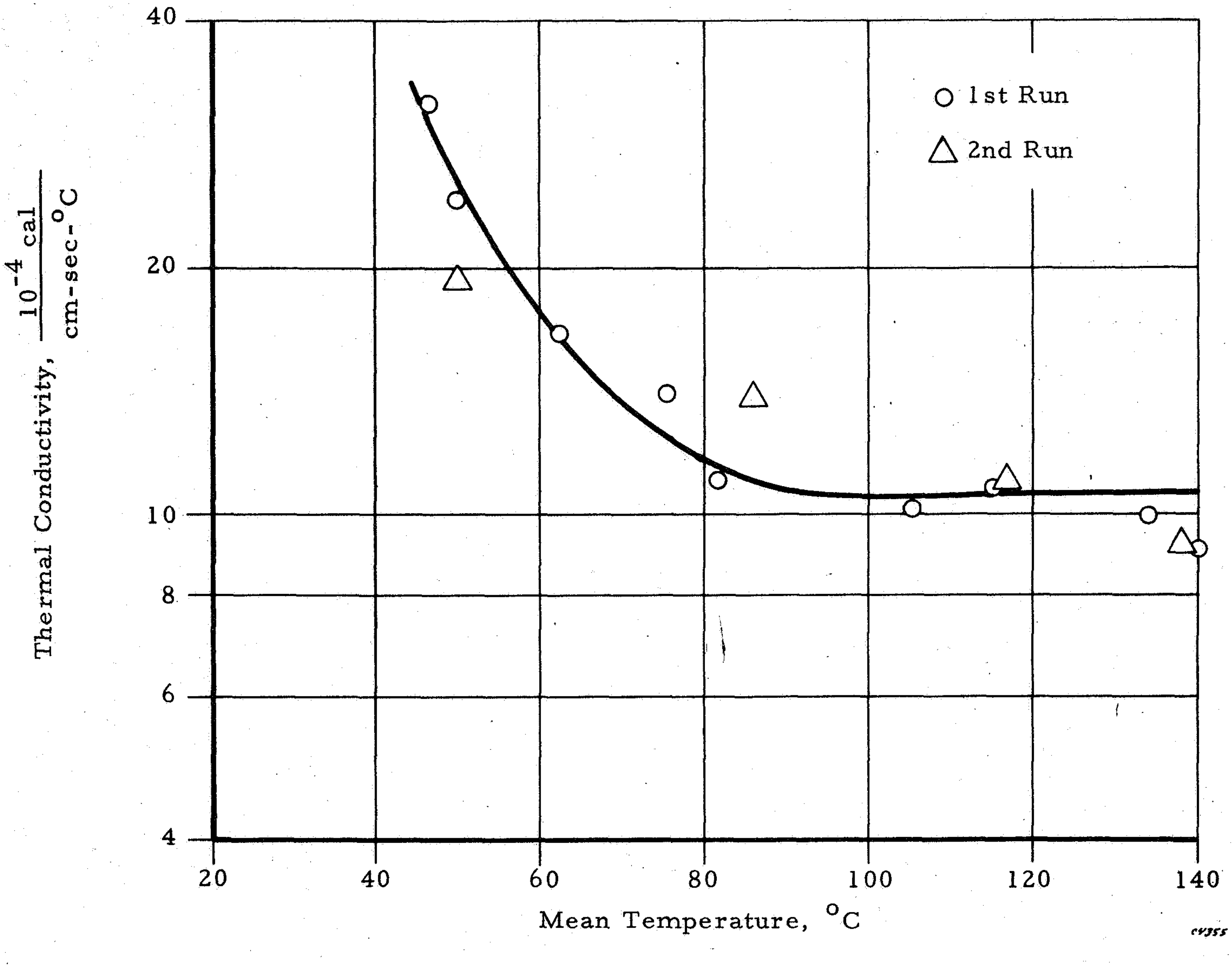

Figure 23. Thermal Conductivity-Temperature Plot of 1, 7-Heptanediamine and p-Benzoquinone

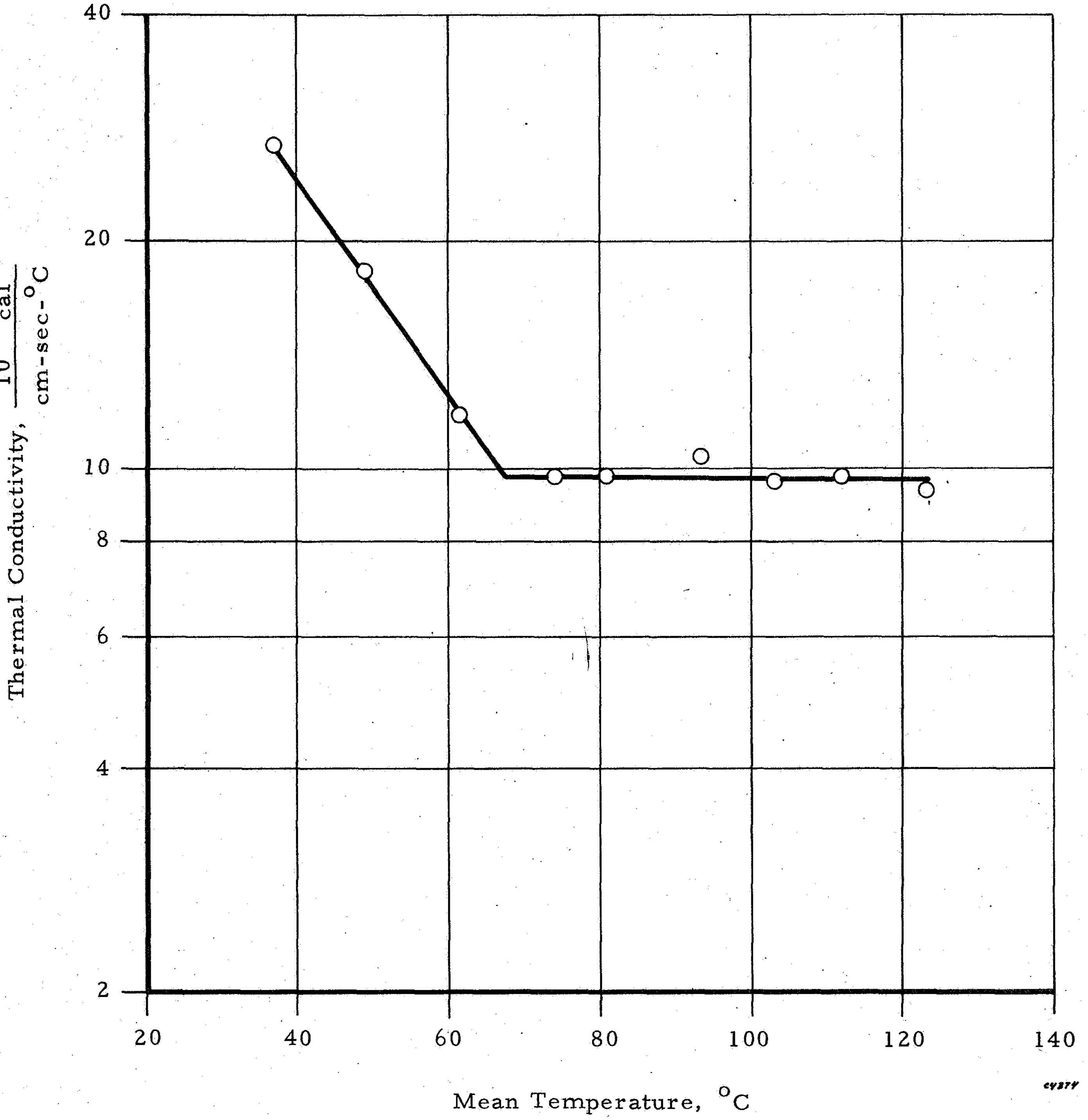

Figure 24. Thermal Conductivity - Temperature Plot of 1,8-Octanediamine and p-Benzoquinone

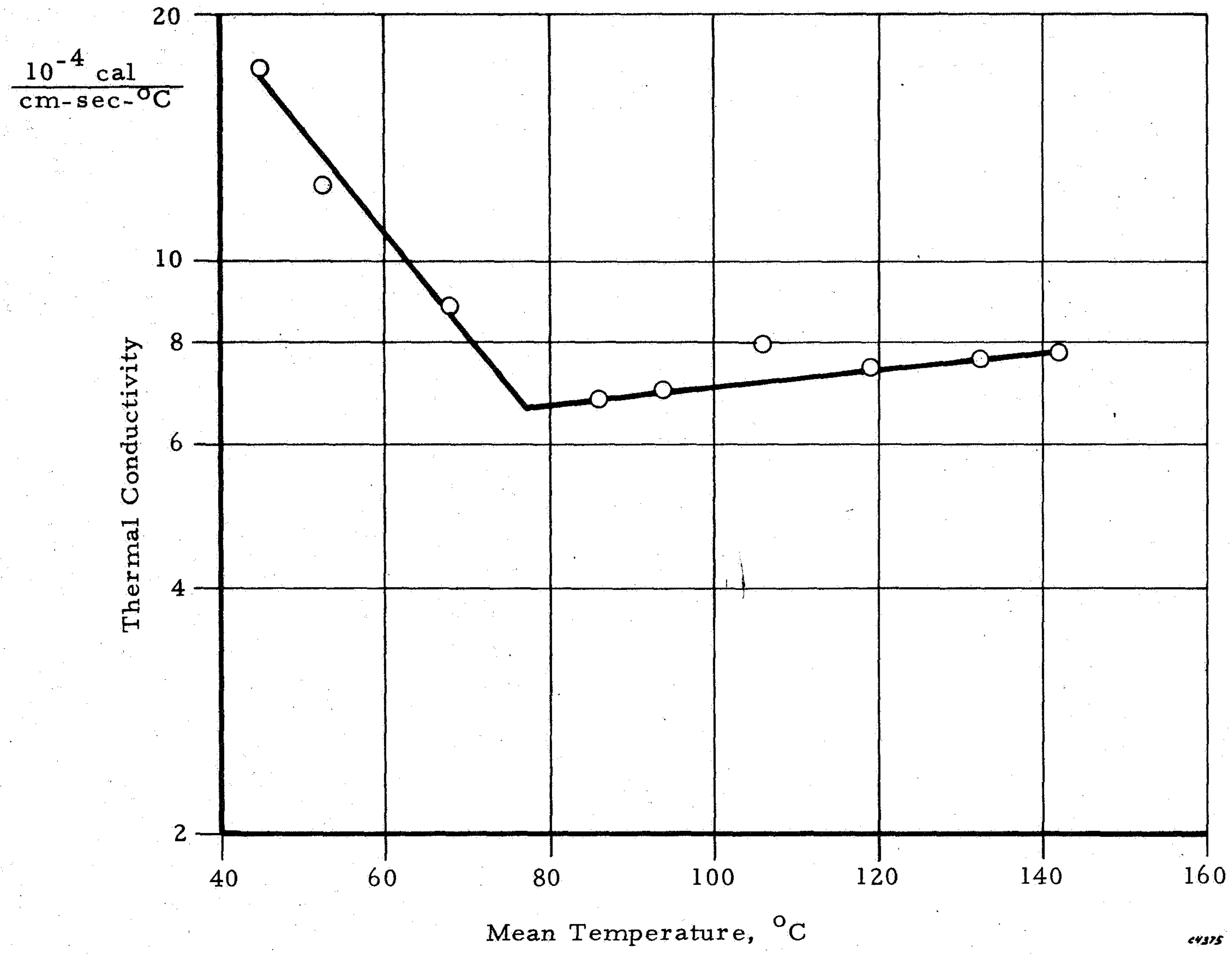

Figure 25. Thermal Conductivity-Temperature Plot of 1, 10-decanediamine and p-benzoquinone

