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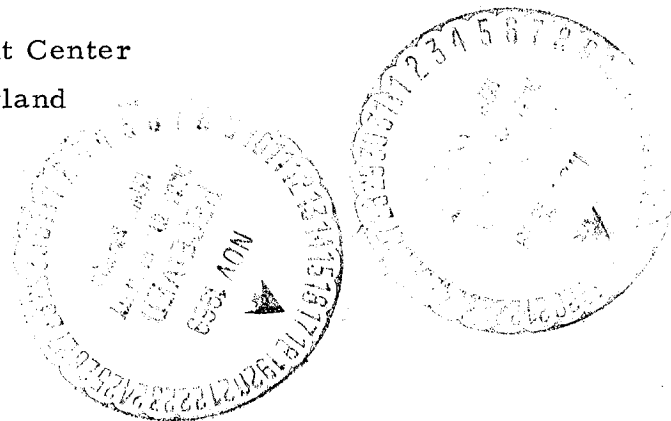
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Final Report
for
Development of High Thermal Conductivity
Polymeric Materials for Spacecraft Use
(1 July 1966 to 31 May 1969)

Contract No.: NAS5-10260

Prepared by
Astropower Laboratory
McDonnell Douglas Astronautics Company
Western Division
McDonnell Douglas Corporation
Newport Beach, California

for
Goddard Space Flight Center
Greenbelt, Maryland



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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- $^{\circ}$ C
Working Temperature	-30 $^{\circ}$ to 200 $^{\circ}$ 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- $^{\circ}$ 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- $^{\circ}$ C.

A family of electron 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 -alkane-diamines in an excess of p-benzoquinone thereby forming a "redox" type polymer containing both the quinone and hydroquinone groups. The quinone-hydroquinone groups in the chain appear to orientate during pressing so that

a charge transfer complex was formed. The formation of this complex yields polymers of high thermal conductivity (10^{-3} cal/cm-sec- $^{\circ}$ 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 equal mole mixtures of 1,7 and 1,10 diamine and also 1,8 and 1,12 reacted with benzoquinone. At higher temperatures, the thermal conductivity values for these two polymers remain above 1.5×10^{-3} cal/cm-sec- $^{\circ}$ C, while at lower temperatures the k values increase to higher values. The flexibility of the polymers increased quite rapidly as the number of (CH₂) groups increased 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.

A second family of electron transfer polymers was prepared by condensing hydroquinone, phenol and formaldehyde at various mole ratios in a basic pH. The resulting water-alcohol soluble "resoles" when cast as films and oven cured, yielded satisfactory thermal conductivities as a function of temperature (about 1.0×10^{-3} cal/cm-sec- $^{\circ}$ C). The film properties ranged from poor to excellent dependent upon the ratio of phenol to hydroquinone. It appears that the optimum mole ratio of 1:1 phenol to hydroquinone is required for the preparation of strong films with good thermal conductivity.

It is suggested that further effort be expended to confirm the results obtained in this investigation; that increased thermal conductivity may be promoted by forming intra and inter molecular charge transfer complexes which in turn yield thermally conducting electron transfer polymers. Once the concept of thermal conductivity-charge transfer complex is understood more completely, synthesis of polymers with wide ranges of properties and usage will become possible.

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Section 1

INTRODUCTION AND SUMMARY

A major problem in the electronics and aerospace industries is the unavailability of polymeric substances for coating and potting 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-xylenes), 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 O₂ 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 $2-8 \times 10^{-4}$ cal/cm-sec-°C (Ref. 1), which is average for 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 polymers evaluated were the ring substituted polyphenylacetylenes having conjugated polyene backbones. 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 transaligned were in most cases transunaligned, thus preventing orientation of the polymers.

The second phase of this program was 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 results in the investigation of this new area, utilizing acceptors such as tetracyanoquinonodimethane, 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, two new series of polymers were prepared using an inter- and intra-molecular charge transfer complexing mechanism which promotes high thermal conductivities as a function of temperature while maintaining good electrical resistivity (Ref. 3). The first series of polymers were prepared by reacting an excess of benzoquinone with various alkanediamines. Their properties ranged 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- $^{\circ}$ C range and may be molded to various shapes under temperature and pressure. These polymers were completely insoluble in laboratory solvents.

A series of polymers was prepared using various mole ratios of phenol, hydroquinone and formaldehyde. Their thermal conductivity response was measured as a function of the mole percentage of monomers to obtain the possibility of measured conductivity due to the probable formation of an intramolecular charge transfer complex between phenol and benzoquinone groups. The polymers containing high mole ratios of phenol to hydroquinone formed excellent films but generally yielded lower thermal conductivity values than the polymers prepared from only hydroquinone and formaldehyde.

The enhanced thermal conductivity of the polymeric system: phenol, hydroquinone and formaldehyde, as compared to the basic phenolic resin, appears to be due to charge transfer coupling of phenol-benzoquinone and hydroquinone-benzoquinone. The benzoquinone was generated by oxidation of hydroquinone during polymer synthesis under basic pH conditions.

Section 2

THEORY

2.1 THEORETICAL BACKGROUND

2.1.1 Thermal Conductivity of Saturated Polymers

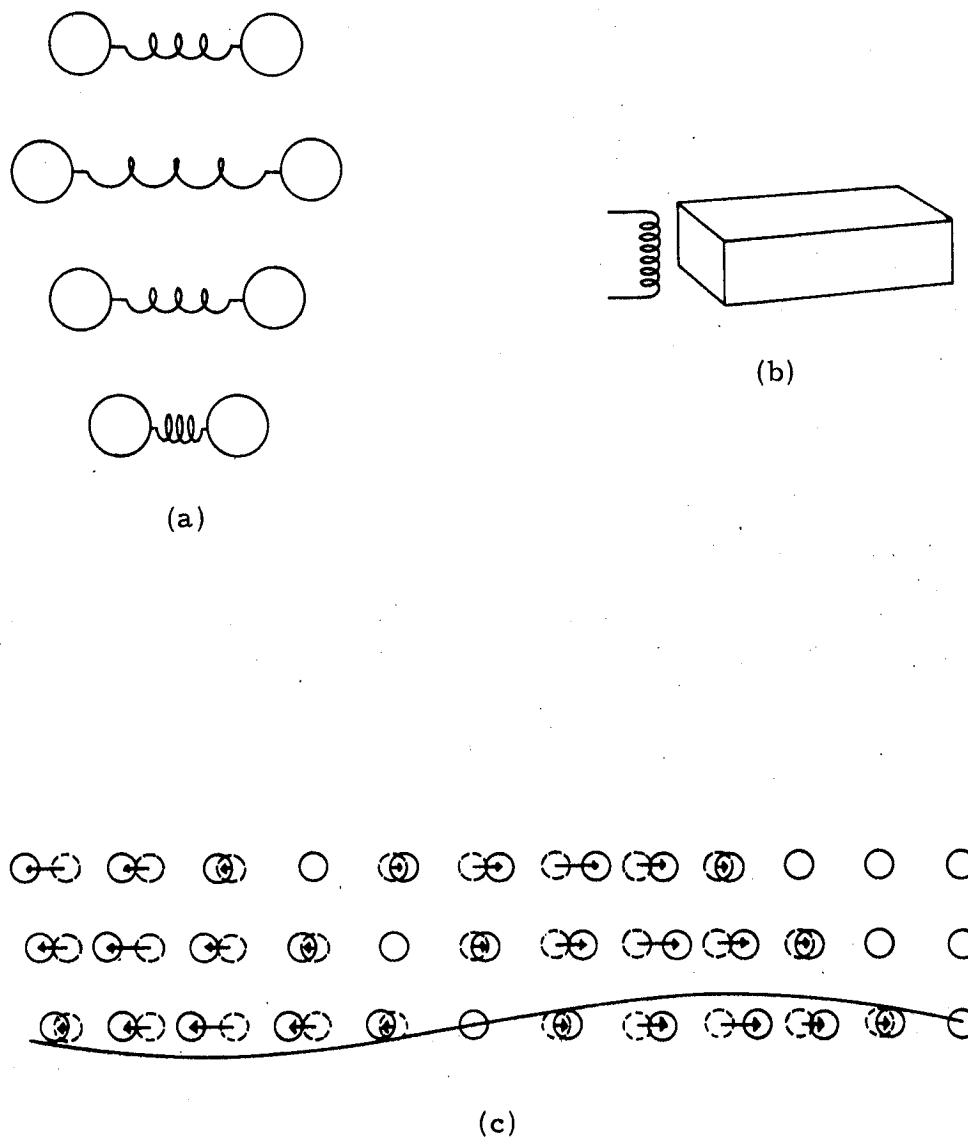
The transfer of energy in a solid may be accomplished by coupling of the lattice vibrations (phonon) or by the electronic movement and collision with atoms. In ordered crystal structures at low temperature, the phonon process of energy transfer is adequately described by:

$$k = 1/3 C \bar{v} \lambda \quad (1)$$

where k is the thermal conductivity, C the specific heat, $\bar{v}$ 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 amorphous phase of the polymer also contributes to thermal conductivity and is generally 6.0×10^{-4} cal/cm-sec- $^{\circ}\text{C}$ or less. The thermal conductivity of both phases are additive but appear to reach maximum values in the low 10^{-3} cal/cm-sec- $^{\circ}\text{C}$ 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)

• 43%

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

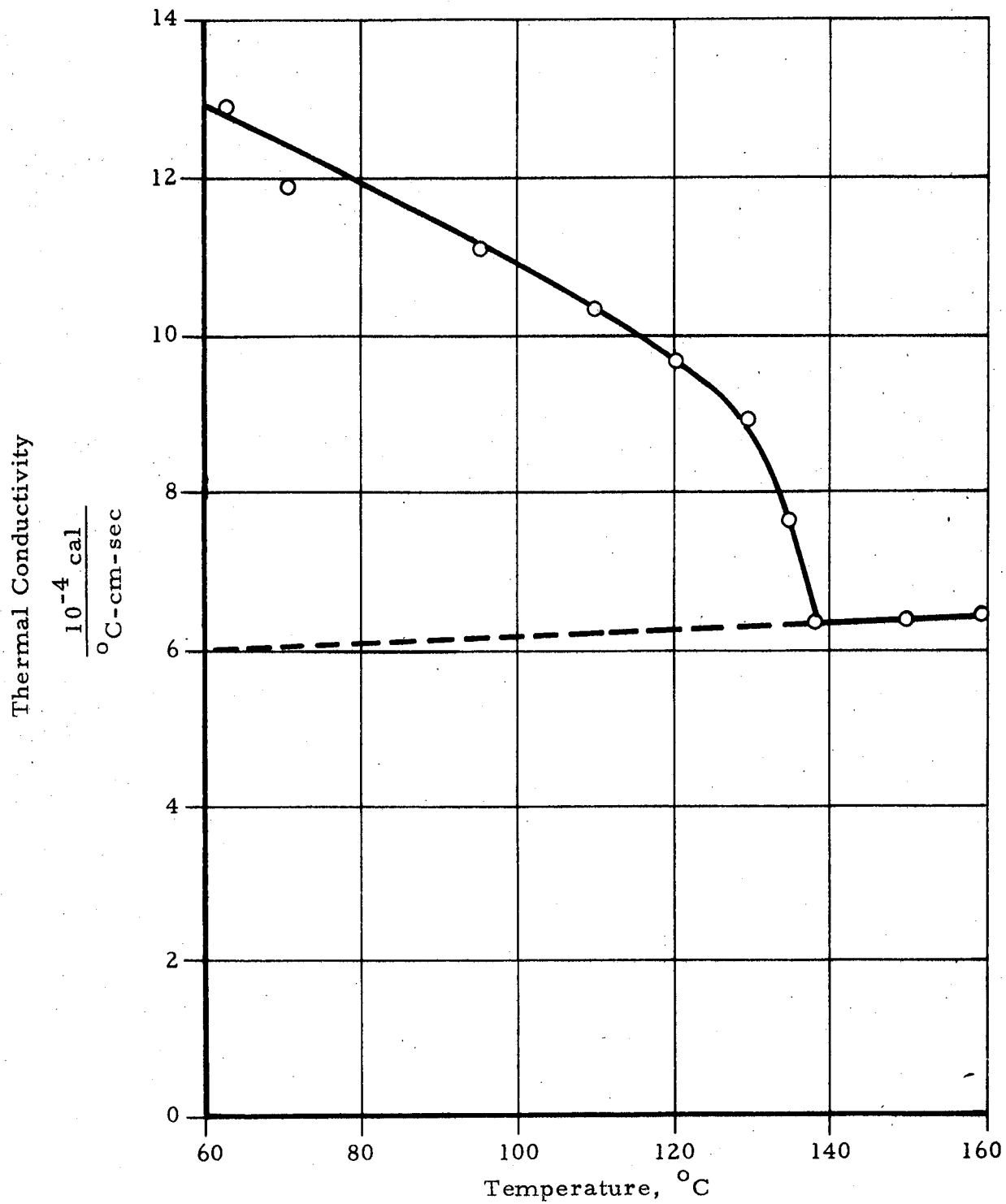


Figure 2. Thermal Conductivity of Linear Polyethylene as a Function of Temperature

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 (T_g) the polymer is elastic; below the T_g , 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 T_g , and then drops off sharply; for polyethylene (Figure 4), the conductivity also approaches a maximum at the T_g , but then slowly increases to a room temperature value of about 6.0×10^{-4} cal/cm-sec- $^{\circ}\text{C}$, 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 Polymeric Charge Transfer Complexes

Inter- and intra-molecular charge transfer complexes in polymeric systems give rise to electron transfer polymers capable of enhanced thermal conductivity by a thermal coupling mechanism (Ref. 3). The mechanics of heat

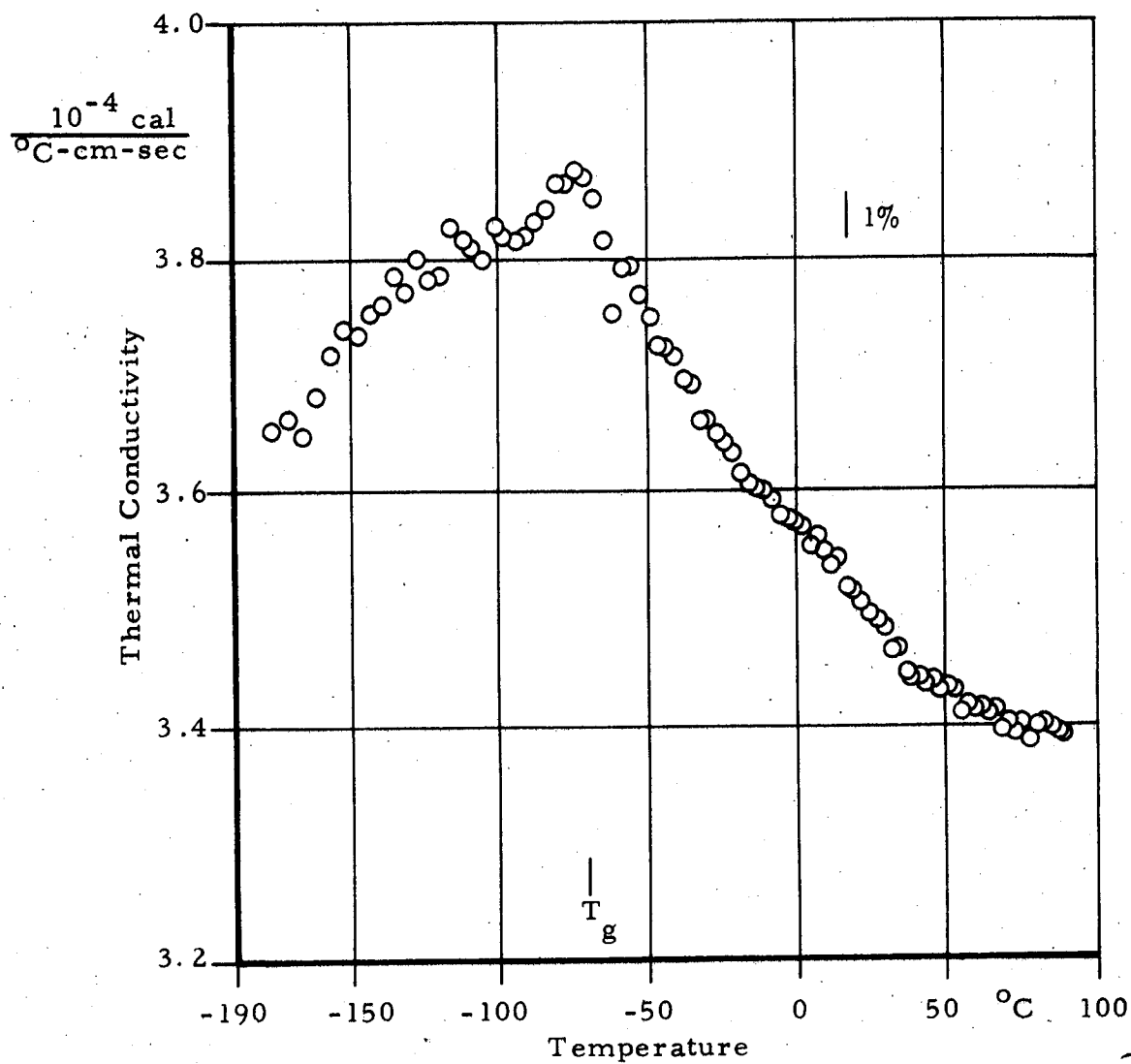
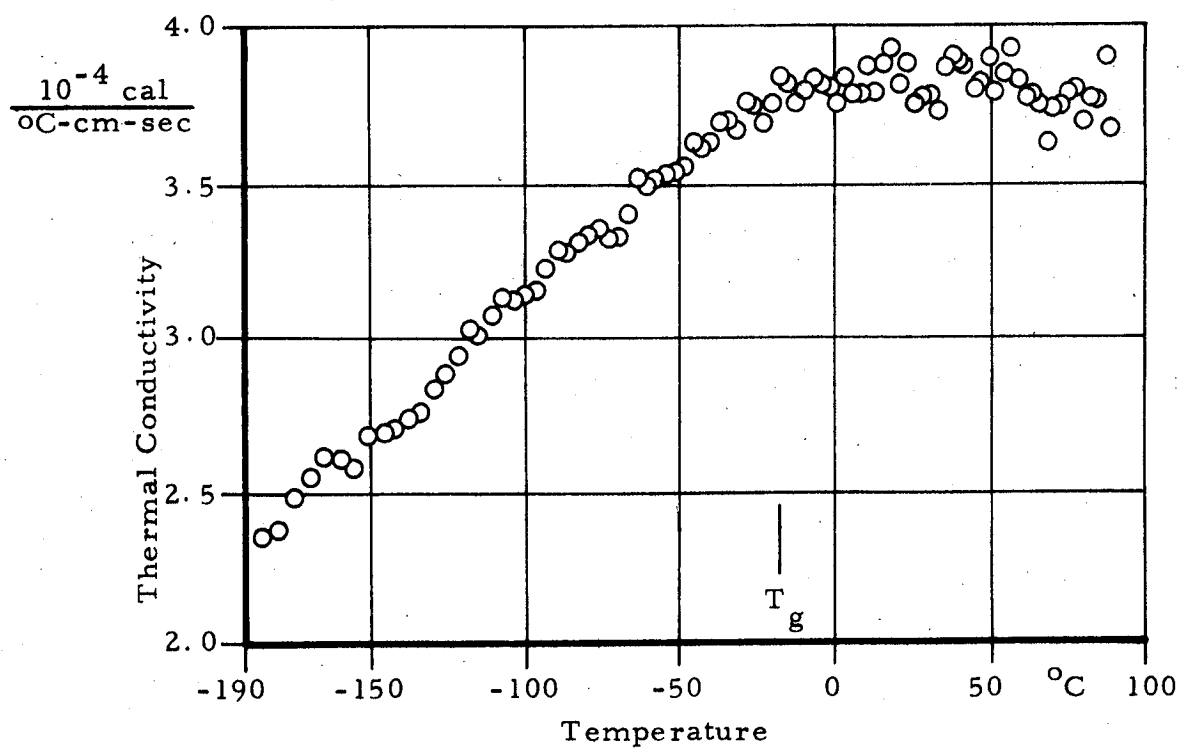


Figure 3. Thermal Conductivity of Natural Rubber
(Ref. 4)



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

transfer from the chain to chain coupling probably is due to the formation of pseudo crystalline regions of donor and acceptor molecules in a stacked graphitic-like structure. Then pseudo crystalline regions in an amorphous matrix give rise to increased phonon and possible electronic flow. Generally, the thermal conductivity of a material may be written as:

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

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

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

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

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

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

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

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)

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

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.