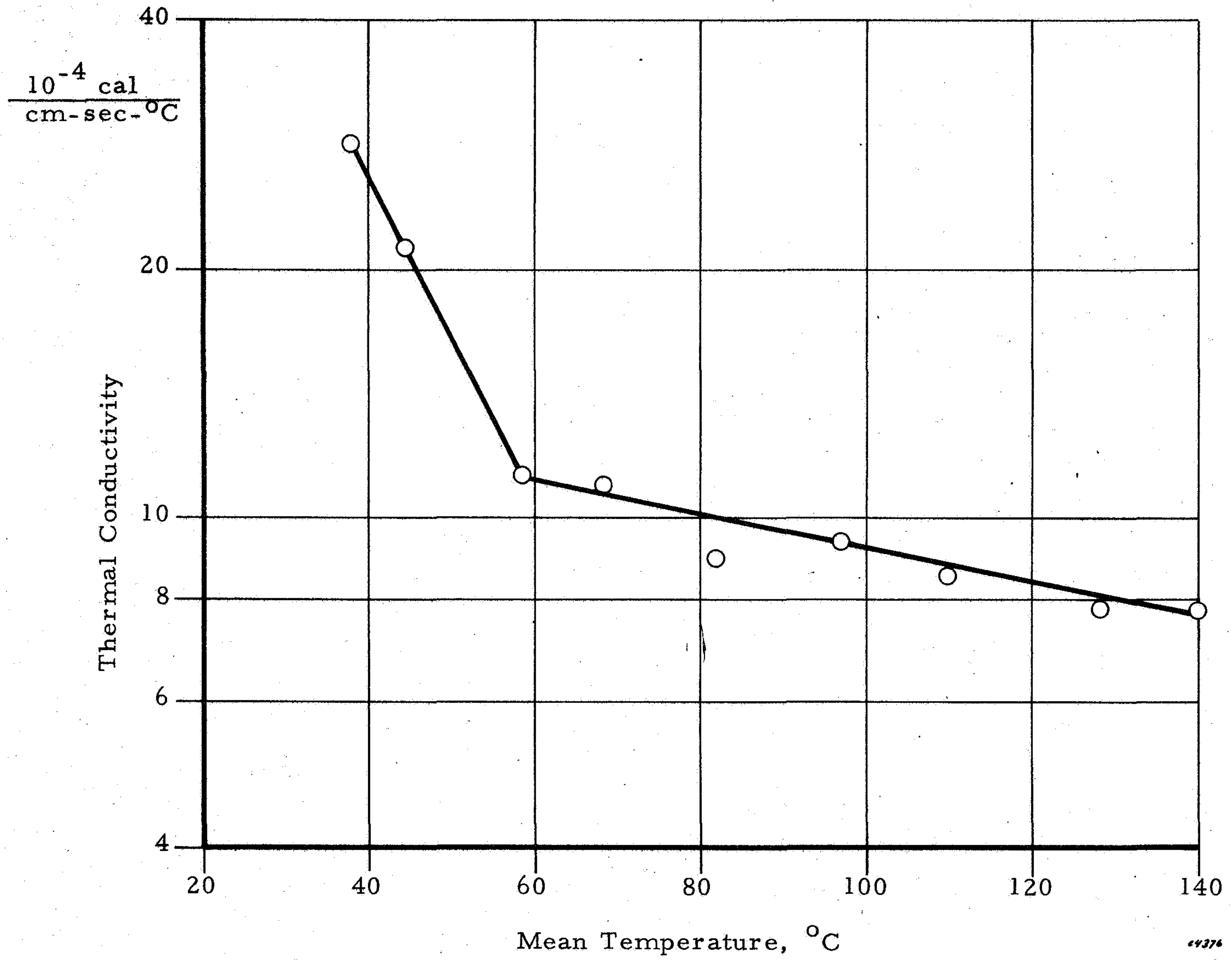

Figure 26. Thermal Conductivity-Temperature Plot of 1, 12-dodecanediamine and p-benzoquinone

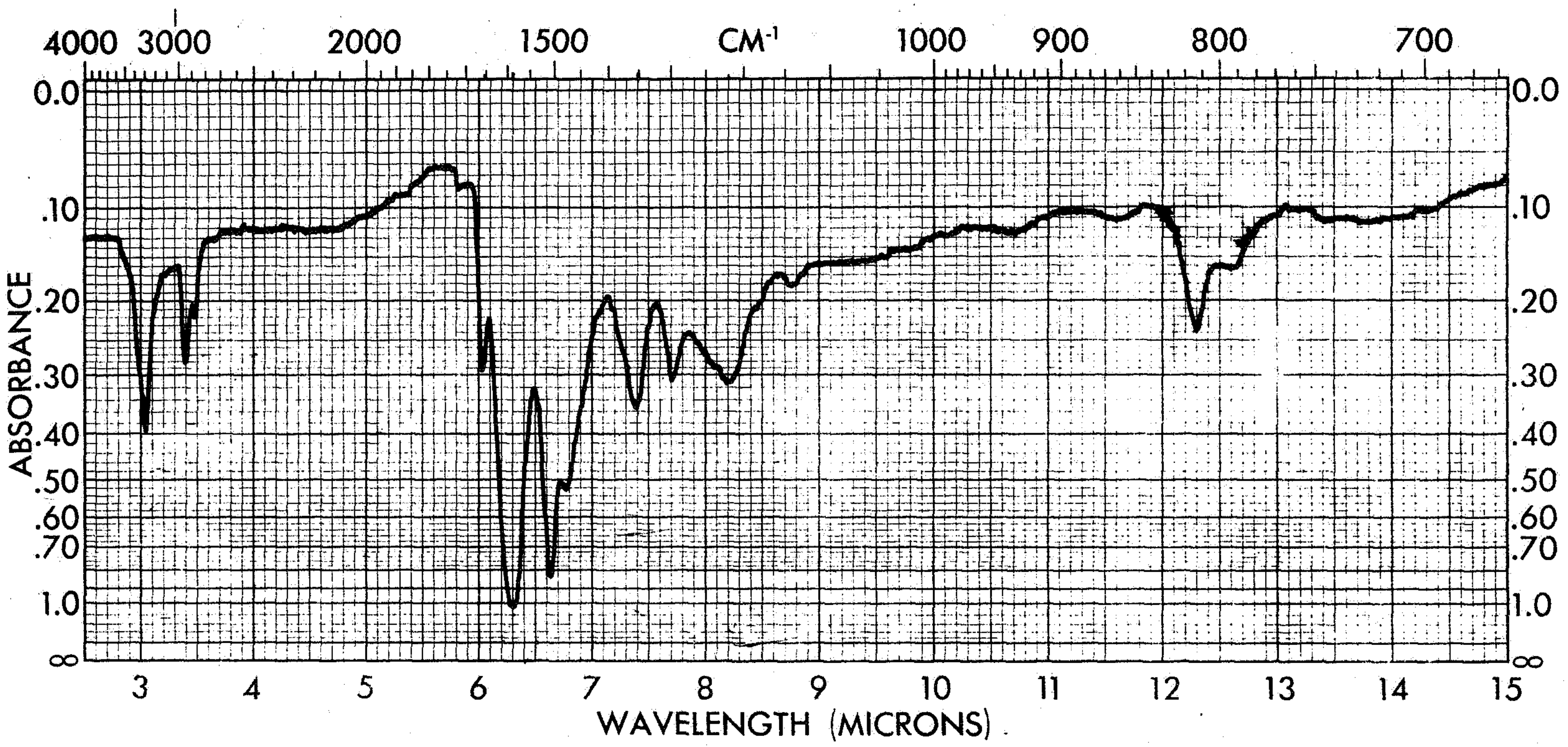

Figure 27. Spectrum of Polymer Prepared From 1,6-Hexanediamine-Benzoquinone

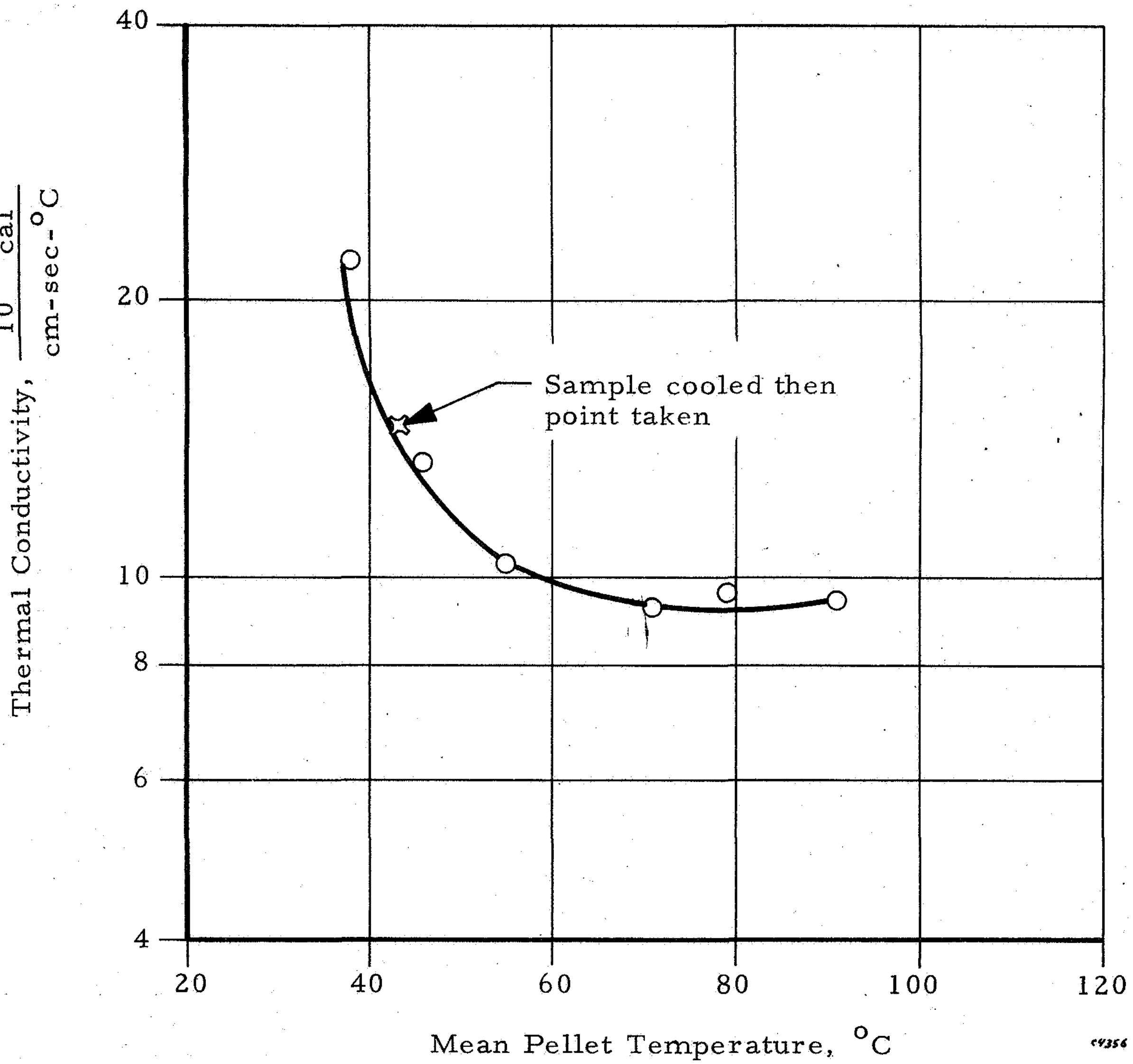

Figure 28. Thermal Conductivity-Temperature Plot of Quinhydrone

Section 4

CONCLUSIONS AND RECOMMENDATIONS

Results thus far gathered in this program strongly indicate that polymeric materials could be prepared with thermal conductivity values in the high 10^{-3} cal/cm-sec-°C range.