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

Section 3

EXPERIMENTAL

3.1 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 to 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,

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

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

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

gives, for a flat slab, the heat flow as

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

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

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

and has the dimensions cal/(sec)(cm)(°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:

$$k_s = \frac{k_{Cu} t_{Cu} x_s}{t_s x_{Cu}} \quad (12)$$

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

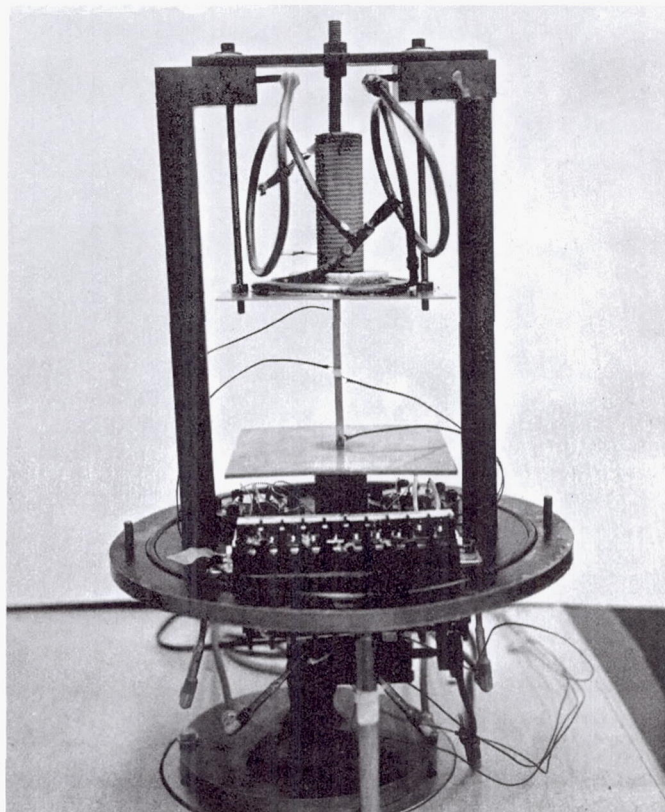
x_{Cu} = distance between thermocouples on lower copper thermode

To ensure good thermal contact between the organic polymer specimen and the copper thermodes, thin foils in indium, 0.005 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.

3.2 ELECTRICAL RESISTIVITY

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

$$\rho = \frac{R \cdot A_e}{L_e} \quad (13)$$



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Figure 5. Thermal Conductivity Apparatus

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.

3.3 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.

3.4 CASTING OF FILMS

Films of the various hydroquinone-phenol-formaldehyde resins were prepared by casting on glass plates covered by aluminum foil. The resins were cured under the following schedule: 120°F — 3 hours, 160°F — 2 hours, and 230°F — 3 hours. The cured films ranged in colors from the typical rose-red of the phenolic-formaldehyde to that of jet-black for the hydroquinone formaldehyde.

3.5 SPECIFIC HEAT

The specific heat of three selected polymers was determined by use of a Perkin Elmer Differential Scanning Colorimeter (DSC-1B) using a comparison technique in which an external standard (sapphire) was used. The DSC was programmed at 20°/min and sensitivity of 4 mcal/sec full scale.

3.6 PELLET PREPARATION

Pellets of the aminoquinone polymers were prepared by pressing at 10,000 psi at a temperature of about 190°C. The press was heated at a rate of about 10°C per minute until 190°C was reached. At this temperature the heating unit was turned off and the die was allowed to slowly cool to 30-40°C. During pressing the material changed from red-brown to blue-black; however, no apparent changes in the infra-red spectra of the material was noted.

3.7 INFRA-RED SPECTRA

All spectra were run on a Perkin-Elmer Model 137 spectrophotometer as films or in KBr disc.

3.8 DYNAMIC MODULUS

The dynamic modulus, E'_{dyn} , of three aminoquinone polymers was evaluated as a function of temperature by use of a vibrating reed technique. Briefly, the vibrating reed apparatus consists of a polymeric cantilever reed which is mounted vertically. The reed is driven into its fundamental frequency of vibration by use of a mechanically linked loudspeaker head driven by a low frequency oscillator. A pin mounted on the free end of the reed generates a sinusoidal signal of varying amplitude as it moves in a linear variable differential transformer. The maximum amplitude of the signal as a function of frequency is taken as the resonance frequency of the polymer. The contribution of the pin may be determined experimentally by observing the resonance frequency of the polymer reed with and without the pin present. The final working equation is:

$$E'_{\text{dyn}} = A \cdot V_r^2 \cdot \rho \quad (14)$$

where E'_{dyn} is the real part of the dynamic modulus, V_r^2 is the squared resonance frequency, ρ is the sample density and A is a constant dependent on the sample's geometry.

Section 4

RESULTS AND DISCUSSION

4.1 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- $^{\circ}\text{C}$ 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 pseudo-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

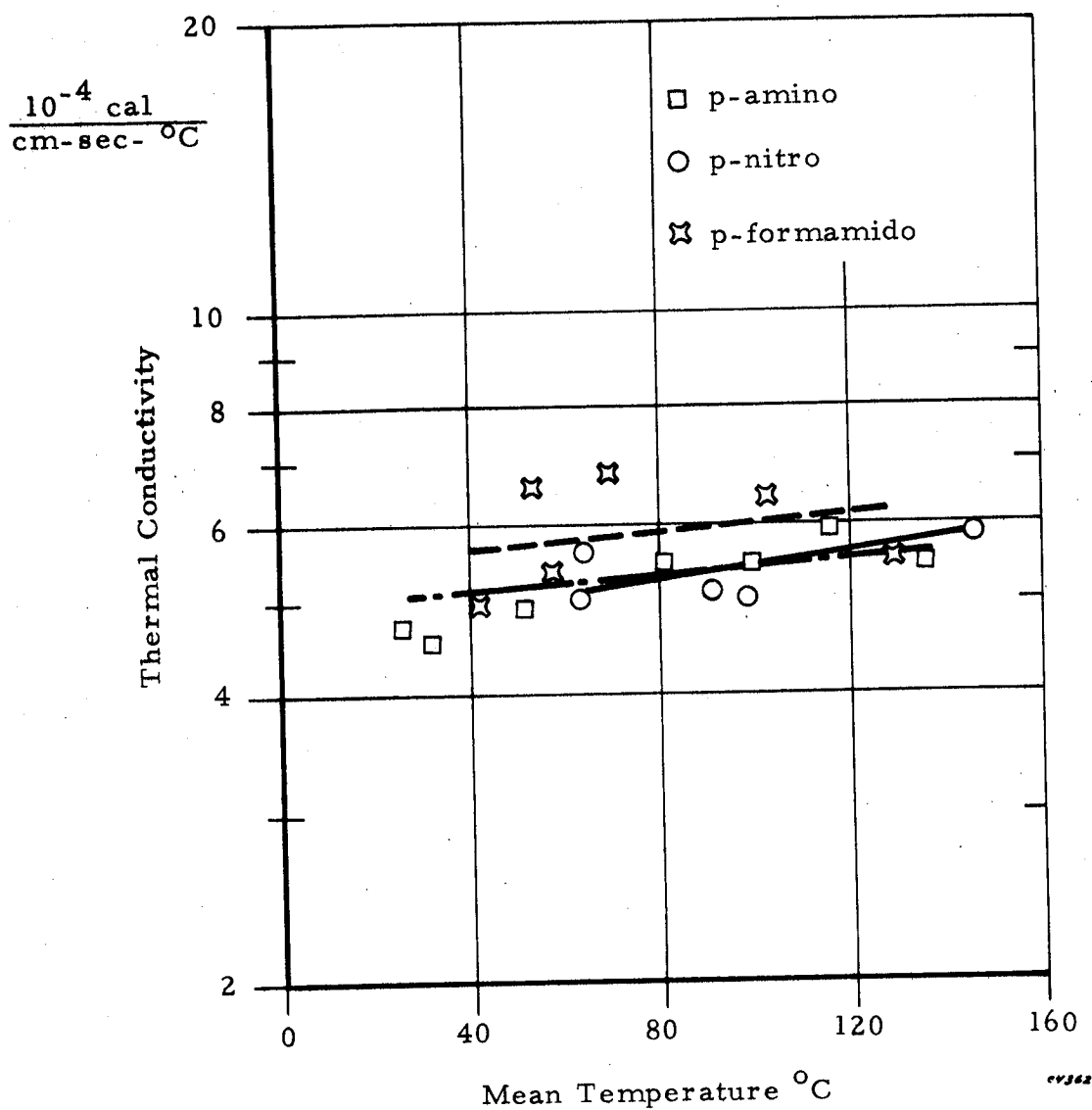


Figure 6. Thermal Conductivity-Temperature Plot of Some Para Substituted Poly(phenylacetylenes)

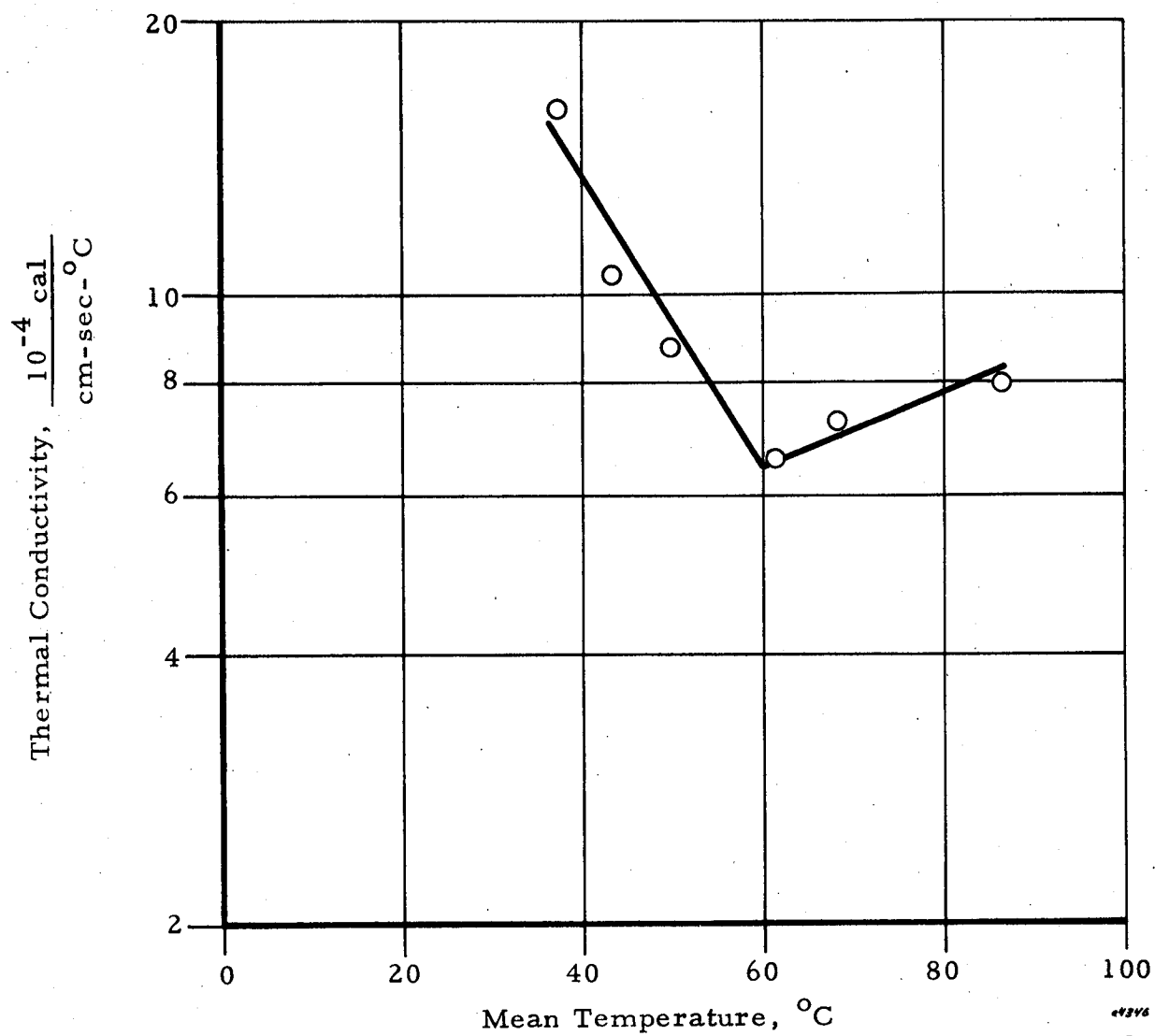


Figure 7. Thermal Conductivity, k , - Temperature Plot of Poly(phenylacetylene), Thermal CuCl_2 Preparation, Cu-In Spacers

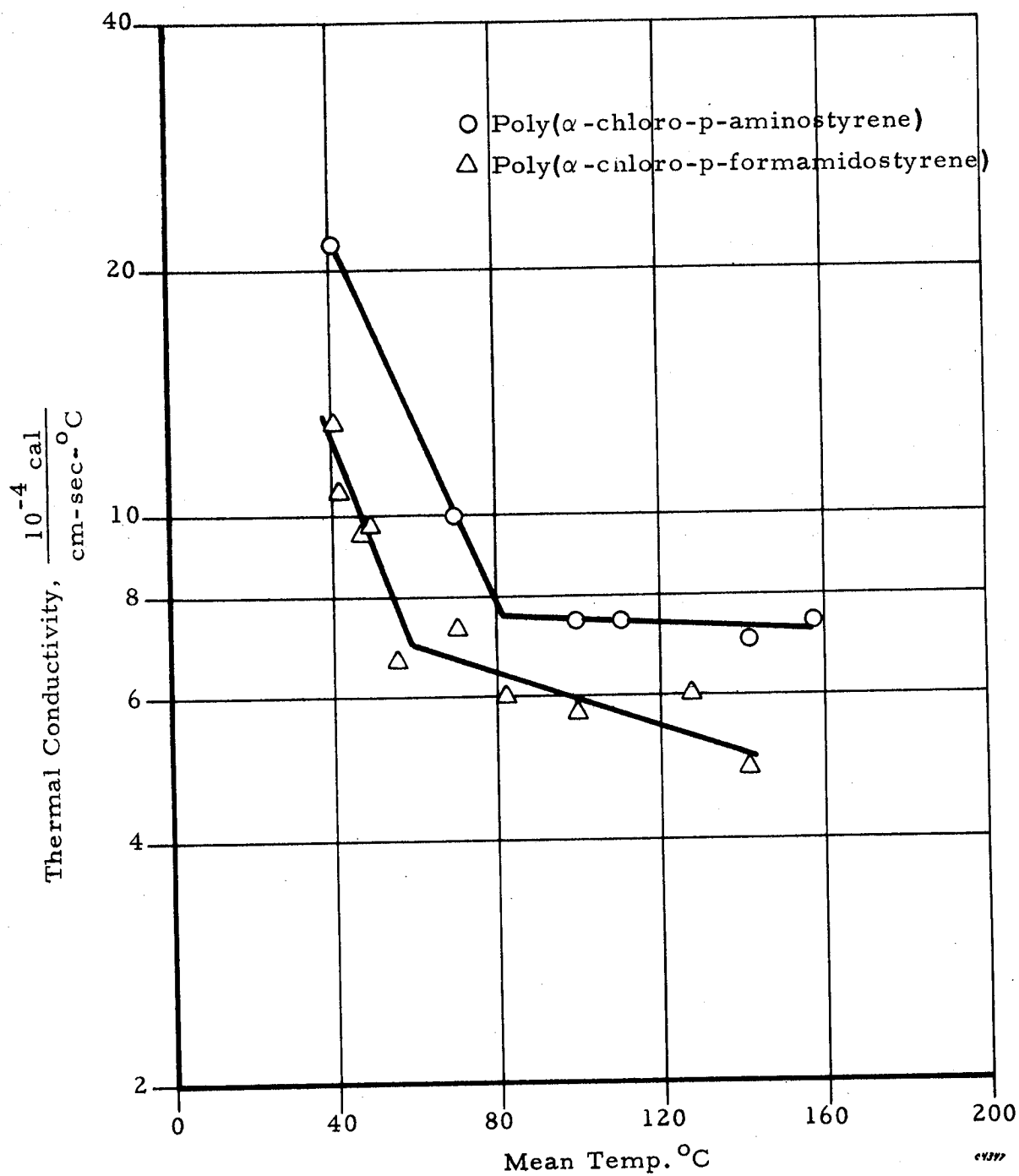


Figure 8. Thermal Conductivity - Temperature Plot of Poly(α -chloro-p-aminostyrene) and Poly(α -chloro-p-formamidostyrene)

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 dehydrohalogenation 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 than the cis; the trans being about 5×10^{-4} cal/cm-sec- $^{\circ}$ C.

4.2 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 mechanism 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-amino-phenylacetylene) 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

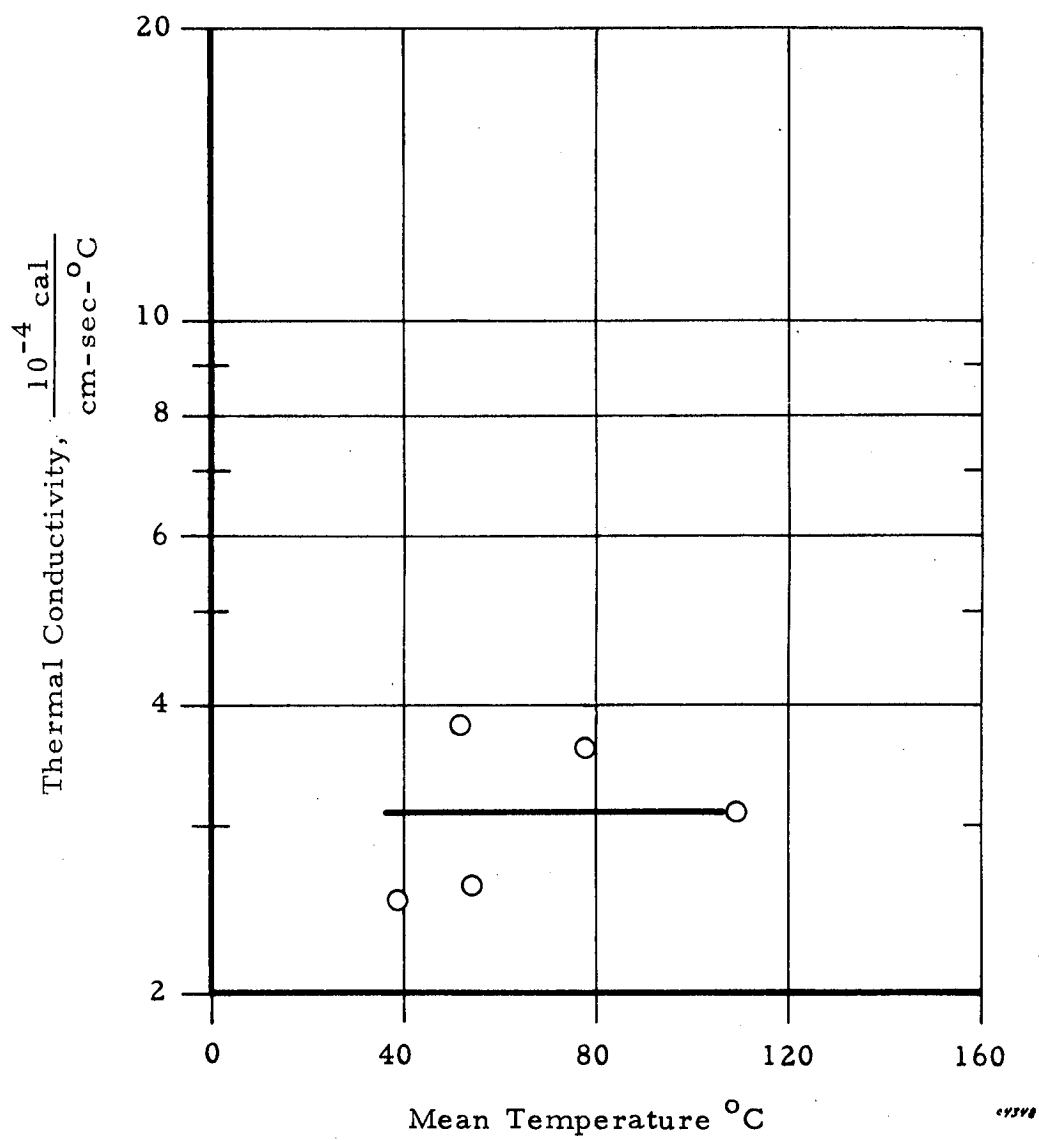


Figure 9. Thermal Conductivity-Temperature Plot of Poly(α -chlorostyrene)

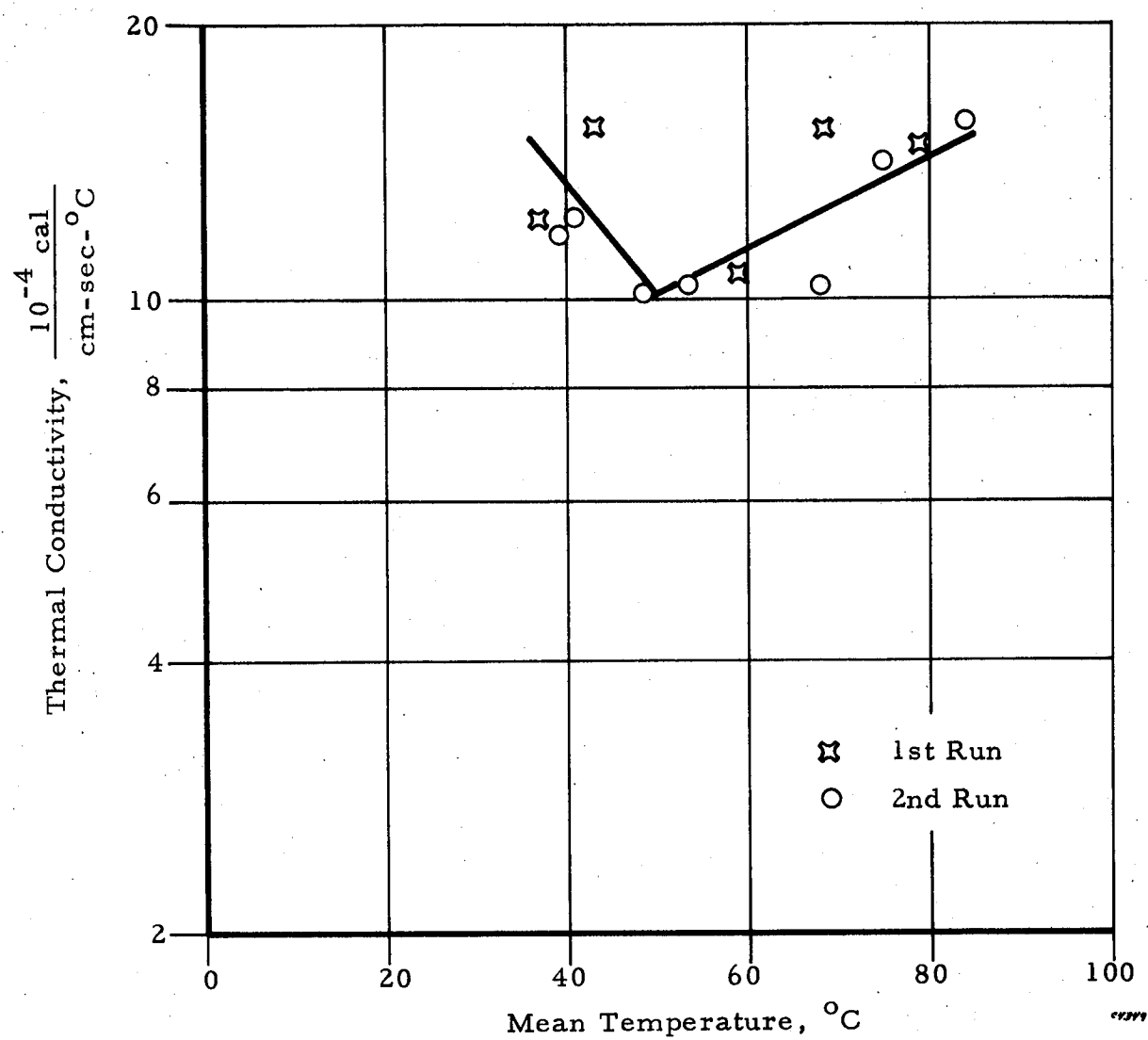


Figure 10. Thermal Conductivity - Temperature Plot of Cis Polyacetylene. Indium Spacers

Mole Ratio of Poly(p-aminophenylacetylene) to Anhydride

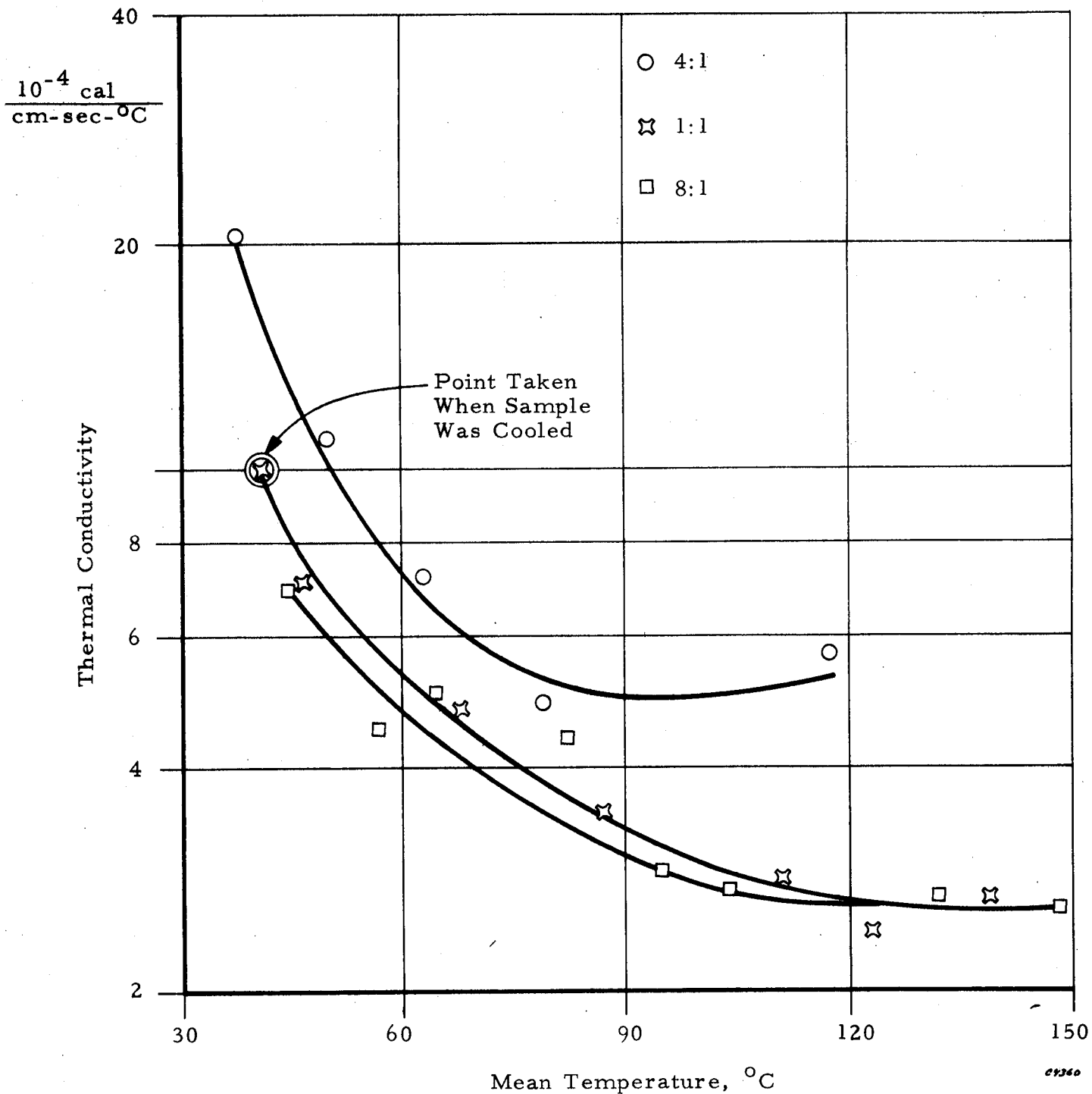


Figure 11. Thermal Conductivity-Temperature Plot of the Reaction Products of PAPA and Pyromellitic Anhydride

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 was 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.10). 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- $^{\circ}$ 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 cross-linked 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.

4.3 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 inter- and 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-

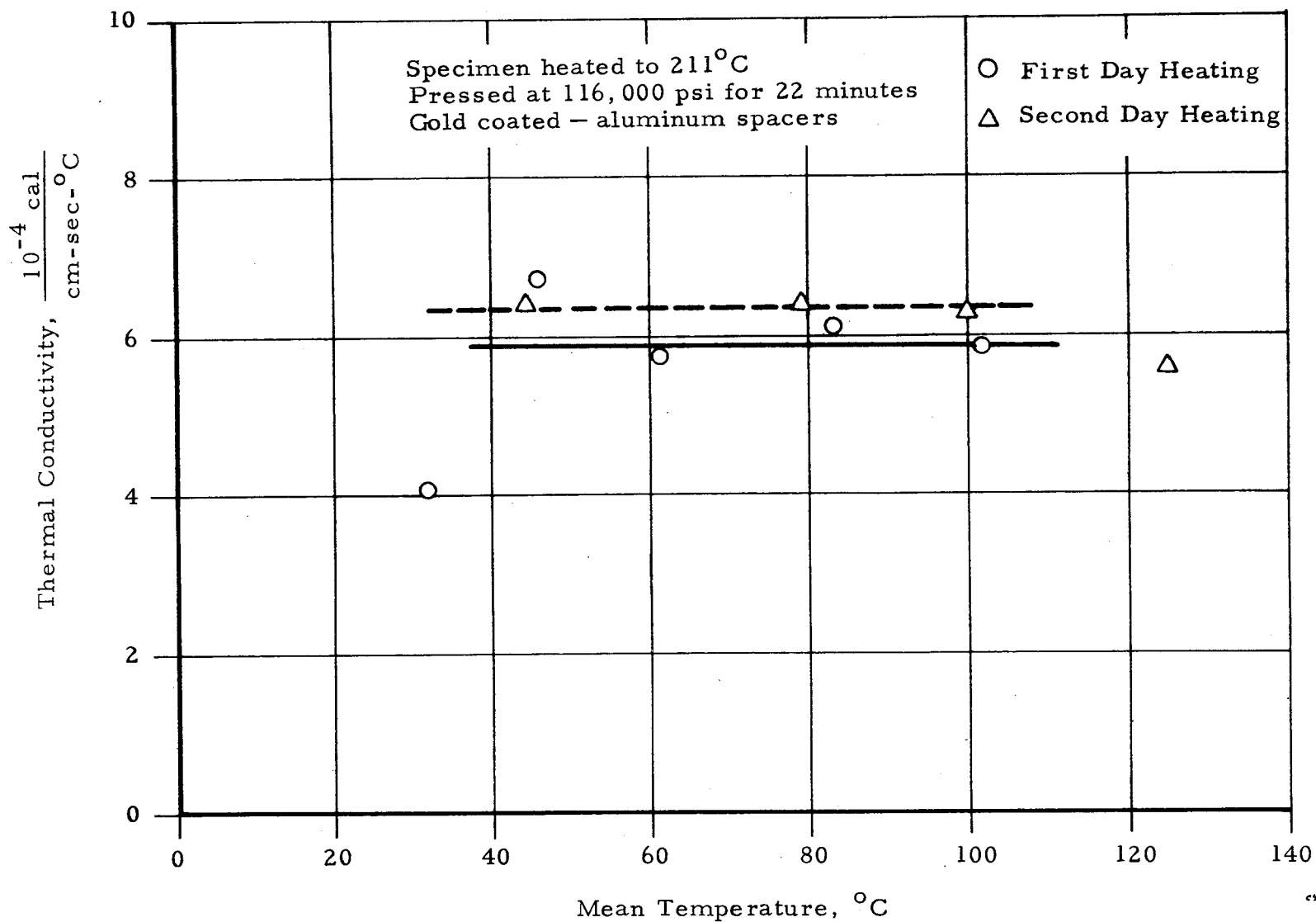


Figure 12. 100% TDI-Crosslinked Poly(p-aminophenylacetylene) (22 Minute Pressing)