The most promising approach is in the area of polymeric charge transfer complexes. Obviously from the discussion presented in this report it is apparent that many types of monomers may be used in the construction of CTC polymers. In addition, the vast number of donor and acceptor molecules available for CTC work allows one an almost unlimited selection of polymer. Therefore, a continuation of the present program is suggested to evaluate and improve the new class of polymers. In particular, the program should be directed into the area of polymer characterization so that some physical properties of the polymer may be identified. Specifically the dynamic modulus of the polymer as a function of temperature, aging, and length of alkane chain should be studied. This type of study will determine the relative thermal stability of the polymers as well as their glass transition temperatures. In addition, tensile and elongation measurements should be made.

Concurrent with the limited investigation of the physical properties, some work should be performed in an attempt to maximize the thermal conductivity of the polymer by polymerization with mixed diamines.

Some effort must be expended in preparing soluble polymers that will maintain their enhanced thermal conductivity. The quest for solubility is obviously required for coating and potting evaluations.

Finally, the possibility of extending the general reaction from alkane diamines to diols, dimercaptans and diacidchlorides should most certainly be investigated as well as replacing part or all of the benzoquinone with other molecular quinones.

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APPENDIX I

SYNTHESIS OF POLYMERS

Appendix I
SYNTHESIS OF POLYMERS

1.0 INTRODUCTION

A considerable materials synthesis effort was expended during the course of the program. Many reactions were studied in attempting to develop a good thermally conducting organic polymer. The first phase used a conjugated polyene and some of its derivatives, i.e., the poly(para-substituted phenylacetylenes). Since materials of this nature were considered to be organic semiconductors, it was anticipated that their thermal behavior would be analogous to certain inorganic semiconductors, such as bismuth telluride whose thermal conductivity versus temperature curve is shown in Figure I-1. The first portion of the curve depicts the phonon contribution to thermal conductivity; with decreasing thermal conductivity due to phonon scatter as the temperature is increased. Subsequently, the thermal conductivity increased with increasing temperature presumably due to the electronic contribution.

As was subsequently observed, the organic conjugated polyenes did not appear to follow this curve completely. Although some started reasonably high at ambient temperatures, increasing temperatures caused a dropping off in thermal conductivity, with little, if any, subsequent rise. Therefore, in seeking out a polymer system that could make both a phonon as well as an electronic contribution to thermal conductivity, a large amount of synthesis was undertaken. Figures I-2 to I-8 depict some of the general synthesis schemes, and the following describes the actual synthesis of the large number of polymers that were evaluated.

2.0 SYNTHESIS

2.1 Preparation of Unsaturated Polymers

2.1.1 Preparation of Poly(α-chlorostyrene)

Two grades of polystyrene, H-100 and PS-2, were utilized in the preparation of the polyacetylene derivatives. PS-2 is a low molecular weight fraction of $\overline{M}_v$ = 27,000 whereas H-100 has a $\overline{M}_v$ = 355,000. The chlorination procedure is identical for both fractions.

One mole of polystyrene (PS-2 or H-100), with a viscosity average molecular weight, $\overline{M}_v$, of 27,000/355,000, was dissolved in 600 ml of CCl_4 in a reaction vessel equipped with a mechanical stirrer, N_2 and Cl_2 inlets, and reflux condenser. The solution was cooled to 10°C and irradiated with a 400 watt

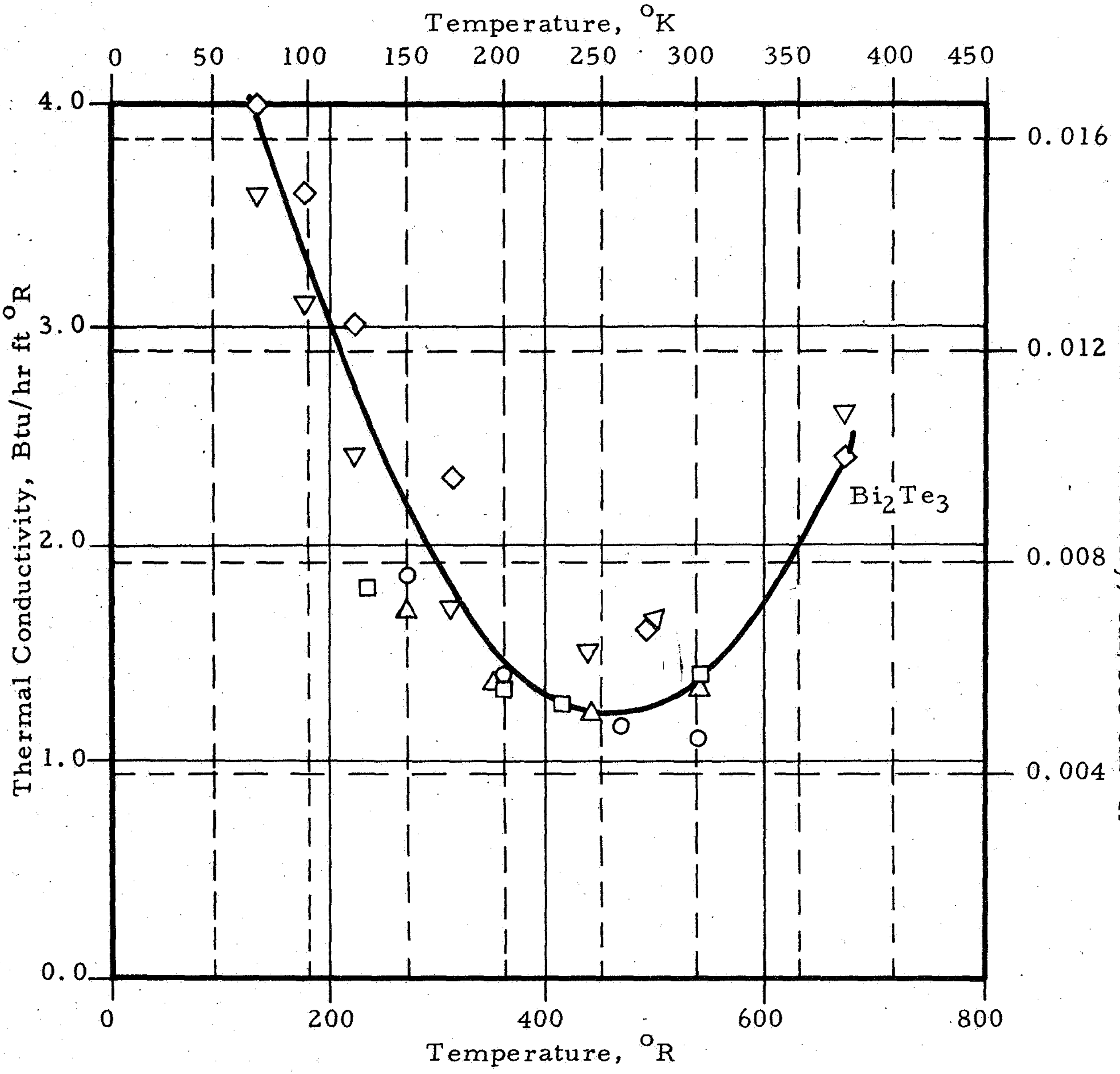

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Figure I-1. Thermal Conductivity — Bismuth Telluride

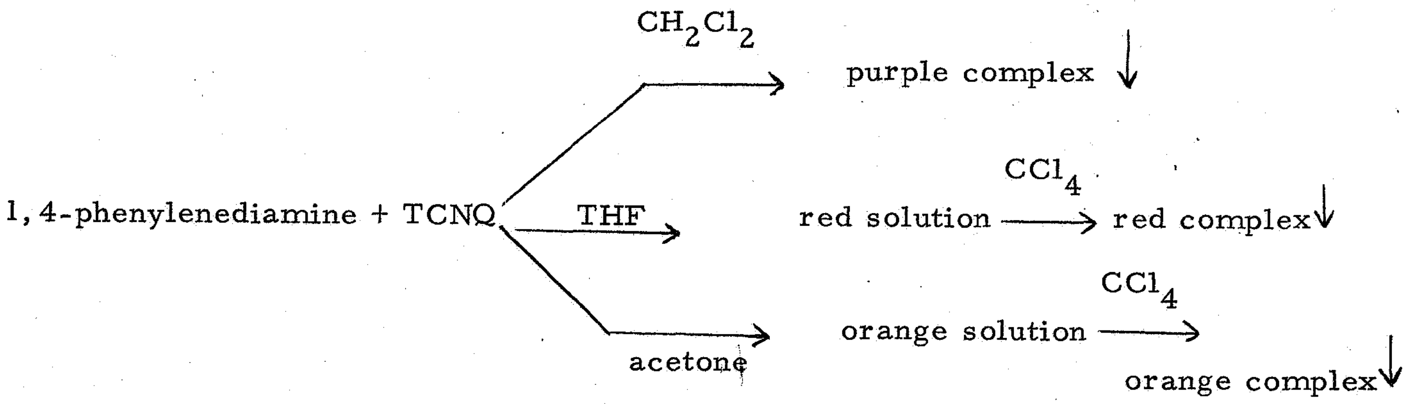

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Figure I-2. Reactions of 1,4-Phenylenediamine With TCNQ in Different Solvents