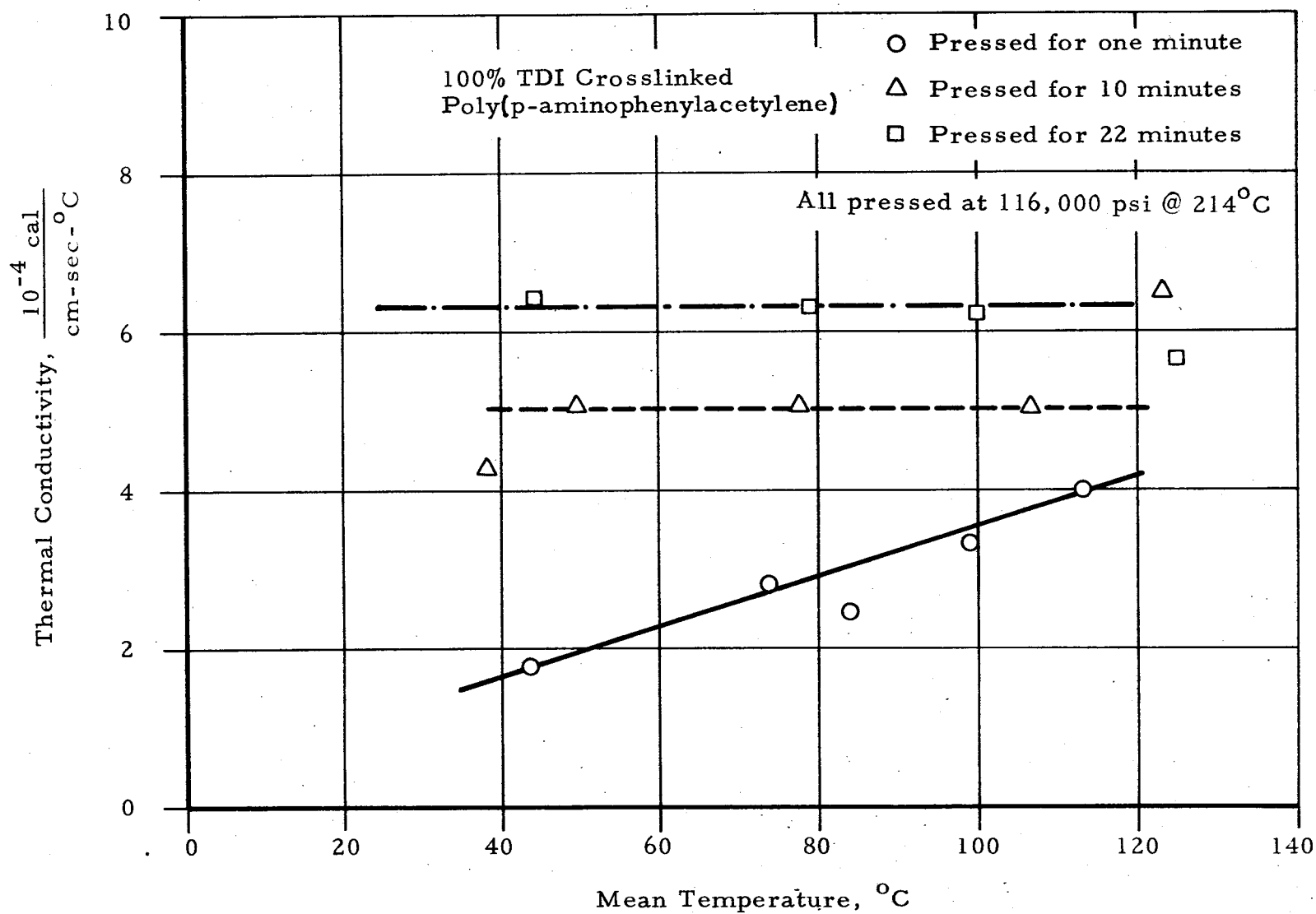


Figure 13. Comparison Plot of Effect of Pressing Time on Thermal Conductivity

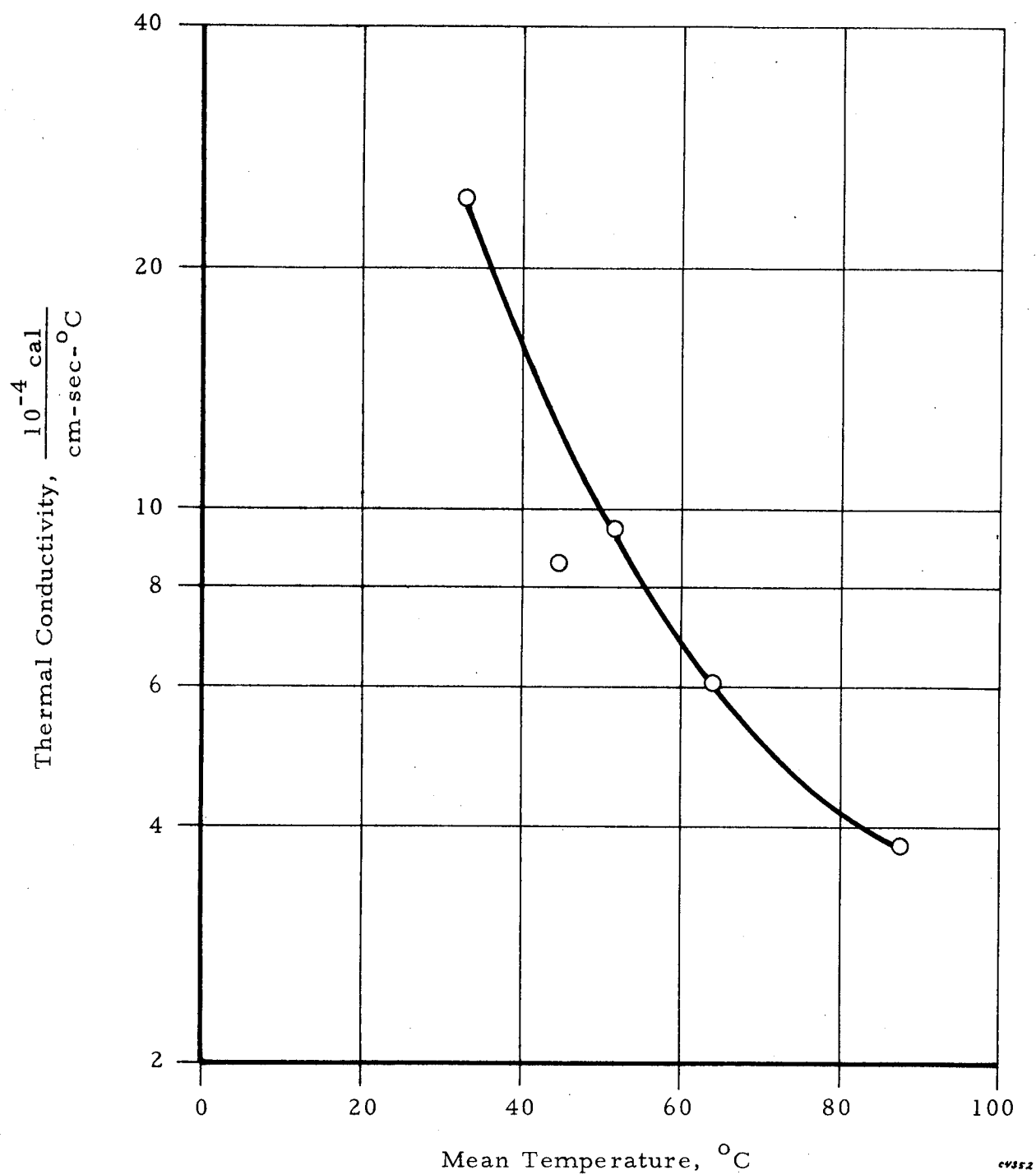


Figure 14. Thermal Conductivity – Temperature Plot of the Charge Transfer Complex of Poly(p-aminophenylacetylene) and Pyromellitic Dianhydride Prepared in CH_2Cl_2

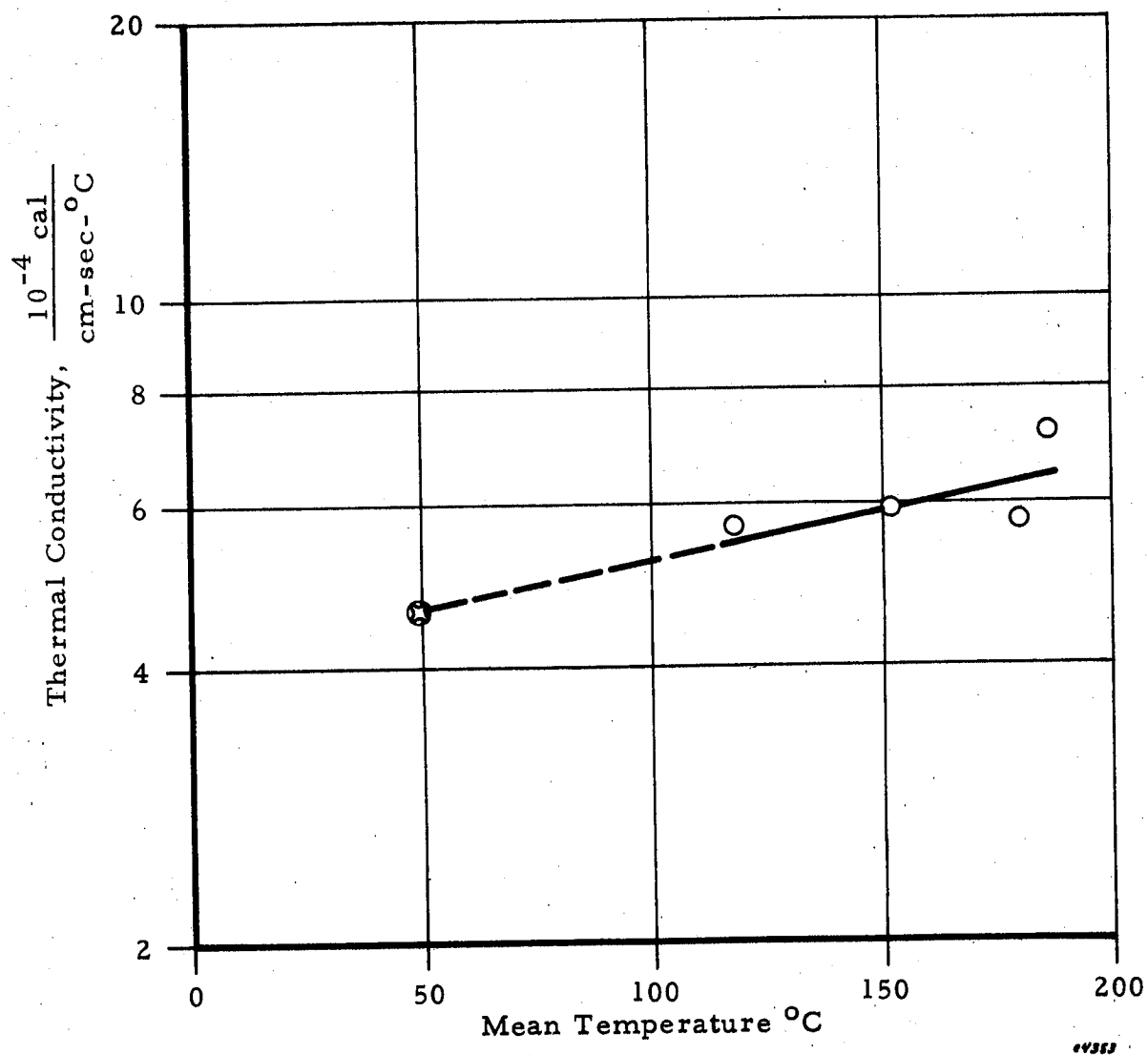


Figure 15. Thermal Conductivity – Temperature Plot of the Reaction Product from Poly(p-aminophenyl-acetylene) and Chloranil, 4:1 Mole Ratio

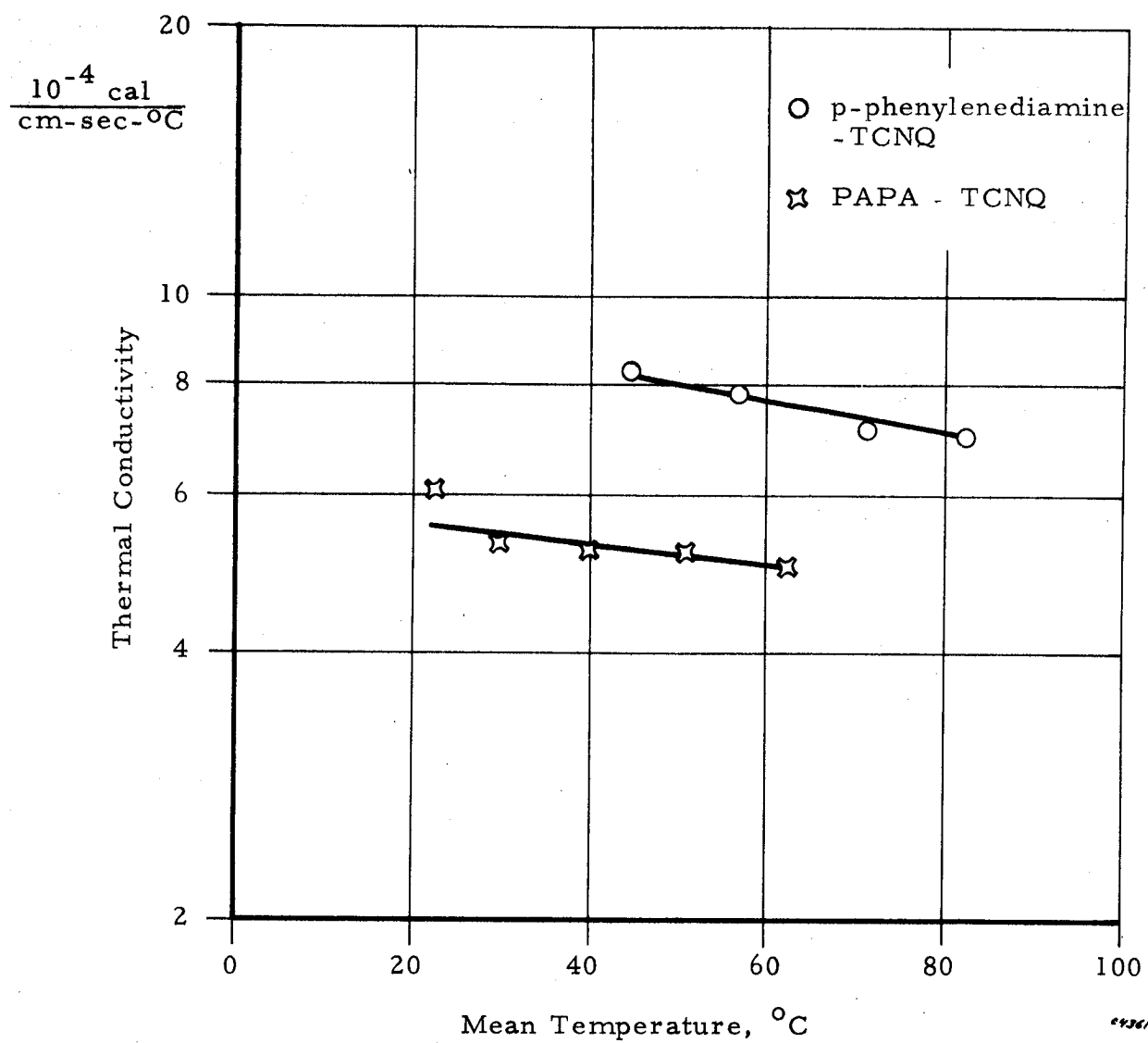


Figure 16. Thermal Conductivity-Temperature Plot of the Charge Transfer Complex from p-phenylenediamine and Tetracyanoquinodimethane and PAPA - TCNQ

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- $^{\circ}$ C over the temperature range studied. In addition, the curve decreases initially, with temperature, up to about 65 $^{\circ}$ 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.

4.4 ELECTRON TRANSFER POLYMERS

A new series of charge transfer polymers was 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- $^{\circ}$ C range) as a function of temperature. The number of (CH₂) groups in the alkanediamine controls the flexibility of the polymer.

The reaction sequence, as shown in Figure 18, 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, and may quite readily form chelates with various metal ions.

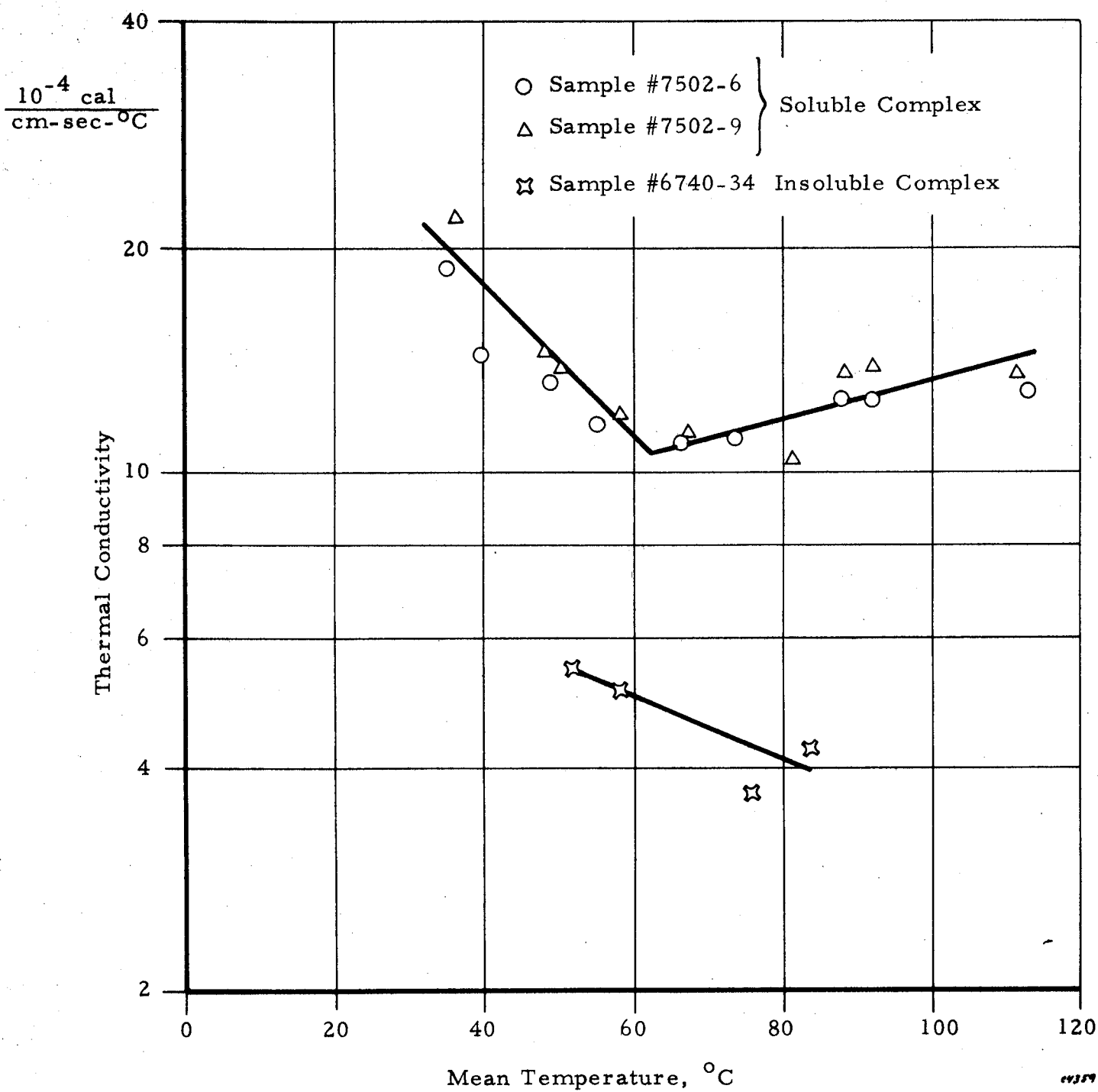
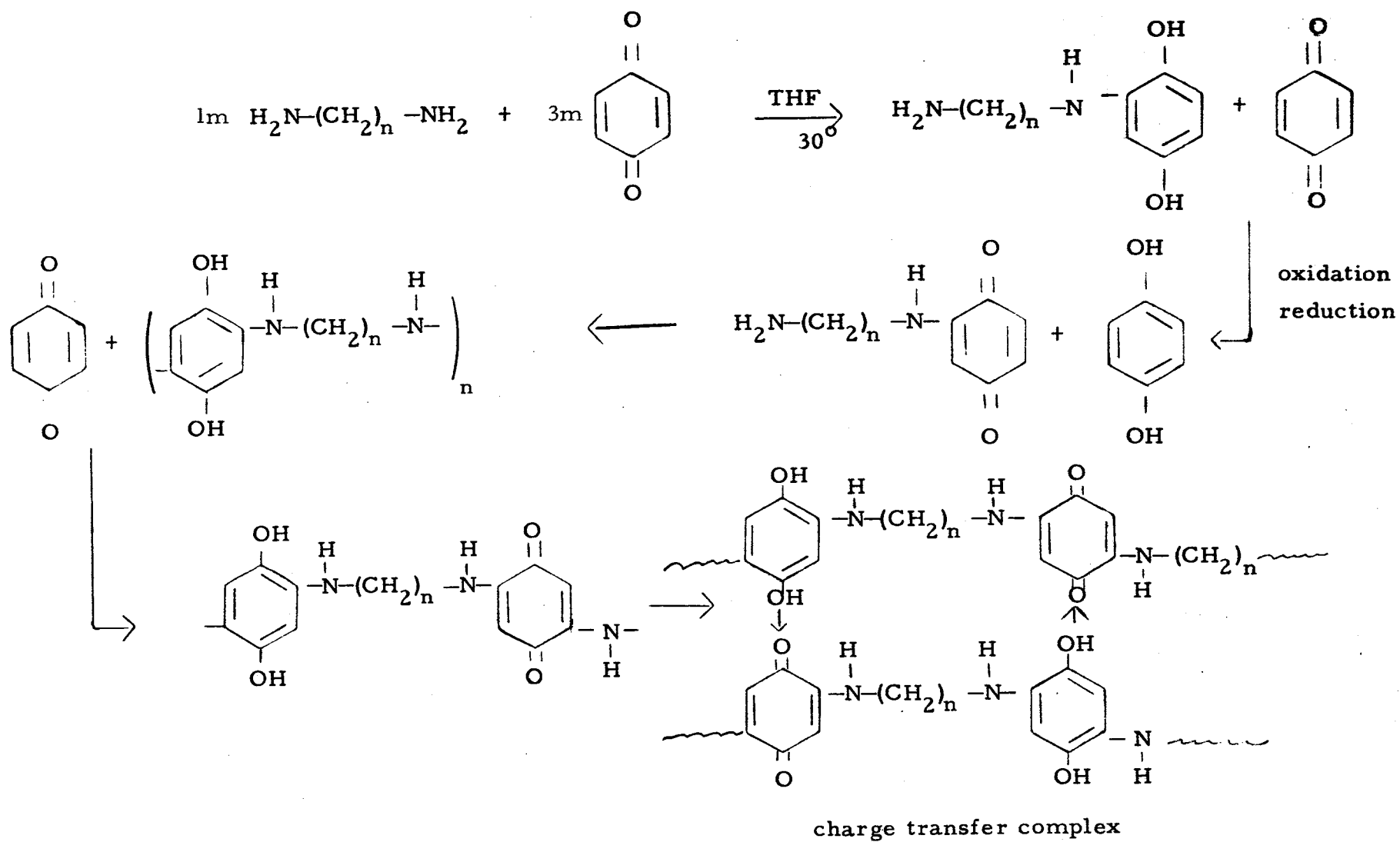


Figure 17. Thermal Conductivity – Temperature Plot of Chloranil and Poly(p-aminophenylacetylene) Complex

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)



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Figure 18. Proposed Reaction Sequence of Benzoquinone With α, ω Alkanediamines

The thermal conductivity-temperature (k - T) behaviors of the polymers prepared from benzoquinone and the α, ω -alkanediamine series are shown in Figures 19 through 24. In all cases, except for the polymer prepared from the 1,9-nonanediamine (Figure 22), the (k - T) curves at low temperatures are quite high followed by a rapid decrease of k with increasing temperature. Generally, the polymers attain a constant value of k as a function of temperature except for the 1,9-nonanediamine which has a constant thermal conductivity value of about 1.1×10^{-3} cal/cm-sec- $^{\circ}\text{C}$, throughout the temperature range studied. In addition the 1,6-hexanediamine polymer has a very high initial k value of about 5.0×10^{-3} cal/cm-sec- $^{\circ}\text{C}$, which gradually decreases as a function of temperature until the thermal conductivity is reduced one order of magnitude. The constant value of k as a function of T at higher temperatures is probably due to the influence of the quinhydrone complex whose (k - t) curve is shown in Figure 22. The similarities of the (k - T) curves of quinhydrone and the aminoquinone polymers indicates those polymers which appear to possess the necessary freedom of main chain rotation, to allow alignment of donor and acceptor groups for the formation of the quinhydrone complex. It appears that the optimum number of methylenic groups in the α, ω -diamines required to provide maximum thermal conductivity of the polymer, is from 7 to 11 as evidenced by data shown in Figure 25. In addition, the polymers prepared from the odd numbered α, ω -diamines display increased thermal conductivity as compared to neighboring even-numbered diamines. Apparently, a certain degree of main chain packing is required to promote maximum inter and intra molecular complex formation; such a packing arrangement is enhanced by use of odd-numbered diamines containing at least 5 methylenic groups.

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 at 10,000 psi the polymers changed to blue-black. See Table II.

The polymers displaying the best overall (k - T) results were prepared from a mixture of 1,7 - 1,10 and 1,8 - 1,12 diamines (see Figures 23 and 24). At higher temperatures, the thermal conductivity values for these two polymers remain much greater than 1.5×10^{-3} cal/cm-sec- $^{\circ}\text{C}$; and at lower temperatures the k values increase quite substantially. The flexibility of the polymers increases rapidly as the number of (CH_2) groups increase from 2 to 12.

Figure 26 depicts two typical infra-red spectra for this class of polymer. The spectra were prepared from the reaction products of (1) benzoquinone and 1,11-undecanediamine, and (2) benzoquinone and 1,7-hexanediamine. The assignments of absorption bands to definite groups is somewhat precarious in that extensive overlapping occurs from the sec amine, amine substituted quinone, amine substituted hydroquinone, and quinhydrone groups. A major new absorption band at 1590 cm^{-1} has been assigned to the amine substituted quinone. This strong band is present in each polymer prepared in the series and represents a carbonyl frequency shift of about 70 cm^{-1} due

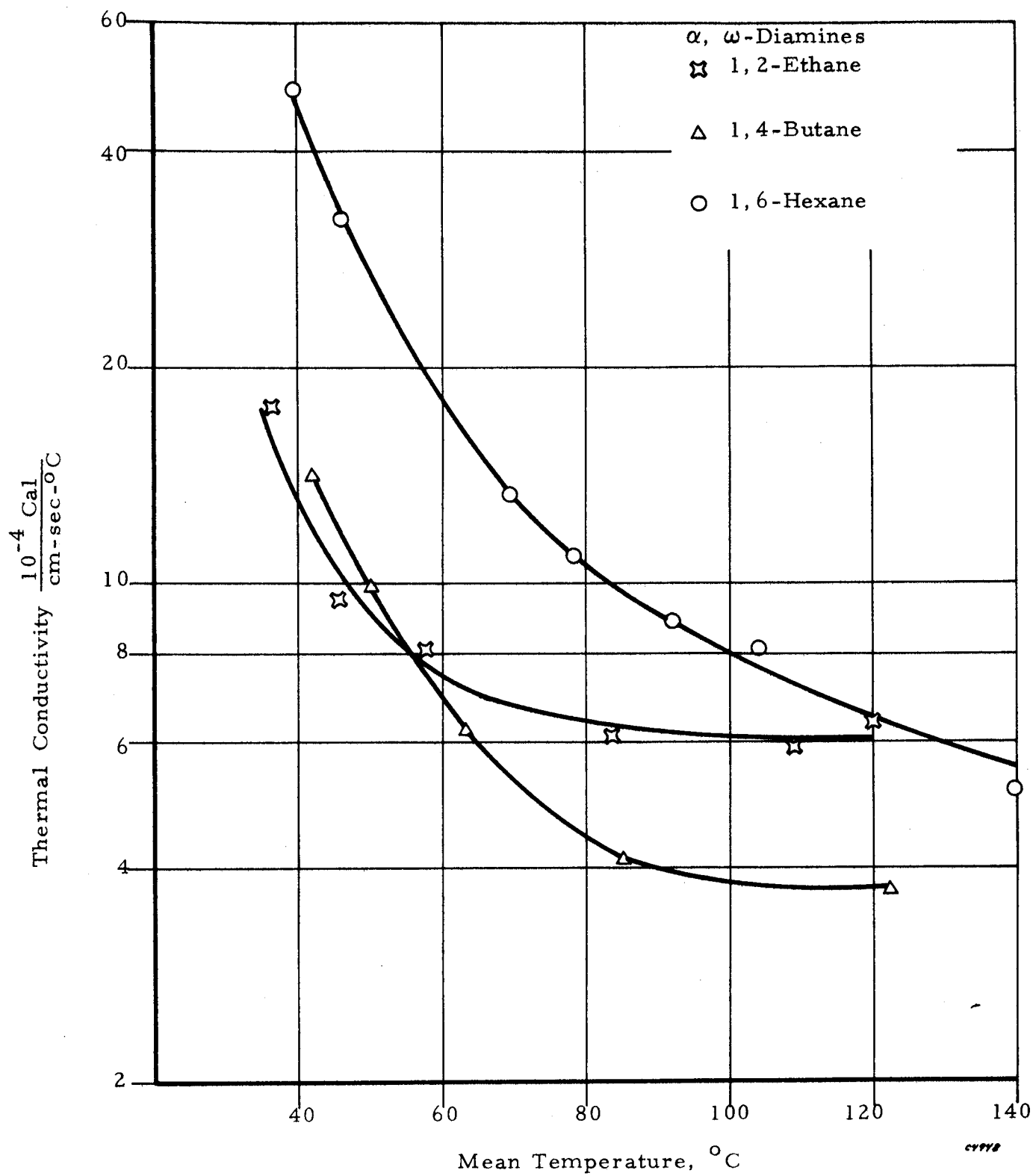


Figure 19. Thermal Conductivity - Temperature Plot of Polyaminoquinones

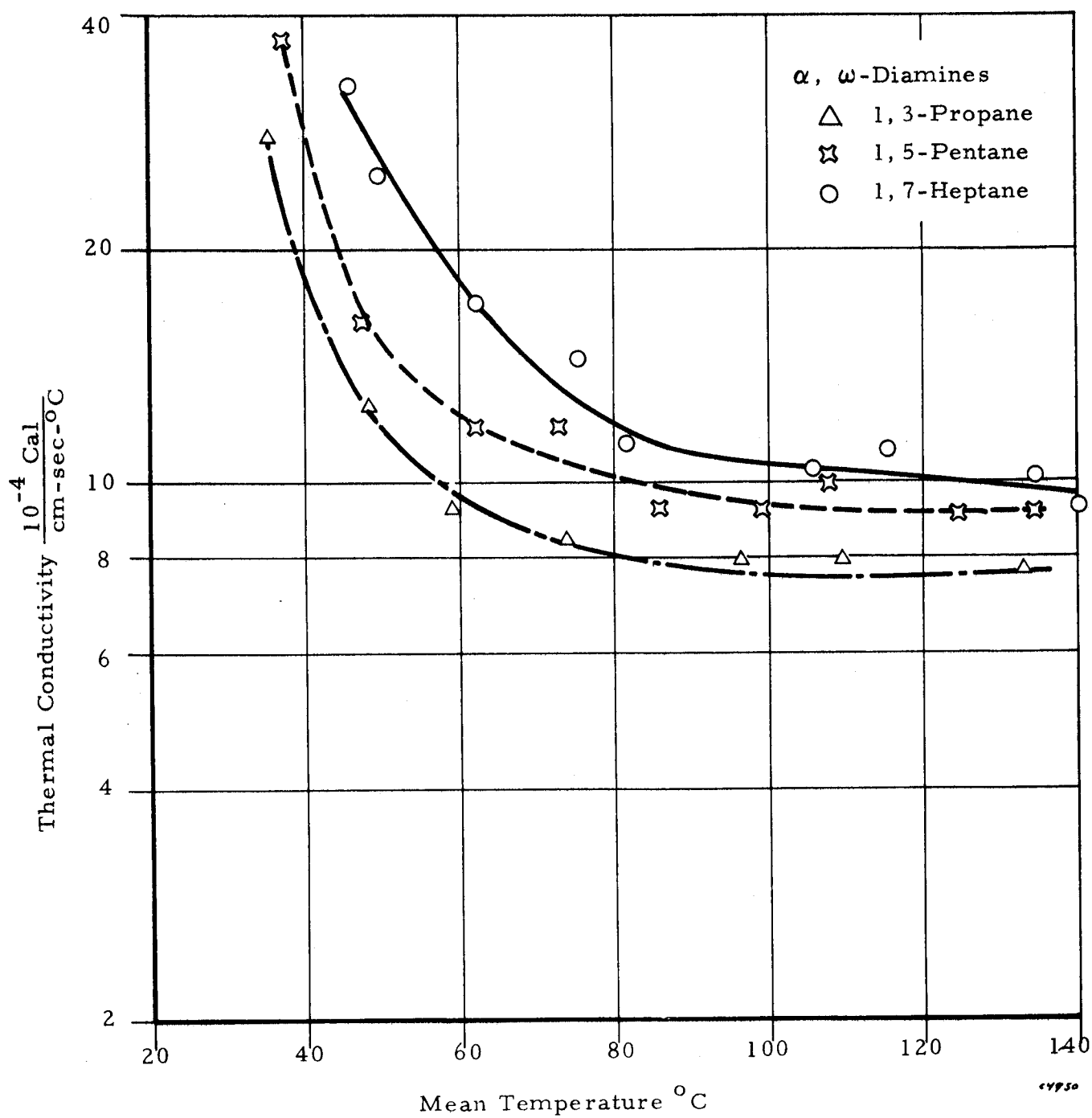


Figure 20. Thermal Conductivity - Temperature Plot of Polyaminoquinones

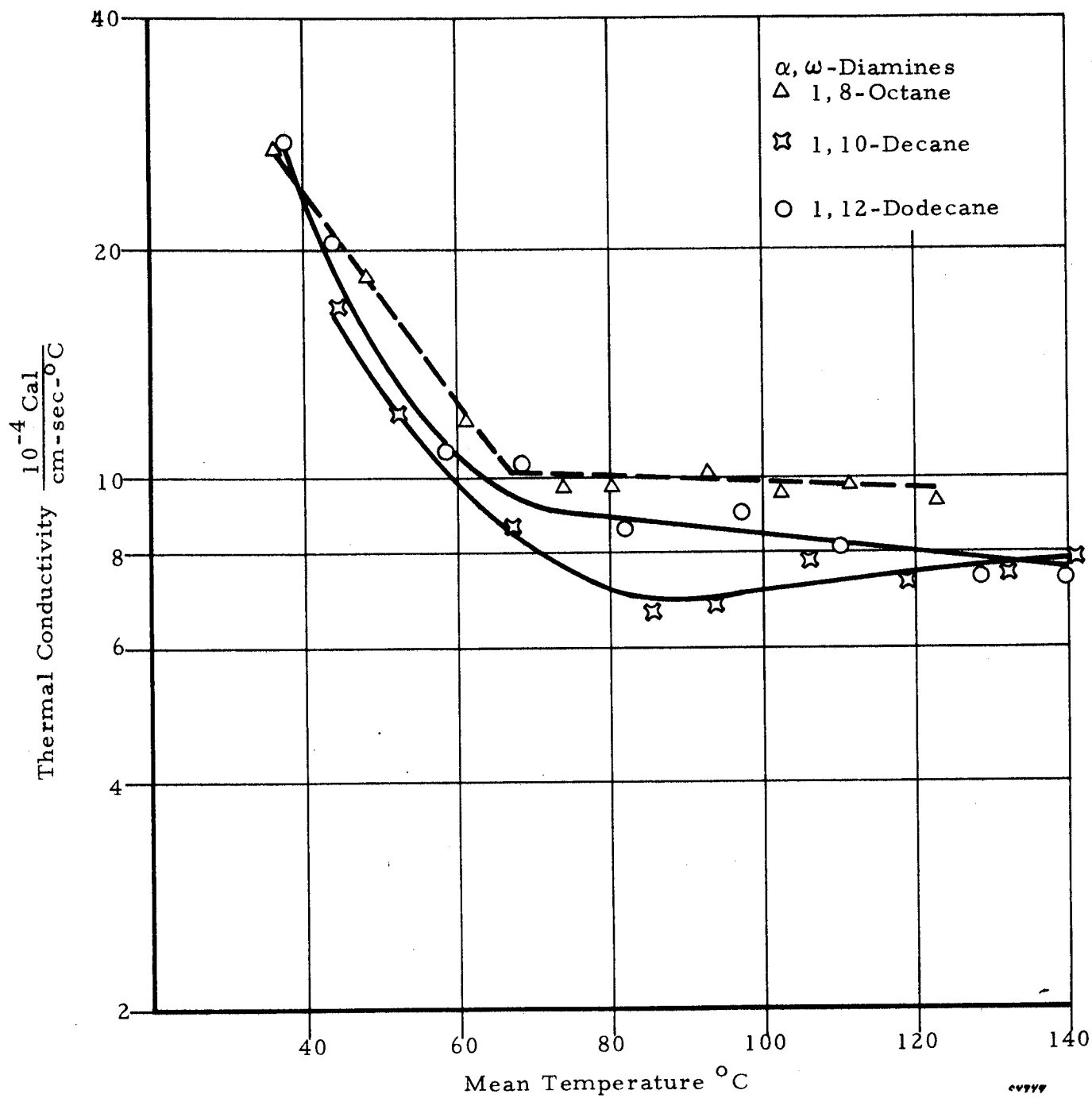


Figure 21. Thermal Conductivity - Temperature Plot of Polyaminoquinones

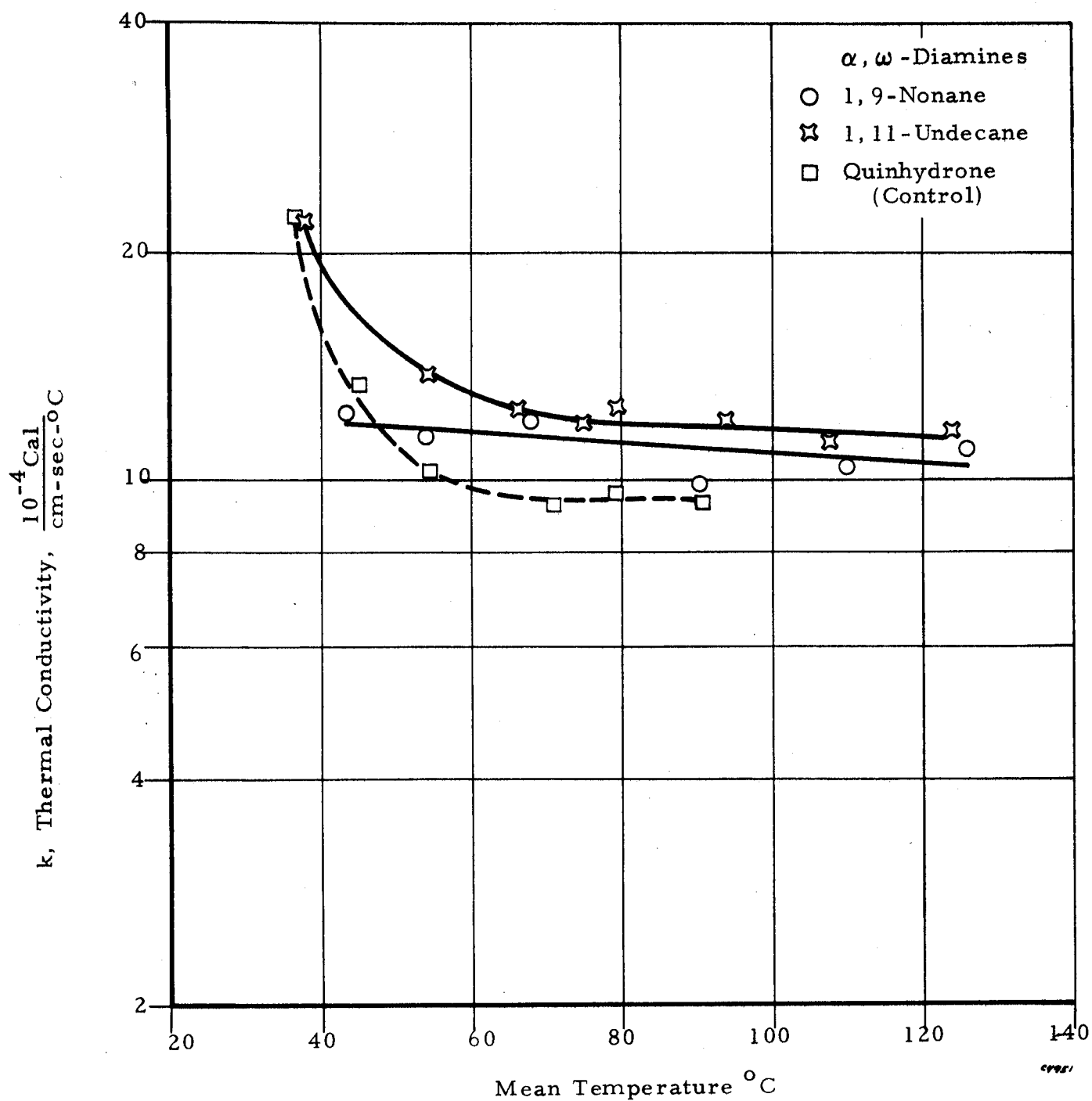


Figure 22. Thermal Conductivity - Temperature Plot of Polyaminoquinones

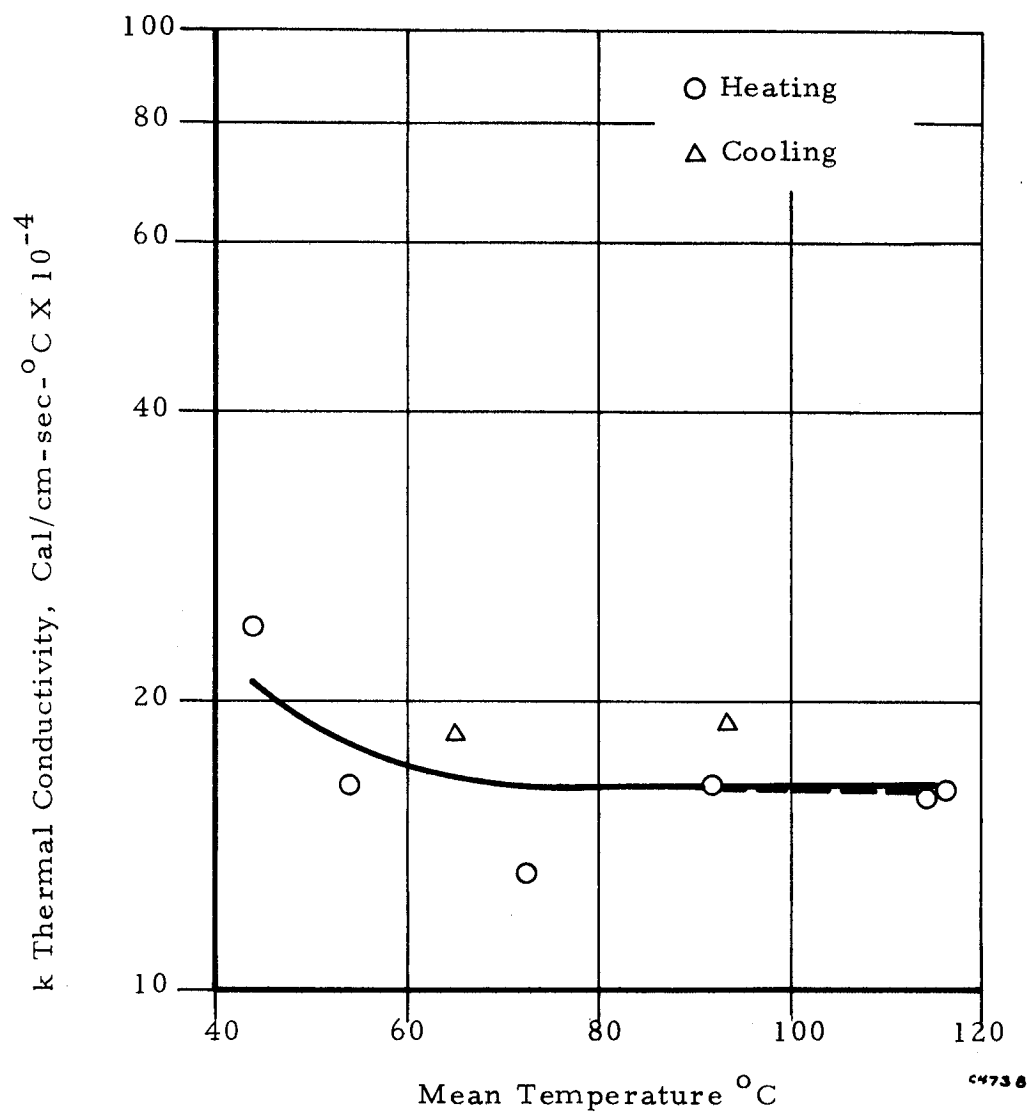


Figure 23. Thermal Conductivity - Temperature Plot of 1,7-Heptane Diamine and 1,10-Decanediamine and p-Benzoquinone

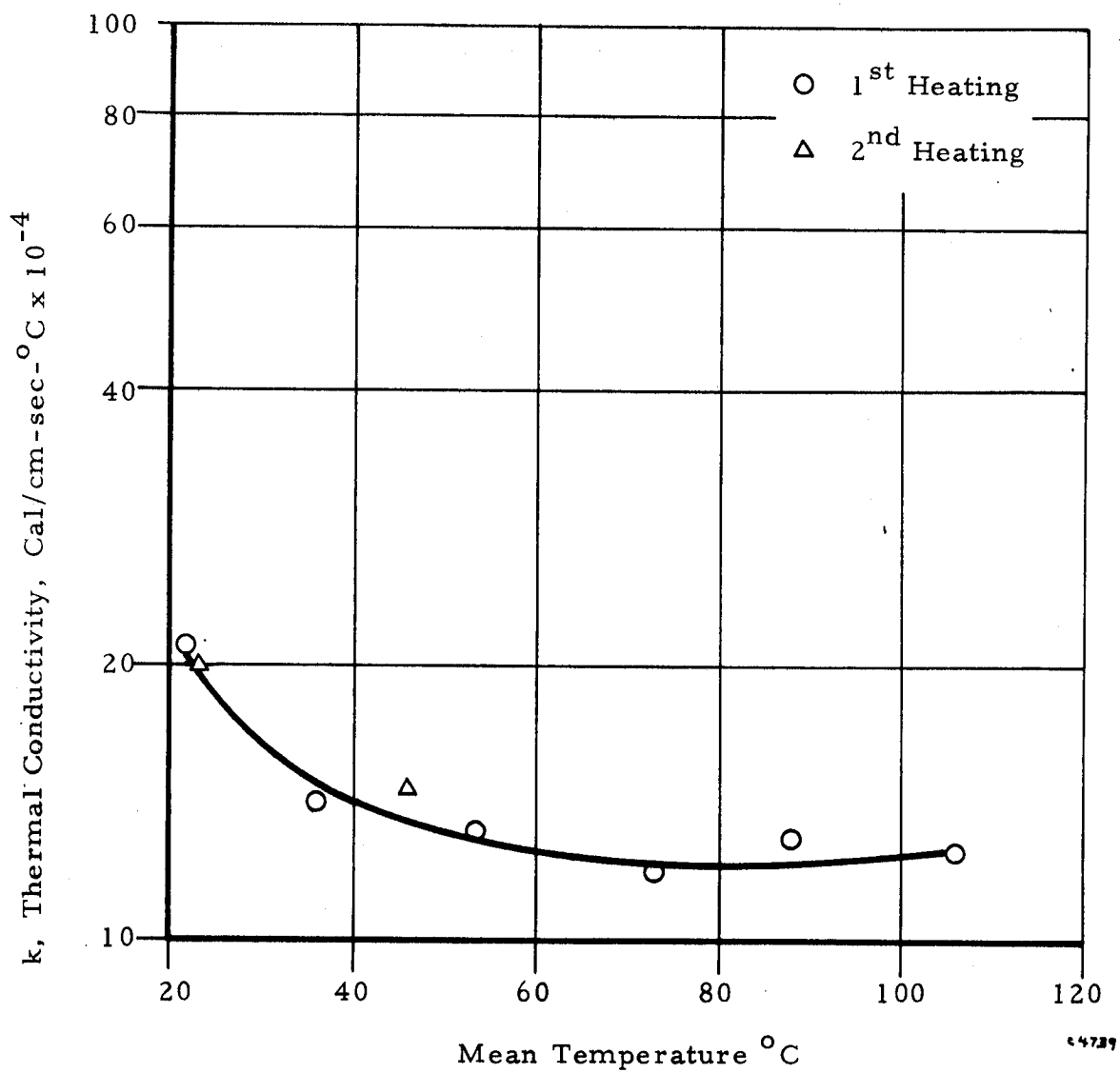


Figure 24. Thermal Conductivity - Temperature Plot of 1,6-Hexanediamine and 1,12-Dodecanediamine and p-Benzoquinone

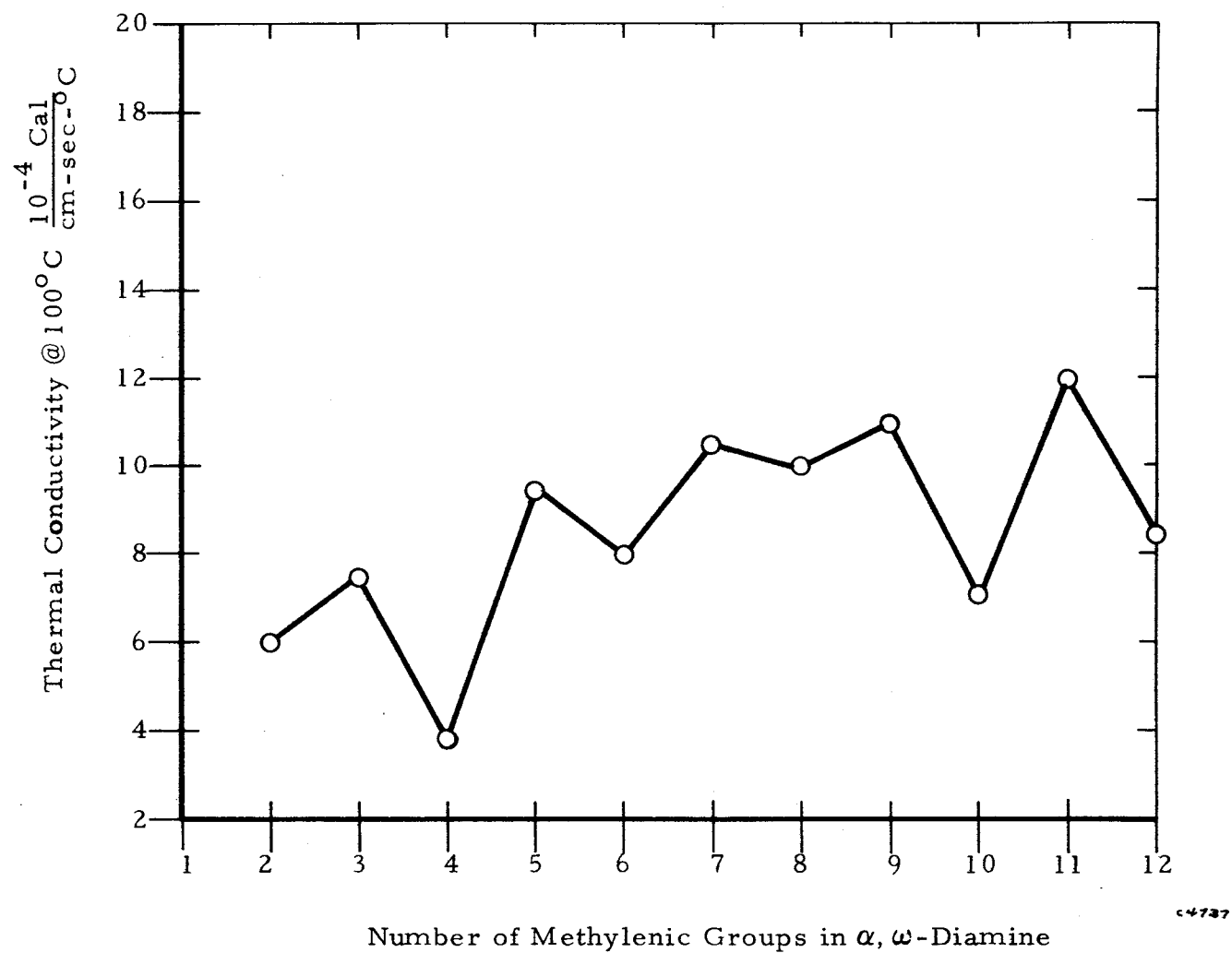


Figure 25. Thermal Conductivity as a Function of Methylenic Groups in the α, ω -Diamines

TABLE II

REACTION CONDITIONS AND PROPERTIES OF SOME POLY(ALKANE DIAMINOQUINONES)

Diamine	Solvent	Atmosphere	Temp.	Mole Ratio Amine/ Benzoquinone	Pressed Disc	Specific Heat Cal/g-°C (120°C)	Fisher-Johns Melting Point Apparatus		Density g/cm ³	Dynamic Modulus E dynes/cm ² (25°C)