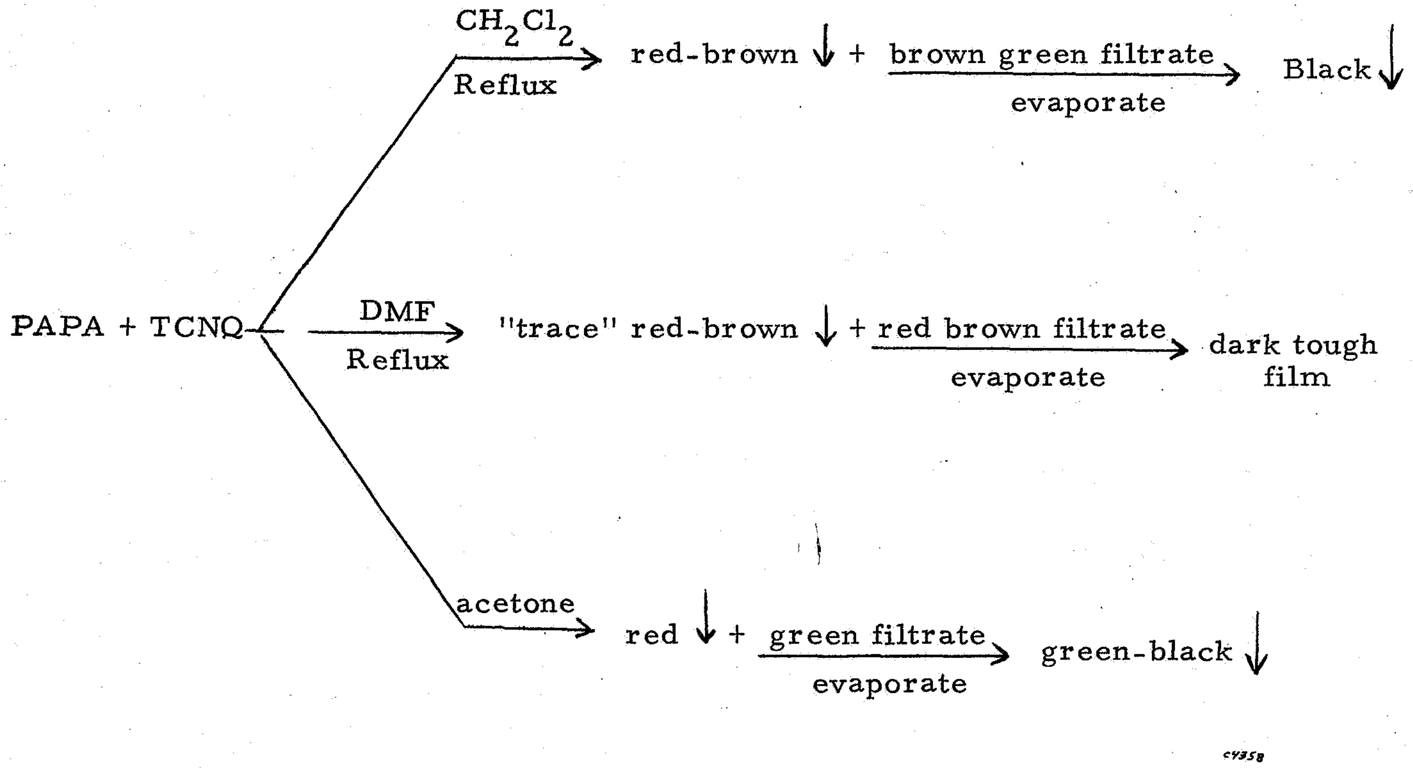

Figure I-3. Reaction of Poly(p-aminophenylacetylene) With TCNQ in Different Solvents

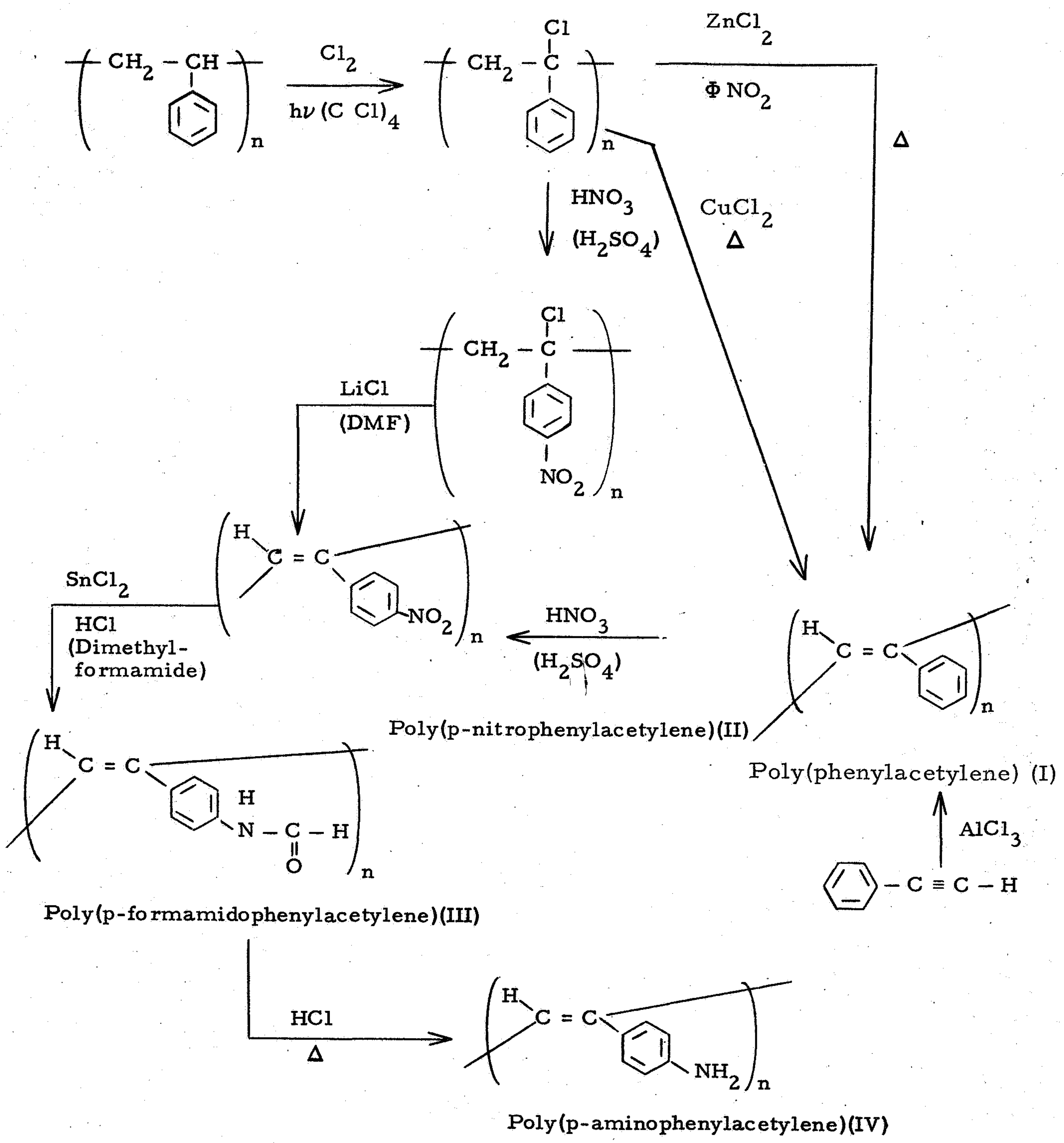

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Figure I-4. Reaction Sequence Used in Preparation of Some Poly(phenylacetylenes)

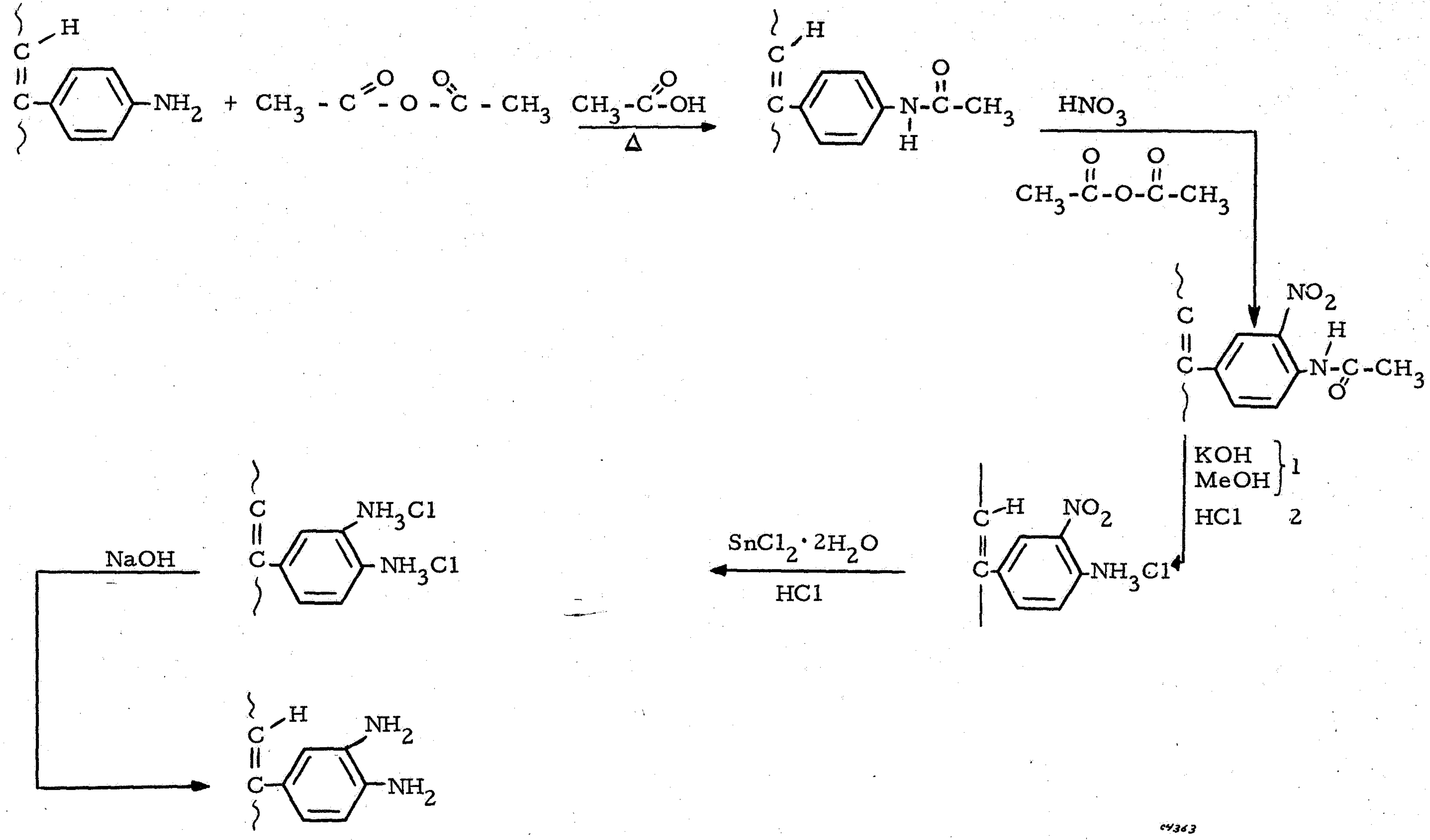

Figure I-5. Synthesis of Poly(3, 4-diaminophenylacetylene)