							Color Change - Temp	Melting Point		
1,2-Ethane	THF	N ₂	30°	1:3	Hard & brittle	0.430	Red Brown → Dark Brown 230°	> 300°	1.45	5.0 × 10 ¹⁰
1,3-Propane	↓	↓	↓	↓	Hard & brittle		Red Brown → Dark Brown 243°		1.30	
1,4-Butane	↓	↓	↓	↓	Hard & brittle		Red Brown → Dark Brown 250°		1.308	
1,5-Pentane	↓	↓	↓	↓	Hard & tough		Red Brown → Dark Brown 252°		1.232	
1,6-Hexane	↓	↓	↓	↓	Semi flexible		Red Brown → Dark Brown 276°		1.235	
1,7-Heptane	↓	↓	↓	↓	Flexible & tough	0.447	Red Brown → Brown 270°	↓	1.200	
1,8-Octane	↓	↓	↓	↓	Flexible & tough		Red Brown → Brown 250°		1.183	
1,9-Nonane	↓	↓	↓	↓	Flexible & tough		Red Brown → Brown 235°		1.113	
1,10-Decane	↓	↓	↓	↓	Flexible & tough		Red Brown → Brown 200°		1.177	
1,11-Undecane	↓	↓	↓	↓	Flexible & tough		Red Brown → Brown 232°		1.065	
1,12-Dodecane	↓	↓	↓	↓	Flexible & tough	0.432	Orange Brown → Brown 190°		1.091	
Mixtures	↓	↓	↓	↓						
1,7 + 1,10	↓	↓	↓	↓	Flexible & tough				1.141	2.1 × 10 ¹⁰
1,8 + 1,12	↓	↓	↓	↓	Flexible & tough			↓	1.142	2.13 × 10 ¹⁰

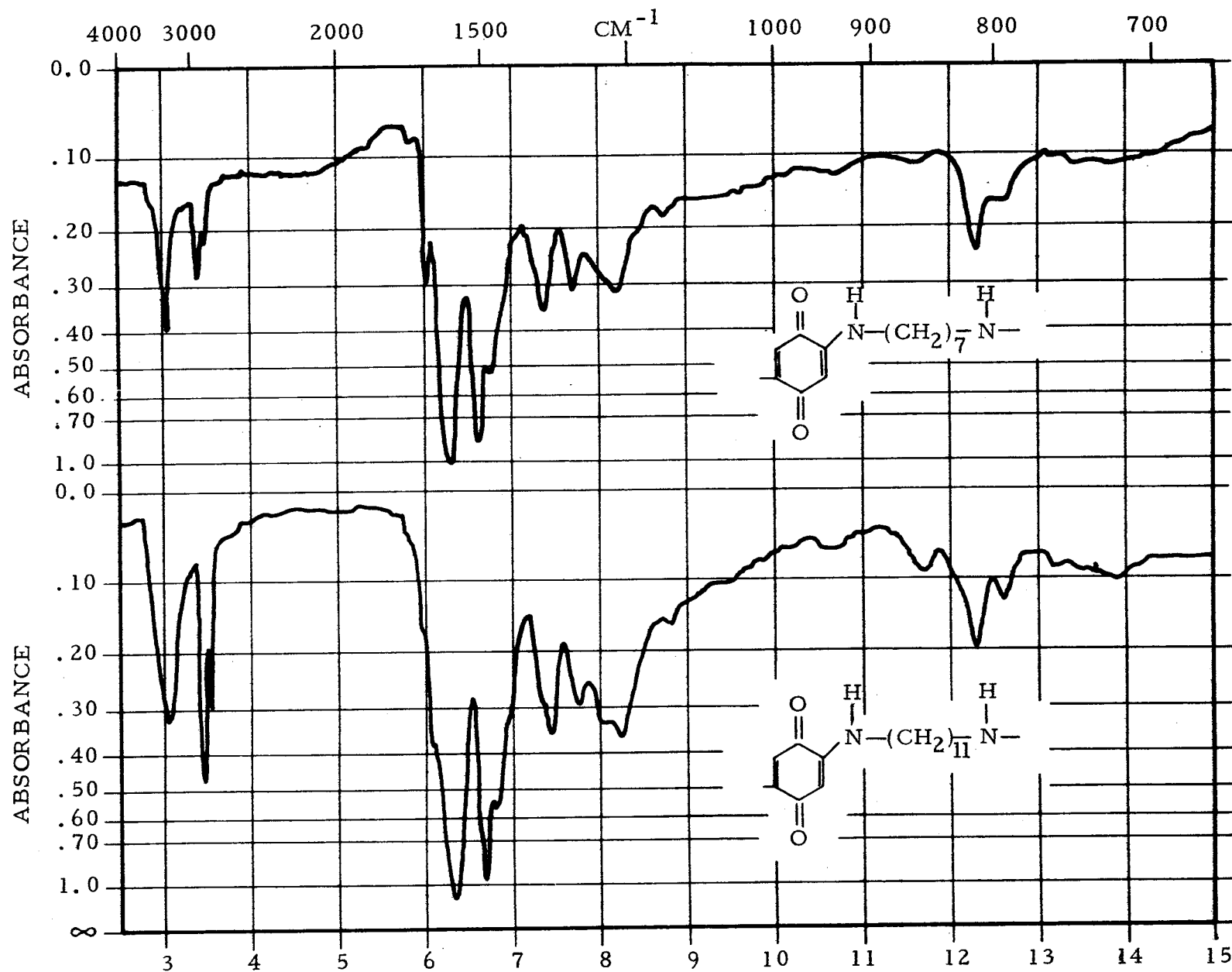


Figure 26. Infrared Spectra of Some Polyaminoquinones

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to the amine-carbonyl interaction. Additional, tentative, absorption band assignments are given in Table III.

Figure 27 depicts the relative modulus/temperature curves of the polymer prepared from the mixed α , ω -diamines and benzoquinone. The mixed amines were 1, 7 and 1, 10. The relative modulus is given as frequency squared (V^2) and is adequate to describe any changes in the polymer due to crosslinking, scissioning or phase transitions. Actually, the absolute dynamic modulus is calculated using Equation 7. The equation is then simplified by lumping the geometry factors together arriving at

$$E'_{\text{dyn}} = A \cdot V^2 \quad (15)$$

Inspection of Figure 27 indicates a glass transition, T_g , occurring at about 150°C followed by extensive crosslinking at temperatures greater than 180°C. This phenomenon is identical to that reported by Jenkins and Kane (Ref. 11) in their study of the cure behavior of an epoxy system, in which extensive cure occurred at temperatures above T_g . This behavior was attributed to main chain rotation thus allowing intimate positioning of reactive functional groups. The second heating curve of Figure 27 indicates the extent of crosslinking and the displacement of the T_g at increased temperatures.