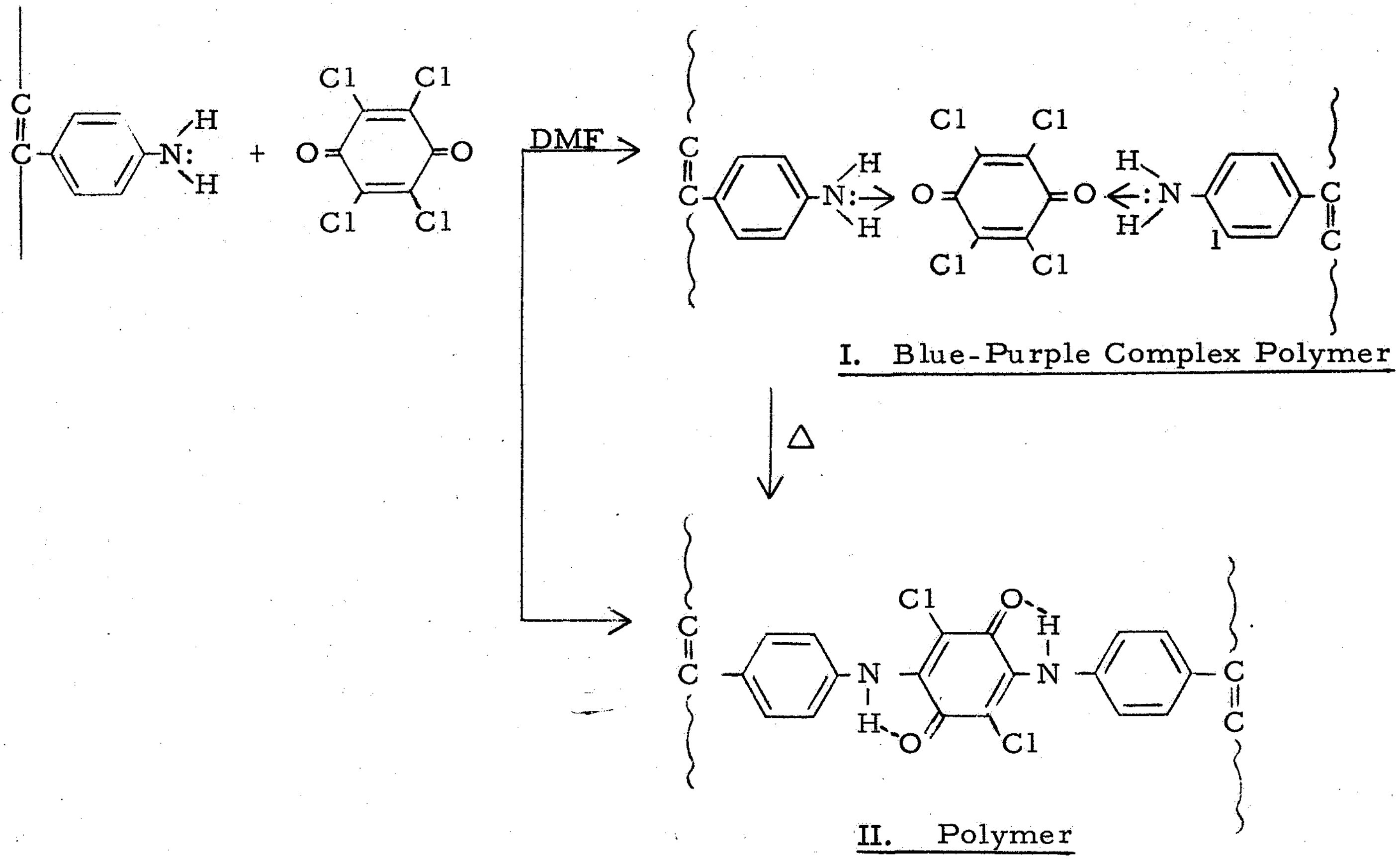

Figure I-6. Reaction of PAPA and Chloranil

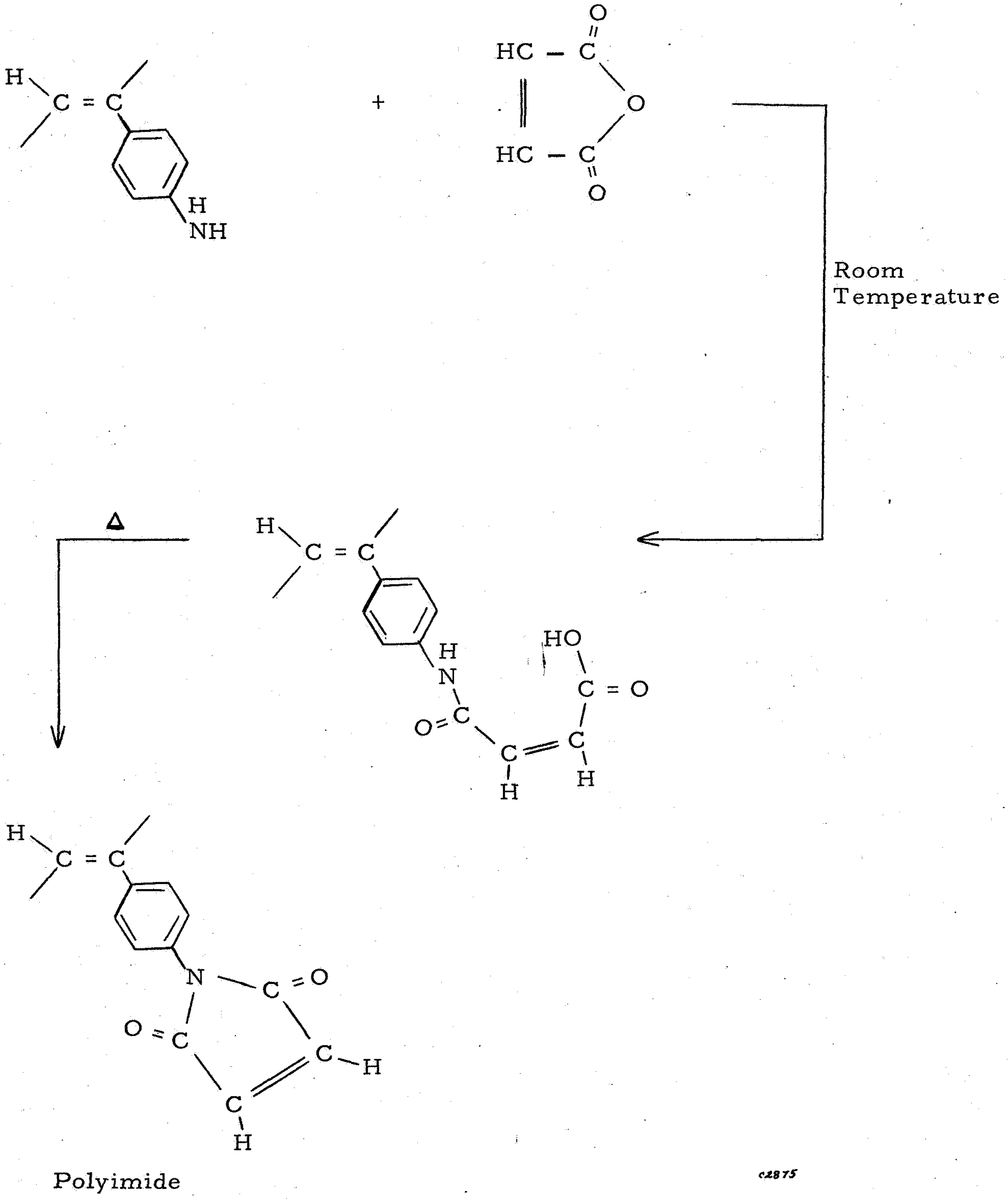

Figure I-7. Preparation of Poly(p-N-maleiimidephenylacetylene) from Poly(p-aminophenylacetylene) and Maleic Anhydride

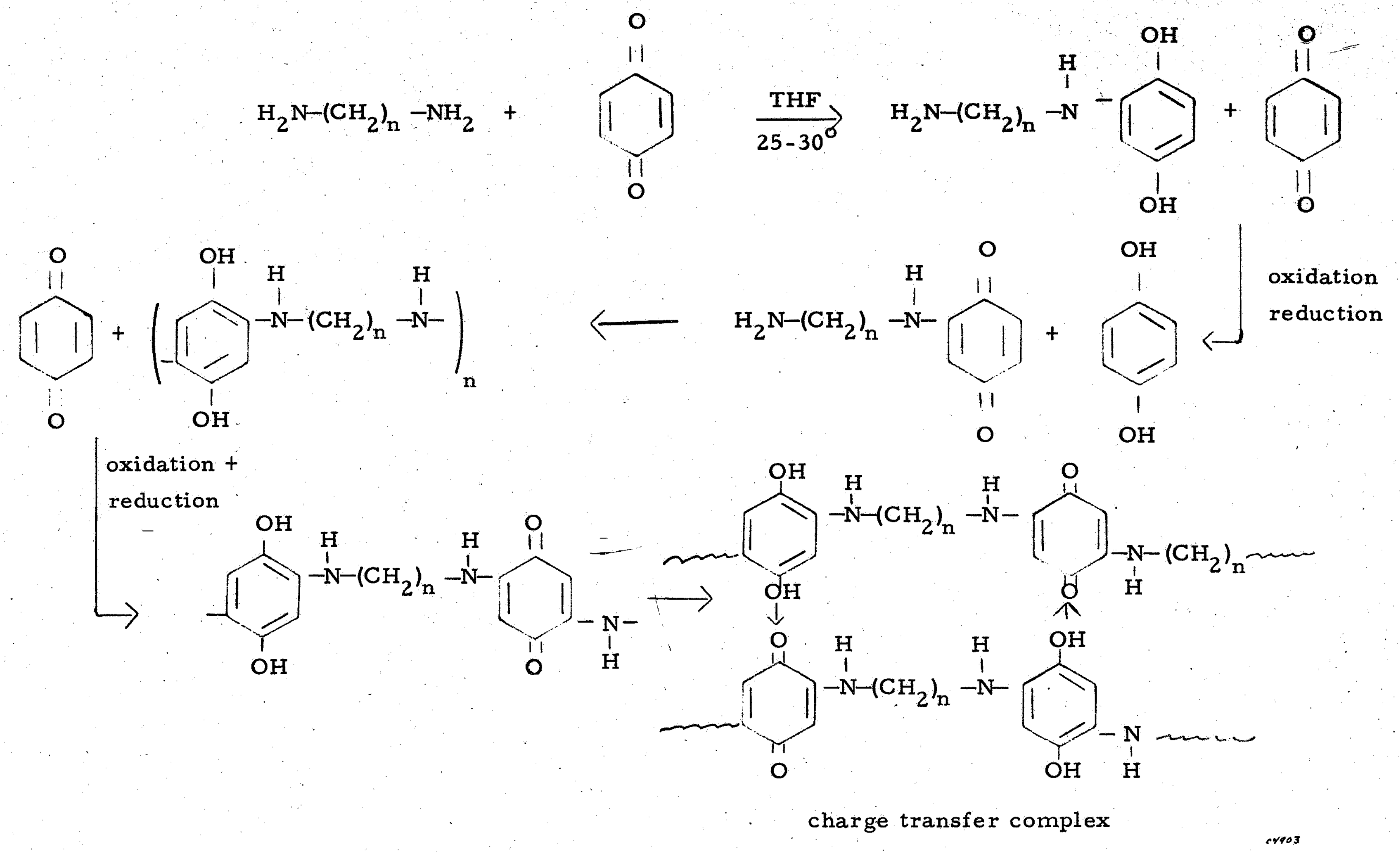

Figure I-8. Proposed Reaction Sequence of Benzoquinone With Alkanediamines mercury lamp while a slow stream of Cl_2 gas was bubbled into the solution. The chlorination reaction began immediately, as evidenced by the evolution of HCl. Approximately six hours were required to complete the addition of chlorine to the polymer. The polymer (poly α-chlorostyrene) was precipitated in a large volume of isopropyl alcohol and dried in a vacuum oven at 50°C overnight.