The thermal conductivity of a hydroquinone-formaldehyde polymer pressed from powder under temperature and pressure was found to yield a value of about 1.5×10^{-3} cal/cm-sec-°C over a moderate temperature range. See Figure 32. Recent synthesis work in the area of phenol-hydroquinone and formaldehyde has produced resins of comparable conductivities (about 1.1×10^{-3} cal/cm-sec-°C) with film properties ranging from fair to excellent. In addition, it appears that the concept of enhanced thermal conductivity by main chain coupling by inter and intra molecular charge transfer complexing has been further substantiated by use of a phenol-hydroquinone-formaldehyde system. This system exhibits increased thermal conductivity because both phenol and hydroquinone form strong charge transfer complexes with benzoquinone which, when polymerized, will allow increased phonon transfer across the main chains of the polymer. Although benzoquinone is not present initially in the resin preparation, it is easily generated "in-situ" by the oxidation of substituted hydroquinone. Figures 28-32 depict the thermal conductivity response as a function of temperature for a series of phenol-hydroquinone-formaldehyde resins prepared in this laboratory. Notice that generally the k - T response is linear whereas previous results obtained with the aminoquinone polymers indicated a strong k dependency on temperature.

The probable structure of the phenol-hydroquinone-formaldehyde resin when cured is depicted in Figure 33.

Figure 34 depicts the thermal conductivity at 80°C as a function of mole fractions of phenol and hydroquinone reacted with formaldehyde. It is interesting to note that as the mole fraction of hydroquinone increases a corresponding increase in thermal conductivity occurs. It is suggested that this

TABLE III
INFRA-RED ASSIGNMENTS

Absorption (cm^{-1})	Functional Group(s)
3280	> N-H and hydroquinone
2936, 2860	> CH_2
1660	Quinhydrone complex
1590	Amine substituted quinone
1220	Hydroquinone

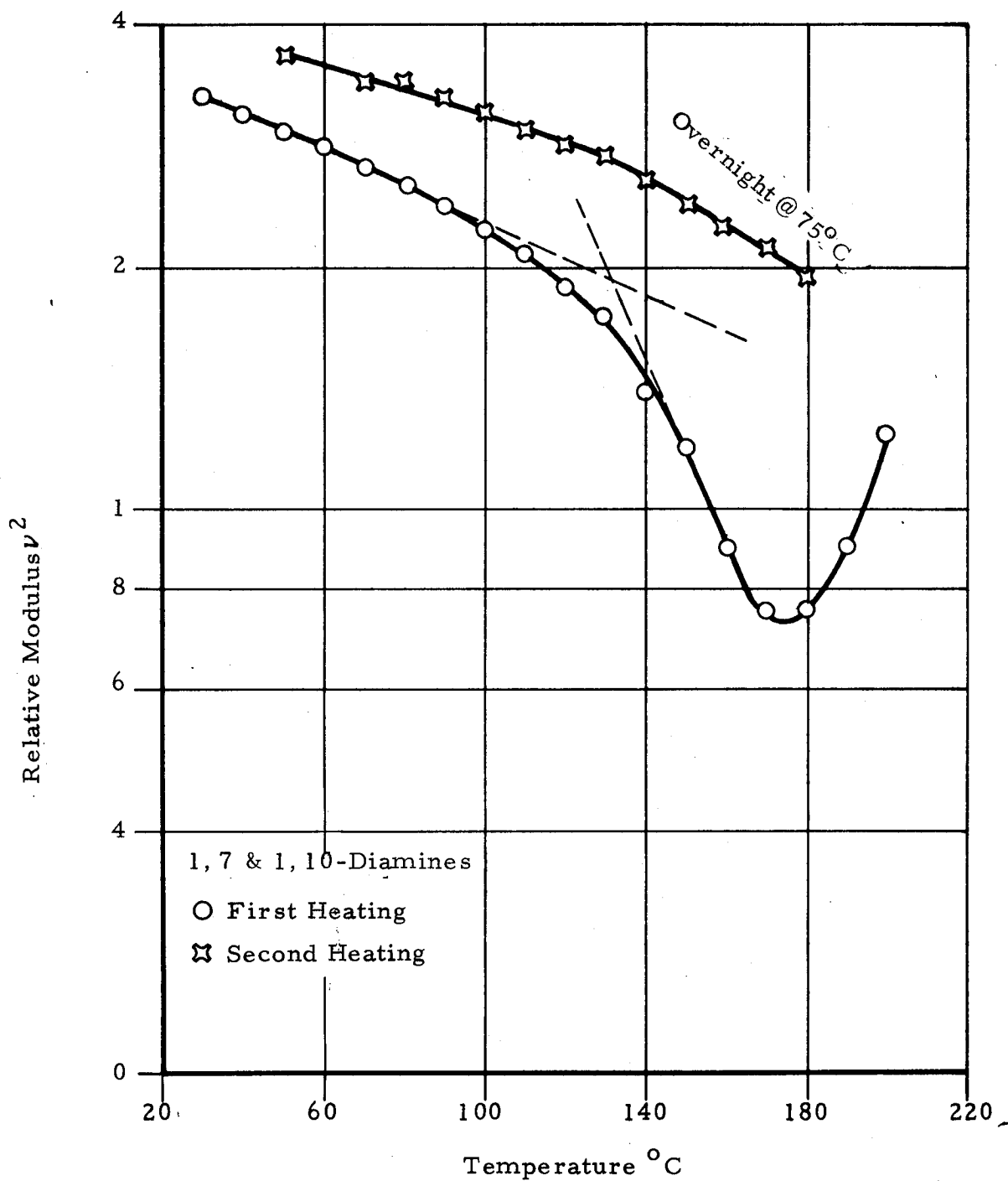


Figure 27. Relative Modulus - Temperature Curve for the Polymer Prepared From 1,7- 1,10-Diamines with Benzoquinone

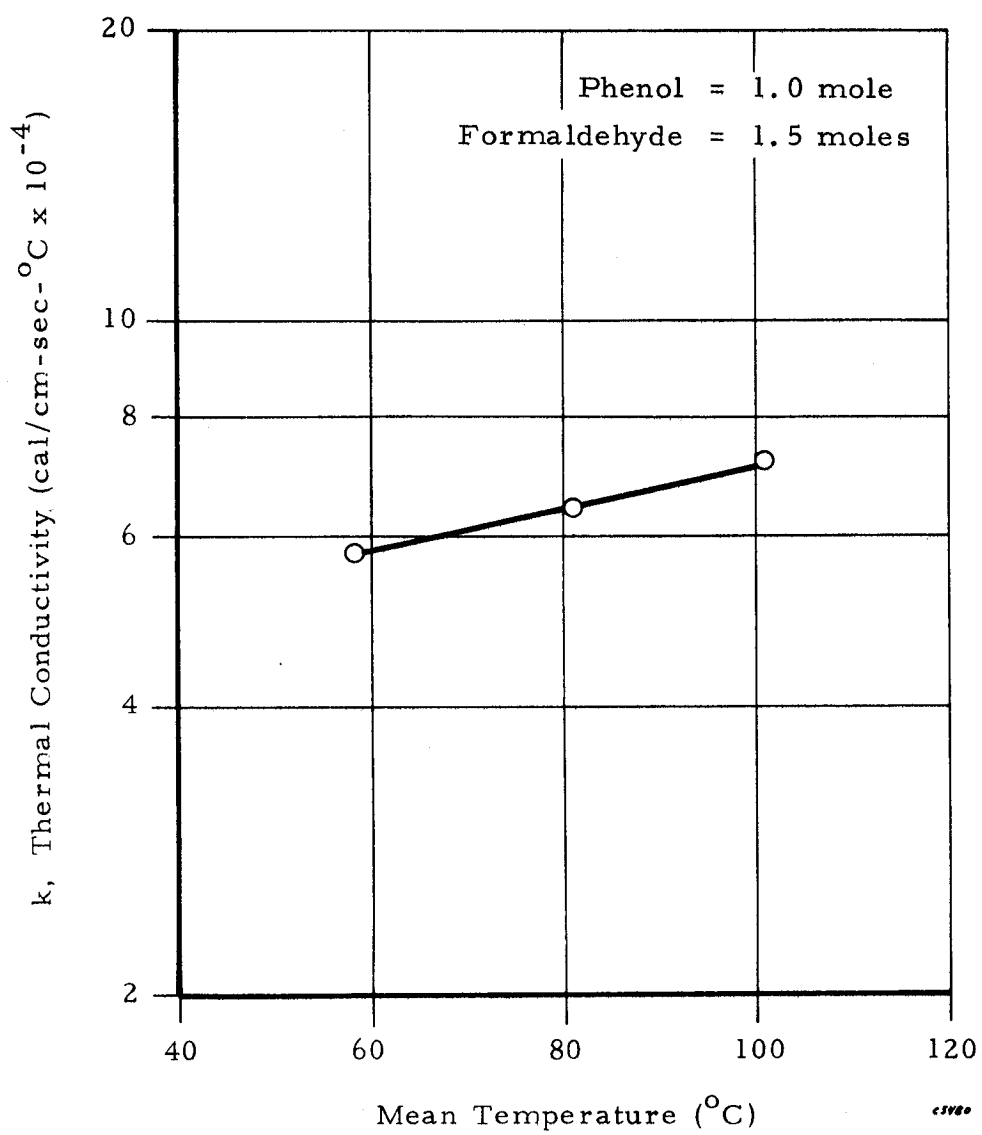


Figure 28. Thermal Conductivity - Temperature Plot of Phenol and Formaldehyde

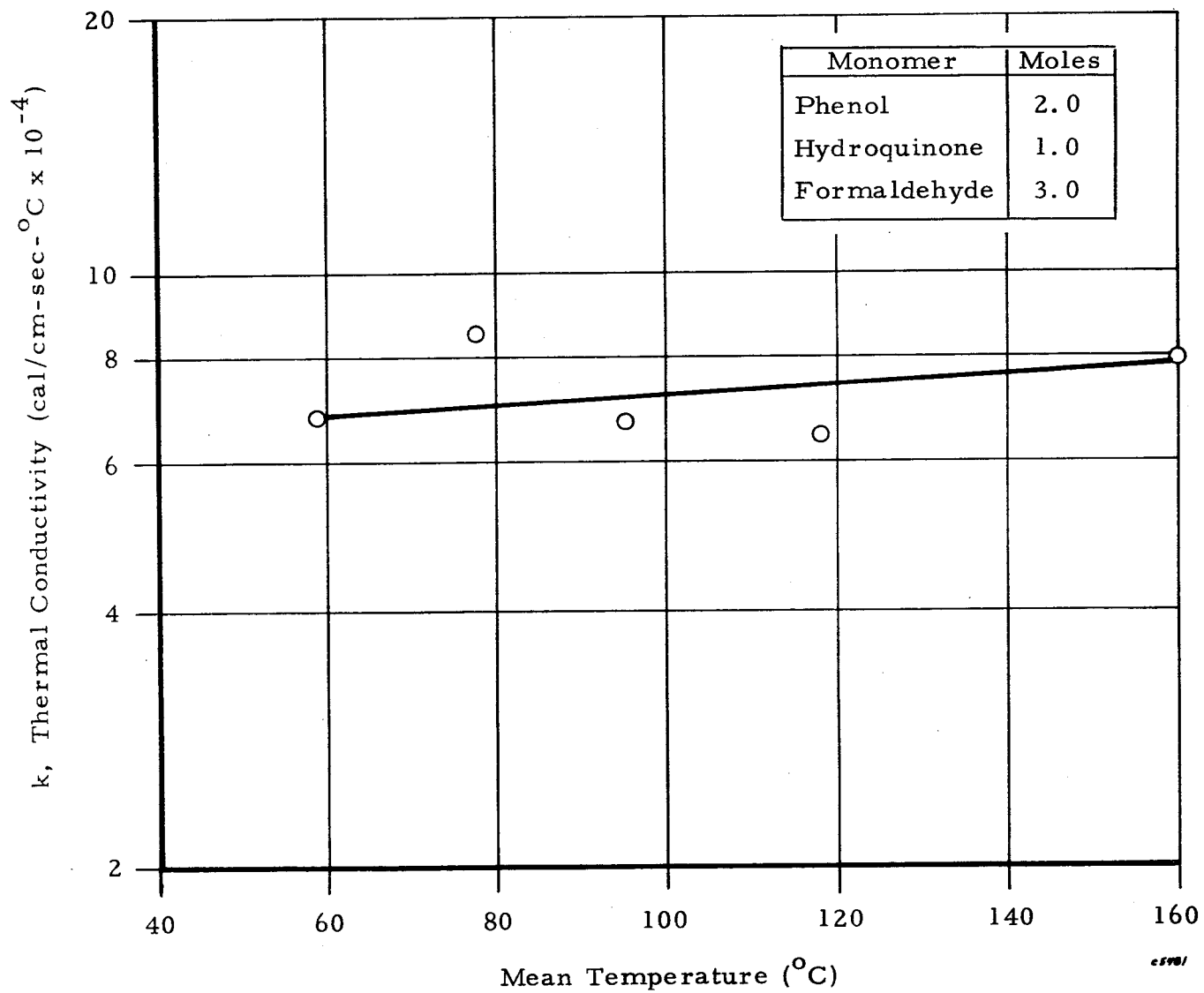


Figure 29. Thermal Conductivity - Temperature Plot of Phenol, Formaldehyde and Hydroquinone

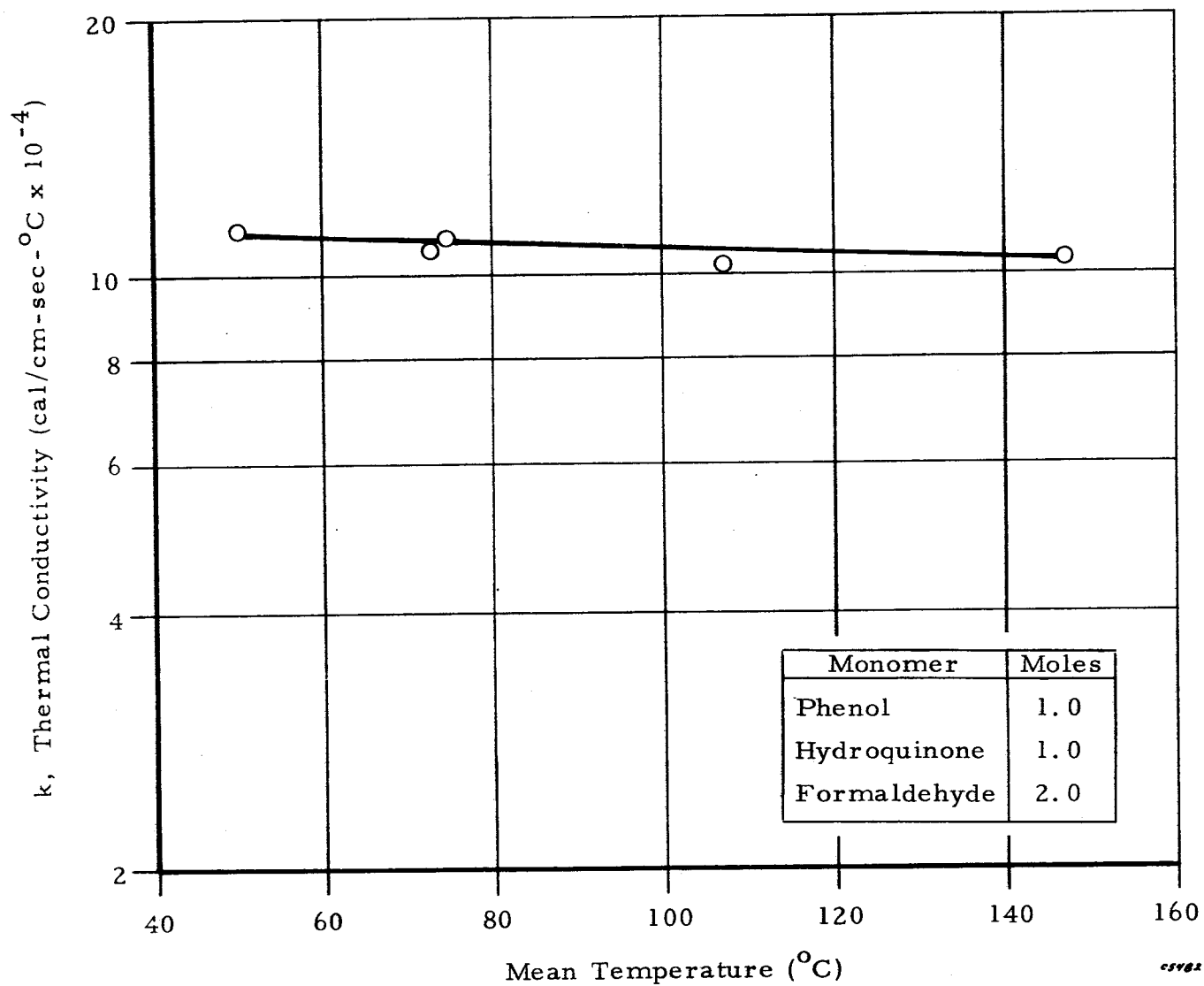


Figure 30. Thermal Conductivity - Temperature Plot of Phenol, Formaldehyde and Hydroquinone Reaction