Elementary Analysis of (Cl-H-100)

	% C	% H	% Cl
Found	69.14	5.08	25.83
Theoretical	69.35	5.05	25.60

2.1.2 Preparation of Poly(α-chloro-p-nitrostyrene)

One mole (138.5 g) of poly(alphachlorostyrene) was dissolved in 800 ml of carbon tetrachloride and cooled to 10°C. To this was added, dropwise and with vigorous stirring, a mixture of 520 ml 90% nitric acid and 130 ml 98% sulphuric acid. The mixture was kept at, or below, 10°C. As the nitration proceeded, the reaction mixture became viscous, and the nitrated product came out of solution. After the addition of the acid mixture was completed, the reaction mixture was poured into two liters of water and stirred vigorously. It was decanted and washed several times with water, filtered, and washed with water again. The solid was gound with a mortar and pestle to release trapped acid in the particles and then washed with water, filtered, and washed until washings were neutral. A final wash was made with acetone and the product dried. The product, poly(α-chloro-p-nitrostyrene), was obtained in 93.5% yield.

Elementary Analysis

	% C	% H	% N	% Cl
Found	52.17	3.50	7.48	19.10
Theoretical	52.33	3.30	7.63	19.31

2.1.3 Preparation of Poly(p-nitrophenylacetylene)

2.1.3.1 LiCl Procedure — Dimethylformamide (500 ml) was added to a flask containing 91.75 g (0.5 mole) poly(α-chloro-p-nitrostyrene) plus 90 g lithium chloride. The polymer and salt were dissolved and the mixture heated to reflux for 48 hours. (Caution: CO is evolved.) The mixture was cooled and poured into two liters of water, filtered, and washed with water. It was dried in a vacuum oven at 50°C to yield poly(p-nitrophenylacetylene).

Elementary Analysis

	% C	% H	% N	% Cl
Found	65.53	4.04	8.68	2.58
Theoretical	65.30	3.40	9.50	0.0

2.1.3.2 Thermal Procedure — Poly(α-chloro-p-nitrostyrene) (40g) was dissolved in 200 ml of sulfolane and heated at about 190°C for a period of 5 hours with good stirring. Evolution of HCl was evident during the reaction. Following the dehydrohalogenation, the solution was cooled and the polymer precipitated in 500 ml of H_2O. It was difficult to filter the colloidal-like precipitate; therefore, the mixture was coagulated by steam distillation. It was then rapidly filtered, washed several times with water, dried overnight at room temperature and finally dried at 75°C in vacuum for a period of 48 hours. Approximately 29 g of poly(p-nitrophenylacetylene) was recovered.

Elementary Analysis

	% C	% H	% N	% Cl
Found	63.3	3.5	8.2	4.8
Theoretical	65.3	3.4	9.5	0

2.1.4 Preparation of Poly(p-formamidophenylacetylene)

Ten grams of poly(p-nitrophenylacetylene) were dissolved in 50 ml dimethylformamide (DMF). A solution of 35 g anhydrous stannous chloride in 75 ml DMF plus 25 ml concentrated HCl was added slowly to the nitro polymer solution. The mixture was heated to 100°C for five hours, cooled, and poured into 500 ml of H_2O made basic with concentrated NH_4OH. The precipitate was filtered, washed with water, and dried. The mixture of polymer and tin salts was extracted with DMF, the extract filtered, and then precipitated into water made basic with ammonium hydroxide. The precipitate was filtered, washed with water, and dried to yield 6.90 g of a dark brown polymer.

Elementary Analysis

	% C	% H	% N	% Cl
Found	72.3	5.7	10.4	2.6
Theoretical	74.5	4.8	9.6	0

2.1.5 Preparation of Poly(p-aminophenylacetylene)

Poly(p-formamidophenylacetylene) was hydrolyzed to the free amino derivative by the following procedure. Ten grams of poly(p-formamidophenylacetylene) were dissolved in 100 ml concentrated HCl and heated at 100°C for one hour. It was diluted with 500 ml of water and made basic with ammonium hydroxide. The resultant precipitate was filtered, washed with NH_4OH, and finally with water.

Elementary Analysis

	% C	% H	% N	% Cl
Found	77.26	6.19	11.42	2.75
Theoretical	82.05	5.98	11.46	0

2.1.6 Preparation of Poly(phenylacetylene)

Anhydrous $CuCl_2$ (1.0 g) was added to 500 ml of sulfolane in a 1000 ml reaction vessel equipped with a reflux condenser, nitrogen purge and mechanical stirrer. The solution was warmed to 35°C and with vigorous stirring, 50 g of poly(α-chlorostyrene) was added under a heavy stream of nitrogen. The temperature was gradually increased to 250°C. At this temperature the solution had turned black and the evolution of HCl had greatly decreased; therefore, an additional 1.0 g of $CuCl_2$ was added to the reaction vessel with subsequent heavy evolution of HCl. The reaction vessel was cooled overnight and an additional 5.0 g of $CuCl_2$ added. The solution was taken to 240°C and held for 72 hours while HCl continued to evolve. The temperature was finally brought to 290°C for 72 hours, with further evolution of HCl still apparent. At this point, it was concluded that the function of the $CuCl_2$ was not catalytic and that equal molar amounts of $CuCl_2$ to the bound chlorine would be required. Therefore, 10 g of $CuCl_2$ was added portion-wise to the hot polymer solution. Upon each addition of $CuCl_2$ the reaction became very active with copious amounts of HCl being evolved. An additional 5.0 g of $CuCl_2$ was added and the mixture refluxed for four hours. The mixture was cooled and precipitated in boiling H_2O and filtered. The precipitate was washed many times with boiling H_2O, taken up in chloroform, precipitated in boiling H_2O and dried. The polymer was extracted with hot acetone and both fractions recovered and dried.

Elementary Analysis

	% C	% H	% Cl	% O	% Ash
Acetone Soluble	90.77	5.96	2.54	—	—
Acetone Insoluble	91.55	4.69	1.58	1.41	1.39
Theoretical	94.13	5.87	—	—	—

2.1.7 Preparation of Poly(p-nitrophenylacetylene)

Five grams of poly(phenylacetylene), previously prepared by the $CuCl_2$-thermal procedure, acetone soluble fraction, were dissolved in 40 ml of CCl_4 and slowly added to a cold solution (10°C) of 5 ml of concentrated H_2SO_4 and 25 ml of fuming HNO_3 with good stirring and under a nitrogen atmosphere. The addition required approximately 45 minutes. The solution was held at 10°C for an additional 60 minutes and then gradually warmed to about 30°, at which temperature, the solution was poured over ice and water. The precipitated polymer was filtered and washed repeatedly with cold water. The product was taken up in a solution of acetone-diethylether and washed with cold water. The solution was evaporated to dryness and the product dried in a vacuum oven at 50° overnight.

2.1.8 Preparation of Poly(α-chlorophenylacetylene)

Poly(α, β-dichlorostyrene), 20 g, was added to about 50 ml of sulfolane in a reaction vessel equipped with a mechanical stirrer, N_2 inlet, and reflux condenser. The mixture was heated to reflux (~ 250°C) during which time the chlorinated polymer gradually passed into solution. At reflux temperature 20 g of anhydrous $CuCl_2$ was added portion-wise to the polymer solution with the evolution of copious amounts of HCl. The solution immediately turned black with continuous evolution of HCl. The reaction solution was held at reflux for about 6 hours, cooled and precipitated into 500 ml of H_2O acidified with 20 ml of concentrated HCl. This mixture was boiled for 30 minutes then filtered. The filtrate, after standing overnight, consisted of white crystals in a blue solution. The precipitate was slurried and filtered several times from hot HCl - H_2O followed by H_2O then MeOH. The low molecular weight fragments were removed by acetone extraction and the insoluble fraction dried and stored.

Elementary Analysis

(A) Poly(α, β-dichlorostyrene)

	% C	% H	% Cl
Found	51.9	3.8	43.9
Theoretical	55.8	3.5	40.7

(B) Poly(β-chlorophenylacetylene)

	% C	% H	% Cl
Found	76.4	3.3	19.9
Theoretical	70.6	3.7	25.7

2.1.9 Preparation of Poly(3,4-diaminophenylacetylene)

Poly(p-aminophenylacetylene), 0.53 g, was dissolved in 50 ml of glacial acetic acid, and taken to 50 - 60°C. Sixteen ml of acetic anhydride was added dropwise with good stirring, and the solution taken to 100°C for two hours to complete the acetylation. The solution was cooled to 60°C and about 50 ml of acetic acid removed by vacuum distillation. At slightly less than 25°C, a nitrating solution (10 ml of 70% HNO_3 - 70 ml of acetic anhydride) was added dropwise. The solution was held at 30°C for 30 minutes and then poured over a crushed ice - H_2O mixture with the formation of a yellow precipitate. The precipitate was washed a number of times with water and finally air dried for 72 hours. An infrared spectrum of the product depicted strong absorption bands at 5.8 and 7.45 microns indicative of acetamido and nitro functional groups.

The poly(acetamido-nitrophenylacetylene) derivative was slurried in 100 ml of methanol, and, with vigorous stirring, a solution of 20 g KOH in 50 ml of methanol was added. The solution was heated to 60-70°C for 2 hours and poured into crushed ice; the addition of 20 ml of conc. HCl caused the formation of a black precipitate. Infrared analysis indicated the amino-nitrophenylacetylene derivative had been formed.

To a solution of 20 g $SnCl_2 \cdot 2H_2O$ in 50 ml conc. HCl was added the wet nitro-amino derivative previously prepared. The solution was taken to 90°C and held for 1.5 hours. An additional 50 ml of conc. HCl was added and the solution cooled to 0°C. The dihydrochloride salt was filtered, redissolved, in 100 ml of hot H_2O and reprecipated by adding 100 ml of conc. HCl. The dihydrochloride salt was dissolved in 40 ml of H_2O and added to a cold solution (10°C) of 10 g NaOH in 25 ml H_2O. The hydrolyzed product was soluble in the strong NaOH base and was precipitated by titrating the solution to a pH of 7.0 with dilute HCl. The precipitate was dissolved in about 25 ml of DMF, and reprecipitated in a solution of 1 part NH_4OH to 3 parts H_2O. The product was washed several times with water, and dried at 50°C in a vacuum oven for four hours. Infrared analysis of the product depicted strong absorption at 2.95 micron for the diamine and a lessening of the 3.2μ band which indicated more ring substitution. No evidence of nitro or acetamido groups was found in the spectrum.

2.1.10 Preparation of Poly(α-chloro-p-formamidostyrene)

Approximately 40 g of poly(α-chloro-p-nitrostyrene), were dissolved in 250 ml of dimethylformamide (DMF) and added to a 500 ml reaction vessel equipped with a reflux condenser and mechanical stirrer. Anhydrous stannous chloride, $SnCl_2$, (150 g) was dissolved in 250 ml of DMF and acidified with 100 ml of concentrated HCl. This solution was added slowly to the polymer over a period of 20 minutes. The temperature of the polymer solution was held at 70°C for 72 hours, cooled and poured into 1000 ml of cold water made basic with 150 ml of concentrated NH_4OH. The mixture of polymer and tin salts was filtered, washed several times with hot water and redissolved in 1000 ml of hot (70°C) DMF. The mixture [dissolved polymer and the insoluble $Sn(OH)_2$ and $Sn(OH)_4$ salts] was filtered, and the polymer solution concentrated in a Rotovac. The concentrated polymer solution was again filtered, precipitated in boiling water, air dried overnight and finally vacuum dried for 24 hours at 100°C. Thirty grams of a light tan polymer product, identified by infrared and differential scanning calorimetric analysis to be poly(α-chloro-p-formamidostyrene) was recovered.

2.1.11 Preparation of Poly(α-chloro-p-aminostyrene)

The preparation of poly(α-chloro-p-aminostyrene) requires the hydrolysis of the formamido group by either a strong acid or base followed by precipitation in NH_4OH, if acid is utilized. Due to the solubility characteristic of poly(α-chloro-p-formamidostyrene), it was hydrolyzed in concentrated H_2SO_4. Ten grams of poly(α-chloro-p-formamidostyrene) were carefully added to 75 ml of concentrated H_2SO_4 in a 250 ml beaker. The polymer slowly dissolved with the evolution of CO and the formation of a red colored solution. The solution was held at room temperature for 72 hours, transferred to a 500 ml reaction vessel, diluted with 200 ml of H_2O and brought to 100°C for 2 hours. The solution was cooled in an ice bath and enough concentrated NH_4OH added to make the mixture basic to pH paper. The mixture was filtered, air dried, and dissolved in 100 ml of hot DMF. Insoluble gell was removed by centrifuging and the polymer solution precipitated in water made slightly basic with NH_4OH. The mixture was boiled at 100°C for approximately 30 minutes followed by filtration (extremely slow) and air drying.

2.1.12 Preparation of Polyacetylene

A procedure based on Luttinger's method* was used. Methanol (200 ml) was saturated with acetylene gas under nitrogen atmosphere. Sodium borohydride (2.0 g) and cobalt nitrate hexahydrate (1.4 g) were added to the stirring solution. Heat evolution was noted. The system was maintained with sitrring and slow bubbling of acetylene through it, under nitrogen atmosphere for six to seven hours at room temperature. Stirring difficulty was not observed. The product was collected on a funnel under a nitrogen-swept polyethylene bag, and washed with acetone, heptane, alcoholic HCl, water and finally acetone again. After drying over Drierite at 56° under reduced pressure (less than 1 mm Hg) for three hours, 1.6 g of black fluffy polymer was obtained.

2.2 <u>Crosslinking of Poly(p-aminophenylacetylene)</u>

2.2.1 Hexamethylene-1,6-diisocyanate-linked Poly(p-aminophenylacetylene) (Heterogeneous Reaction)

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*Luttinger, L. B., U.S. 3174956 (1965).

Commercial hexamethylene-1,6-diisocyanate (HDI), 0.36 ml, was added to a stirring suspension of 0.51 g of poly(p-aminophenylacetylene) in benzene. The mixture was stirred at room temperature overnight, refluxed for one hour and filtered. The dark brown product was washed with diethyl ether, and dried over Drierite at 56°C under reduced pressure (less than 1 mm Hg) for five hours. A yield of 0.66 g (theoretical yield 0.88 g) was obtained. Thus an estimated 40% of the amino groups of poly(p-aminophenylacetylene) were linked with HDI.

The HDI-linked poly(p-aminophenylacetylene) is insoluble in dimethylsulfoxide, dimethylformamide and concentrated sulfuric acid. The poly(p-aminophenylacetylene) is readily soluble in these solvents. The infrared spectrum of the product shows a shoulder band at 1660 cm^{-1} indicating CO absorption for a substituted urea derivative, -NH-CO-NH-.

2.2.2 Toluene-2,4-diisocyanate-linked Poly(p-aminophenylacetylene) (Heterogeneous Reaction)

Commercial toluene -2,4-diisocyanate (TDI), 0.39 ml, was added to a stirring suspension of 0.53 g of poly(p-aminophenylacetylene) in benzene. The mixture was stirred at room temperature overnight and refluxed for four hours under anhydrous condition. The dark brown product was washed with benzene and diethyl ether and dried over Drierite at 56°C for four hours. A yield of 0.77 g (theoretical yield 1.01 g) was obtained. Thus an estimated 50% of the amino groups of poly(p-aminophenylacetylene) was linked with TDI.

The TDI linked poly(p-aminophenylacetylene) was insoluble in dimethyl formamide and concentrated sulfuric acid.

2.2.3 Multiisocyanate-linked Poly(p-aminophenylacetylene) (Heterogeneous Reaction)

Upjohn's PAPI (polymethylene polyphenylisocyanate) 0.54 ml, was added to a stirring suspension of 0.50 g of poly(p-aminophenylacetylene) in toluene. The mixture, protected from atmospheric moisture by a Drierite-filled drying tube, was stirred at room temperature overnight and refluxed for eleven hours. The dark brown product was washed twice with toluene, then benzene and dried over Drierite at 56°C under reduced pressure (less than 1 mm Hg) for six hours. A yield of 0.9 g was obtained. An estimated 40% of the amino groups of poly(p-aminophenylacetylene) were linked with PAPI.

2.2.4 Reaction Between Poly(p-aminophenylacetylene) and Toluene-2,4-diisocyanate (TDI) (Homogeneous Reaction)

Poly(p-aminophenylacetylene) was dissolved in dimethylsulfoxide which had been dried over $MgSO_4$, and to this was added, with vigorous stirring, a 20% solution of the TDI dissolved in benzene. After the reaction mixture had become gelatinous at room temperature, it was heated at 100°C for five minutes, diluted with benzene, filtered, washed with ether, and then dried.

The dried polymer was subsequently washed with alcohol, water, alcohol, ether, and then dried in vacuum at 100°C. Table I-I shows the results of the reactions with varying amounts of TDI.

2.2.5 Reaction between Maleic Anhydride and Poly(p-aminophenylacetylene) 1:1 Ratio

Poly(p-aminophenylacetylene) (PAPA) (0.6 g) (approximately 0.005 mole) was dissolved in 10 ml dimethylsulfoxide (DMSO) (dried over anhydrous $MgSO_4$), and 0.55 g of maleic anhydride (approximately 0.006 mole), dissolved in 10 ml DMSO, was added to this, with stirring. The reaction was carried out at room temperature for 5.5 hours, and the resultant solution was precipitated into benzene, washed with dioxane and dried in vacuo. Yield was 1.10 g (100%).

2.2.6 Reaction Between Maleic Anhydride and Poly(p-aminophenylacetylene) (50% Reaction Product - 1:2)

Poly(p-aminophenylacetylene) (PAPA) (0.6 g, approximately 0.005 mole) was dissolved in 10 ml dimethylsulfoxide (DMSO) (dried over $MgSO_4$), and 0.28 g (approximately 0.003 mole) of maleic anhydride in 10 ml DMSO was added with stirring, and the solution allowed to stand at room temperature for five hours. The product was precipitated into benzene, filtered, washed with benzene, and dried in vacuo. The yield was 0.85 g (97% based upon one maleic moiety per two amino groups). The infrared spectrum was similar to the 100% (1:1) reaction product prepared previously except that the carbonyl absorption, at 5.85 μ, was less intense.

2.2.7 Reaction Between Epichlorohydrin and Poly(p-aminophenylacetylene)

PAPA (1 g, approximately 0.009 mole) was dissolved in 10 ml dimethylformamide (DMF) (dried over $MgSO_4$), and 0.67 ml (approximately 0.0085 mole) of epichlorohydrin was added with stirring. It was allowed to react at room temperature for 20 hours, and then the solution was divided into two portions. One half was precipitated into benzene, filtered, washed with benzene, and dried in air. The other half was heated at 100°C for three hours and then left standing at room temperature for three days. It was precipitated as above. The infrared spectrum shows the appearance of some new bands. Two strong bands are found at 6.0 and 9.1μ; three weak bands occur at 6.95, 7.1, and 7.25 μ. The former are OH bands, while the latter are aliphatic CH bands.

2.2.8 Reaction Between Poly(p-aminophenylacetylene) and Pyromellitic Anhydride at Various Mole Ratios

Master solutions of PAPA and PMA, were prepared for use in a series of controlled crosslinking reactions. The PAPA solution was prepared by dissolving 4.970 g (0.0425 mole) of PAPA in about 25 ml of dimethylacetamide

TABLE I-I

REACTION BETWEEN POLY(P-AMINOPHENYLACETYLENE) AND VARIOUS MOLE RATIOS OF TDI

Mole Percent of TDI	Wt of Polymer Used (gms)	Volume of 20% Solution of TDI in Benzene (ml)	Wt of TDI Used (gms)	Yield (Wt)
10	0.61	0.18	0.044	0.56
25	0.61	0.45	0.11	0.69
50	0.60	0.90	0.22	0.91
80	0.60	1.44	0.35	1.10
100	0.60	1.80	0.44	1.19

(DMA) and diluting to 100 ml. The titer of this solution was 0.000425 mole/ml. The pyromellitic anhydride (PMA) was recrystallized from acetic anhydride and the PMA solution was prepared in the same manner in DMA at a concentration of 5.4767 g (0.0251 mole) per 100 ml or 0.000251 mole/ml.

2.2.8.1 1:1 Mole Ratio of Amine to Anhydride — About 39.8 ml of the PMA solution (0.01 mole) was added to the reaction vessel previously described. To this stirred solution was added 23.5 ml of PAPA (0.01 mole) dropwise over a period of about 15 minutes. Following the addition of the PAPA solution, about 12 ml of DMA was added to bring the total volume of the solution to 75 ml. The solution was held at room temperature under a nitrogen atmosphere for a period of four hours with the appearance of a small amount of precipitate on the side of the reaction vessel. The mixture was then taken to reflux (165°C), which caused the formation of a heavy precipitate. The precipitate was washed with benzene twice and three times with acetone, filtered, and dried in the vacuum oven at 50°C for a period of four hours. Infrared analysis indicates a new band formation at 5.75 μ that may be associated with the imide structure; in addition, the carbonyl doublet at 5.35 and 5.6 μ is almost extinct, thus indicating that very little of the free anhydride is present.

2.2.8.2 2:1 Mole Ratio of Amine to Anhydride — Reactants used were 25.5 ml of PAPA solution and 20 ml of PMA solution. The amine was added dropwise to the anhydride solution with immediate precipitation and a slight exotherm. About 31.5 ml of DMA was added to the mixture and then held at room temperature for four hours. The mixture was washed and filtered by first decanting the DMA, washing with benzene three times, then washing with acetone three times. The product was dried overnight in a vacuum oven held at 50°C. The filtrate from this reaction was almost clear, indicating that the mole ratio of reactants used were close to the stoichiometric point.

2.2.8.3 4:1 Mole Ratio of Amine to Anhydride — The reactants used were 10 ml of PMA and 23.5 ml of PAPA solutions made up to a total volume of 75 ml by the addition of 43.5 ml of DMA. The addition of the amino polymer caused an immediate precipitate. The reaction mixture was held at room temperature for two hours, followed by decanting, washing, filtering, and finally drying in a vacuum oven at 50°C overnight. The infrared spectrum of the compound showed a sharpening of the band at about 3.0 microns, indicating free NH_2 group.

2.2.8.4 8:1 Mole Ratio of Amine to Anhydride — Reactants consisted of 5.0 ml of PMA and 23.5 ml of PAPA solutions diluted with 46.5 ml of DMA to a total volume of 75 ml. The anhydride was added to the amine solution dropwise at room temperature without forming a precipitate. The solution was held at room temperature over the weekend and filtered. No precipitate was recovered. About 100 ml of acetone was added to the reaction vessel to precipitate a possible reaction product; however, no precipitate formed.

The solution was taken to reflux and held four hours without the formation of a precipitate. Approximately 10 ml of the solution was air dried overnight, followed by vacuum drying at 80°C for four hours. The infrared spectrum of this product showed strong NH_2 absorption.

2.2.9 Reaction Between Poly(p-aminophenylacetylene) and Chloranil at Various Mole Ratios

2.2.9.1 2:1 Mole Ratio of Amine to Chloranil — Approximately 0.005 mole (0.58 g) of PAPA polymer was dissolved in 25 ml of dimethylformamide and added to a 150 ml reaction vessel. The reaction vessel was equipped with a nitrogen inlet, mechanical stirrer, reflux condenser, and dropping funnel. Chloranil, 0.615 g, (0.0025 mole), previously recrystallized from isopropyl alcohol and benzene, was dissolved in 25 ml of DMF. The chloranil solution was added dropwise to the reaction vessel with vigorous stirring while under a nitrogen blanket. The solution was taken to reflux, 152°C, for 2-1/2 hours during which time a precipitate formed. The mixture was cooled, filtered and washed several times with acetone and dried. The filtrate from this reaction was red purple and may have been a charge-transfer complex between PAPA and chloranil.

2.2.9.2 1:1 Mole Ratio of Amine to Chloranil — Equal molar amounts of chloranil (1.23 g) and PAPA (0.58 g) were each dissolved in 25 ml of DMF. The solutions were mixed in a 100 ml volumetric flask, flushed with nitrogen, stoppered, and stored at room temperature for a period of 168 hours. During this time, the solution turned dark brown. A precipitate was formed by adding 300 ml of acetone to the solution and allowing to stand overnight. The mixture was filtered, dried, and bottled.

The acetone filtrate from the above reaction was a dark blue-purple color, probably the PAPA-chloranil complex. The filtrate was evaporated to dryness leaving a purple-black, waxy compound. The material was vacuum dried at 60°C for 4 hours.

2.2.9.3 4:1 Mole Ratio of Amine to Chloranil — This reaction was carried out at the reflux temperature of DMF (152°C) under an N_2 blanket using the reaction vessel previously described. The PAPA polymer (0.004 mole - 0.468 g) was dissolved in 25 ml of DMF and added to the reaction vessel. The chloranil compound, (0.001 mole - 0.246 g), dissolved in 25 ml of DMF, was added dropwise to the stirring solution. The reaction was taken to reflux for 30 minutes during which time a heavy precipitate formed. The mixture was cooled to room temperature and 90 ml of acetone added. The mixture was filtered and the precipitate air dried for 48 hours followed by vacuum drying at 60°C for 4 hours.

2.2.10 Reaction Between Poly(p-aminophenylacetylene) and Terephthalaldehyde at Several Mole Ratios

Equipment used in these reactions consisted of a 150 ml reaction flask equipped with a mechanical stirrer, reflux condenser and dropping funnel.

A solution of the PAPA polymer in dimethylsulfoxide (DMSO) was added to the reaction flask and, with vigorous stirring, a solution of terephthalaldehyde in DMSO was added. The solution was taken to reflux (189°C) and held for about four hours. No precipitate formed. At this point, 3 ml of concentrated HCl was added, and after refluxing another 15 minutes, a precipitate formed. The mixture was cooled, added to about 250 ml of acetone, filtered and vacuum dried at 80°C for eight hours. See Table I-II for reaction conditions.

2.3 Charge Transfer Complexes

2.3.1 Poly(p-aminophenylacetylene) Charge Transfer Complexes

Charge transfer complexes were prepared by adding an acetone solution of PAPA to acetone solutions of tetracyanoquinodimethane (TCNQ), tetracyanoethylene (TCE) and chloranil. The reactants were at equimolar amounts and held at room temperature for a period of 24 hours, evaporated to dryness and redissolved by adding 200 ml of acetone to each beaker. Each complex contained a soluble and insoluble fraction that was separated by filtration and washed several times with acetone. The acetone-insoluble fraction was dried at 50°C in vacuum for 2 hours. The acetone soluble fraction was recovered by evaporation of the solvent followed by oven drying in vacuum at 50°C, for 2 hours. (see Table I-III for details.)

2.3.2 Tetracyanoquinodimethane (TCNQ) + 1,4-Phenylenediamine

Equi-molar quantities of 1,4-phenylenediamine and TCNQ were dissolved in tetrahydrofuran (THF), acetone and dichloromethane, respectively. Each TCNQ solution was added rapidly to the corresponding 1,4-phenylenediamine solution at room temperature. The charge-transfer complex (CTC) formed in CH_2Cl_2 immediately precipitated as a crystalline purple complex; whereas the complexes prepared in THF and acetone formed intensely colored solutions. The complexes in THF and acetone were recovered by precipitation in a large volume of CCl_4. Figure I-2 is a schematic of the reaction sequences.

2.3.3 Chloranil + 1,4-Phenylenediamine

Equi-molar quantities (0.002 mole) of chloranil and 1,4-phenylenediamine were each dissolved in 100 ml of CH_2Cl_2. The 1,4-phenylenediamine solution was added rapidly to the chloranil with an immediate formation of a precipitate. The mixture was filtered and air dried for two days yielding a black fluffy complex.

2.3.4 Polyphenylacetylene-Iodine

Equal weight amounts of poly(phenylacetylene) and I_2 were dissolved in 100 ml of $CHCl_3$ and the solutions added together rapidly at room temperature. The solvent was removed by evaporating the solution in a roto-vac (no heat) at low pressure. The CTC was collected as a dark shiny, violet precipitate.

TABLE I-II

REACTION OF POLY(P-AMINOPHENYLACETYLENE) (PAPA) WITH TEREPHTHALALDEHYDE (TPA)

Mole Ratio PAPA/Terephthalaldehyde	Mole of PAPA	Mole of TPA	Ml of DMSO		Ml HCl Conc.
			PAPA	TPA	
2/1	5×10^{-3} (0.58g)	2.5×10^{-3} (0.335g)	50	25	2.0
4/1	1×10^{-2} (1.17g)	2.5×10^{-3} (0.335g)	100	25	5.0
20/1	1×10^{-2} (1.17g)	5×10^{-4} (0.067g)	100	25	5.0
Control	0.10 g	0	50		2.5

TABLE I-III

PAPA CHARGE TRANSFER COMPLEXES

Moles/Wt. of Acceptor	Moles/Wt. PAPA Donor	Total Vol. Acetone	Precipitates Acetone Sol	Acetone Insol
TCNQ				
0.0025/0.51g	0.0025/0.29g	150	Slight	Large
TCE				
0.0025/0.32g	0.0025/0.29g	150	Large	Slight
Chloranil				
0.0011/0.27g	0.0011/0.13g	100	Slight	Large

2.3.5 Poly(p-aminophenylacetylene) + TCNQ

Equi-molar quantities of poly(p-aminophenylacetylene) (PAPA) and TCNQ were each dissolved in 100 ml of DMF, acetone, and CH_2Cl_2. The TCNQ solutions were added to the corresponding PAPA solutions and gently refluxed for about four hours. The resulting mixtures were cooled to room temperature and allowed to settle out overnight. The mixtures were filtered and dried. Figure I-3 is the reaction sequence.

2.3.6 CTC From Poly(p-aminophenylacetylene) with Pyromellitic Dianhydride

Pyromellitic dianhydride (0.2 g) was dissolved in 100 ml of CH_2Cl_2. To this solution was added 0.1 g of poly(p-aminophenylacetylene) dissolved in 25 ml of CH_2Cl_2. The resultant solution was stirred rapidly, and a light brown precipitate formed almost immediately.

2.3.7 Chloranil with PAPA Prepared in DMF

Chloranil (0.240 g) was dissolved in 25 ml of DMF and added to a solution of 0.117 g of PAPA dissolved in 25 ml DMF. The solution was purged with N_2, stoppered and allowed to stand for two weeks, during which time the solution turned dark brown with evidence of a precipitate. The mixture was added to 200 ml of acetone and filtered, with the recovery of about 0.17 g of a black product and a purple filtrate. The black-purple filtrate was evaporated to dryness to obtain the product. A second batch was prepared using twice the amounts of monomer each dissolved in 25 ml DMF.

2.4 Preparation of Poly(alkyldiaminoquinhydrone) Polymers

The reaction sequence for the formation of poly(alkyldiaminoquinhydrone) consists essentially of adding, dropwise, a dilute tetrahydrofuran (THF) solution of diamine to a 10 wt % THF solution of benzoquinone. The reaction is carried out under nitrogen with good stirring at a temperature of about 30°C. The addition of the diamine causes an instantaneous color change of the benzoquinone solution; going from yellow to red then purple. The reaction is exothermic and requires cooling during the addition of the diamine. Following the addition of diamine a red, solvent-swollen polymer is isolated, washed several times with warm THF, and vacuum dried. The polymers appear to be crosslinked and swell in a number of common solvents. A red filtrate from the above reactions contains the soluble polymer fraction and may be recovered by precipitating in n-heptane. The reaction variables that appear to affect the final polymer products are:

1. Mole ratio of benzoquinone to diamine.
2. Temperature of reaction.
3. Solvent used in reaction.
4. Atmosphere.
5. Number of CH_2 groups in alkanediamine.

Thus far, it appears that the optimum conditions are a 3:1 ratio of benzoquinone to diamine, reaction temperature of 30°, THF as the solvent, a N_2 atmosphere, and possibly an odd number of (CH_2) groups. Table I-IV lists the various polymers prepared under certain reaction conditions.

TABLE I-IV

REACTION CONDITIONS FOR THE PREPARATION OF POLY(ALKANEDIAMINOBENZOQUINONES)

Diamine	Solvent	Atmosphere	Reaction Temperature	Mole Ratio Diamine/ Benzoquinone	Sample Identification
1, 2-ethane	THF	N_2	30°	1:3	7502-31
1, 3-propane	THF	N_2	30°	1:3	7502-30
1, 4-butane	THF	N_2	30°	1:3	7502-29
1, 5-pentane	THF	N_2	30°	1:3	7502-22-A
1, 6-hexane	benzene	N_2	40°	1:3	7470-34
1, 6-hexane	THF	air	50°	1:3	7502-19A
1, 7-heptane	THF	N_2	30°	1:3	7502-16
1, 8-octane	THF	N_2	30°	1:3	7502-25
1, 10-decane	THF	N_2	30°	1:3	7502-26
1, 12-dodecane	THF	N_2	30°	1:3	7502-21