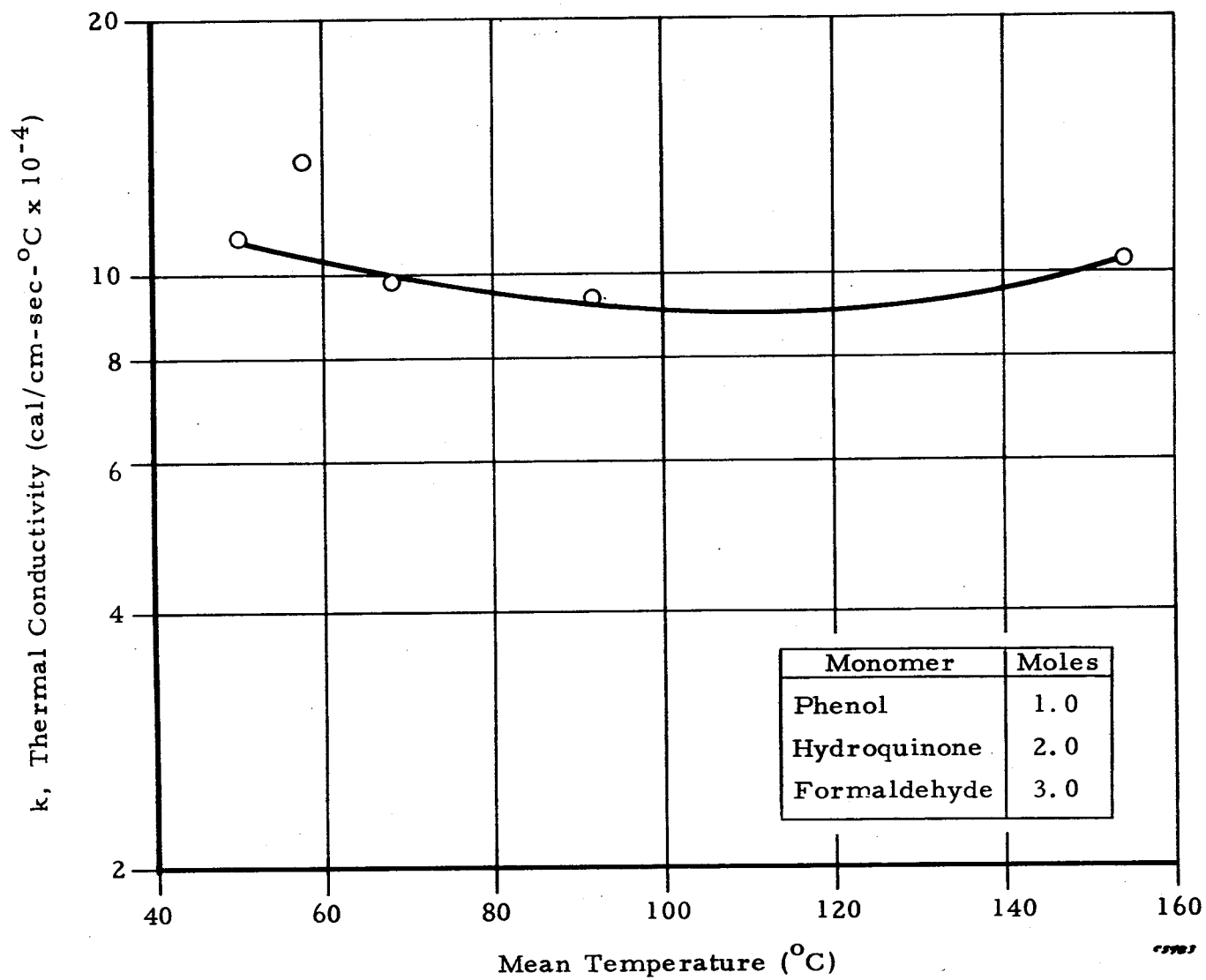


Figure 31. Thermal Conductivity-Temperature Plot of Phenol, Formaldehyde and Hydroquinone Reaction

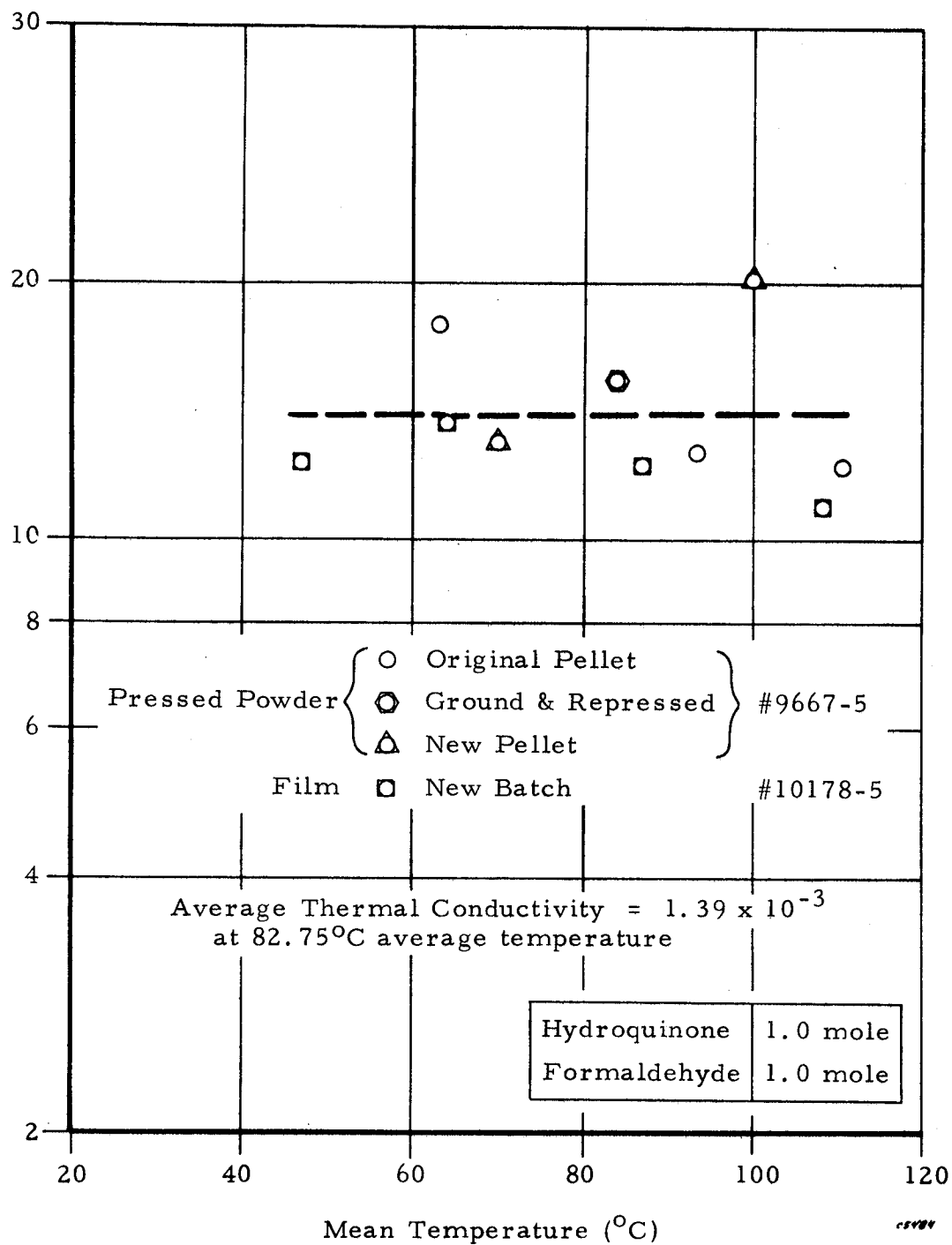
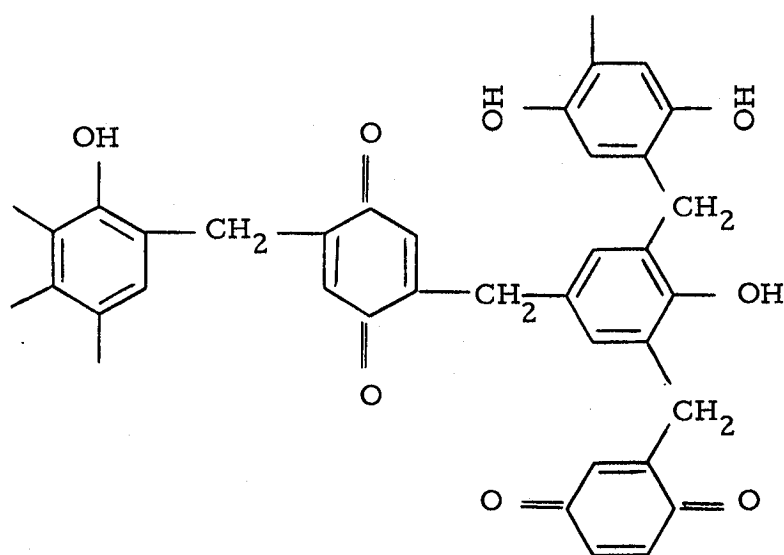


Figure 32. Thermal Conductivity - Temperature Plot of the Polymer From Hydroquinone and Formaldehyde



c5570

Figure 33. Probable Structure of Phenol-hydroquinone-formaldehyde Resin

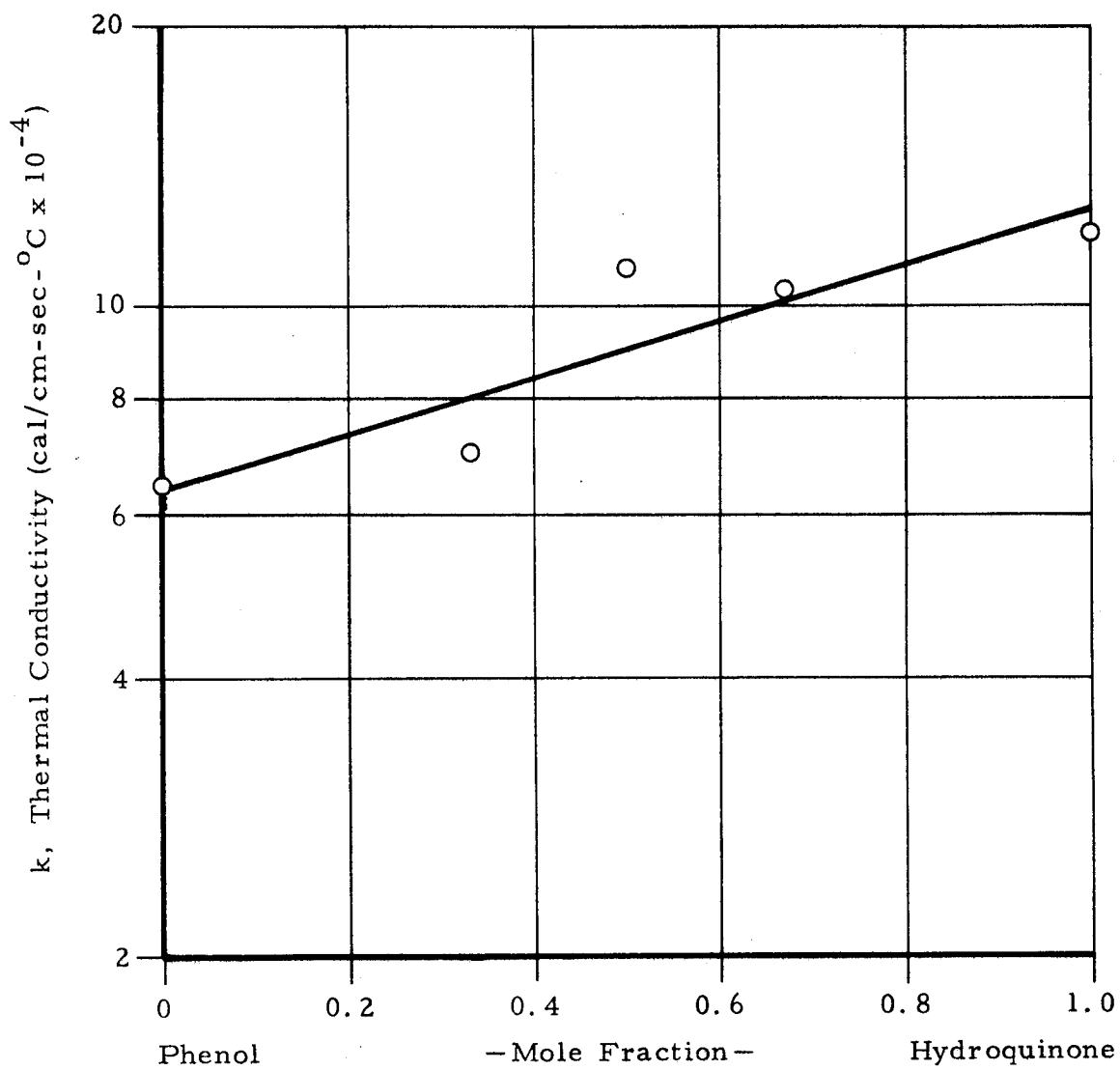


Figure 34. Thermal Conductivity at 80°C of the Polymer System Phenol-Hydroquinone Formaldehyde

increase may be explained by the increase in quinone groups available for complexing as the mole ratio of hydroquinone is increased.

4.5 MISCELLANEOUS POLYMERS

A number of reactions involving thionyl chloride and sulfur monochloride with both hydroquinone and benzoquinone were investigated to determine if the reaction products would yield increased thermal conductivity, presumably through charge transfer complexing. Unfortunately, the reactions yielded low molecular weight compounds (~400 number average when measured with a vapor pressure osometer) that remained either as tarry gums or were extremely sensitive to moisture.

Section 5

CONCLUSIONS AND RECOMMENDATIONS

Perhaps the most notable achievement in this program has been the development of a new concept in which enhanced thermal conductivity in unfilled polymeric materials may be achieved by main chain coupling through the formation of inter- and intra-molecular charge transfer complexes. This concept has been partially verified experimentally by the synthesis and thermal testing of two families of electron exchange polymers. The first polymer system studied was the polyaminoquinone in which strong charge transfer complexing arose from the donating groups of hydroquinone and amine and the strong acceptor benzoquinone. These polymers when pressed and cured exhibited excellent thermal conductivity as a function of temperature. The second class of electron transfer polymers studied were the water-alcohol soluble condensation products obtained from the reaction of hydroquinone, phenol and formaldehyde. During the condensation of the monomers in a basic pH media, most of the substituted hydroquinone was oxidized to the quinone form thus allowing strong charge transfer complexes to exist between phenol-benzoquinone and hydroquinone-benzoquinone groups. The polymers cured to strong, glassy films with all the advantages and disadvantages of typical cured phenolics except that their thermal conductivity is about two to three times greater.

It would appear that further effort in this area is warranted. The concept of enhanced thermal conductivity by coupling with charge transfer complexes should be further substantiated by preparing polymers containing known acceptors and donors either as pendant groups or incorporated in the main chain. Various constituents on both the acceptors and donors would change the electrical potential of the system thus providing a method to determine the influence of the strength of the complex on the thermal conductivity. Some effort should be expended to prepare pre-polymers terminated with reactive functional groups such as epoxy or isocyanate. Such a system could be formulated into a "neat" polymer system. One additional area of interest is the polymer-filler systems that could quite possibly exhibit much higher thermal conductivities than the rule of mixtures would predict due to synergism from polymer-filler interaction. The probable nature of this synergism would be by chelation of the aminoquinone to the metal surface.

REFERENCES

1. Modern Plastics Encyclopedia, McGraw-Hill, New York, 1966.
2. Ehrlich, P., R. J. Kern, E. D. Pierron, and T. Provder, J. Polymer Sci., 5, 911 (1967).
3. Jenkins, R. K., N. R. Byrd, J. L. Lister, and C. Vest, "Thermally Conducting Electron Transfer Polymers," J. Appl. Polymer Sci., in press.
4. Eiermann, K., J. Poly. Sci., C, 6, 157 (1964).
5. Hansen, D. and C. C. Ho., J. Poly. Sci., A, 3, 659 (1965).
6. Eiermann, K., Rubber Chem. & Tech., 39, 866 (1966).
7. Ziman, J. M., Electron and Phonons, Oxford University Press, 1962.
8. Kingery, W. D., Introduction to Ceramics, John Wiley and Sons, Inc., New York, 1960.
9. Jenkins, R. K., J. Polymer Sci., 2, 999 (1964).
10. Jenkins, R. K. and N. R. Byrd, "High Thermal Conductivity Polymeric Materials for Spacecraft Use," Report SM-49143-M17, Contract NAS 5-10260, February 1968.
11. Jenkins, R. K. and L. Karre, J. Appl. Poly. Sci., 10, 303 (1966).

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 phenyl-acetylenes). 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 follow this curve. 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-7 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 $\bar{M}_v = 27,000$ whereas H-100 has a $\bar{M}_v = 355,000$. The chlorination procedure is identical for both fractions.

One mole of polystyrene (PS-2 or H-100), with a viscosity average molecular weight, $\bar{M}_v$, 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

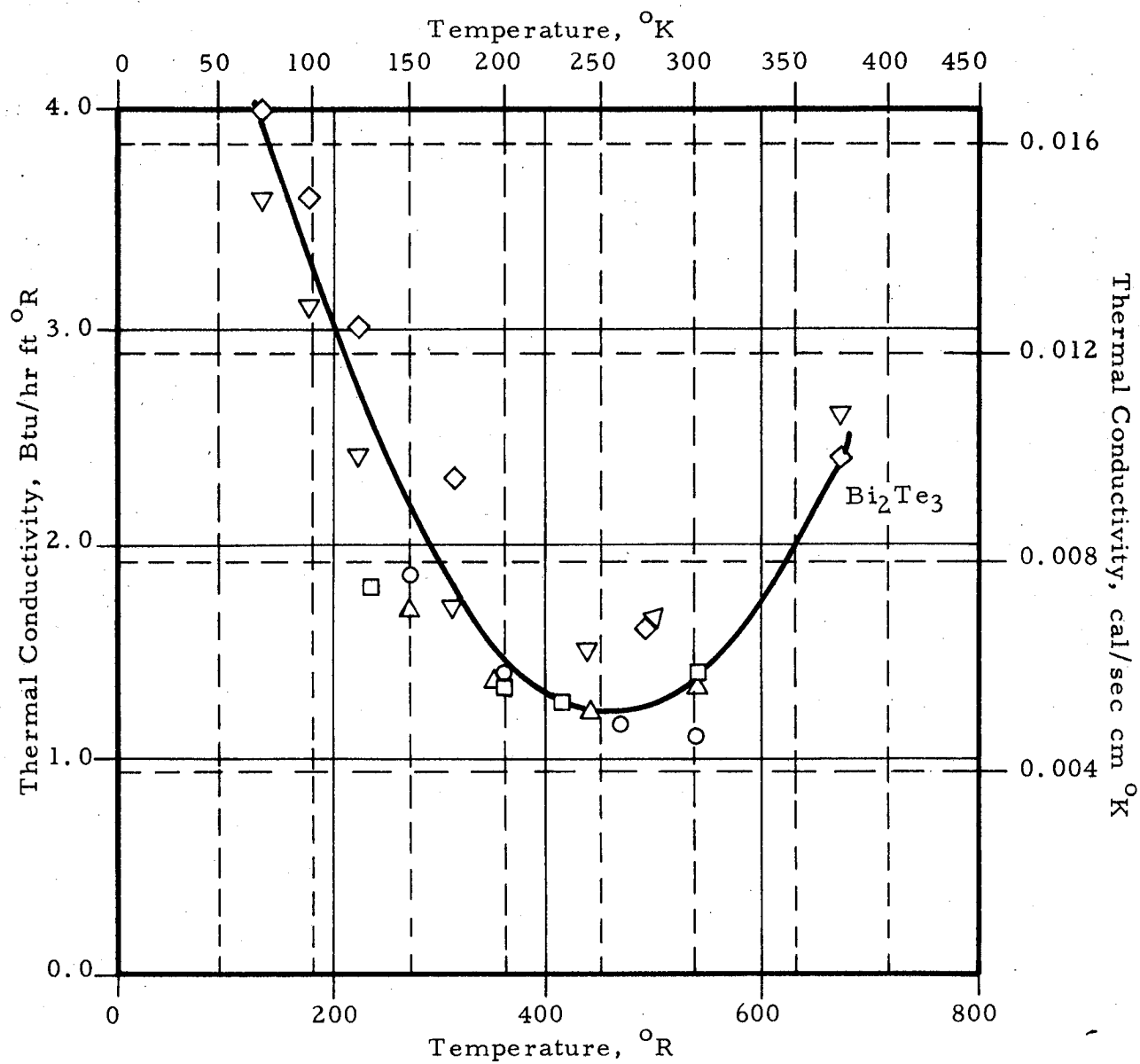


Figure I-1. Thermal Conductivity - Bismuth Telluride

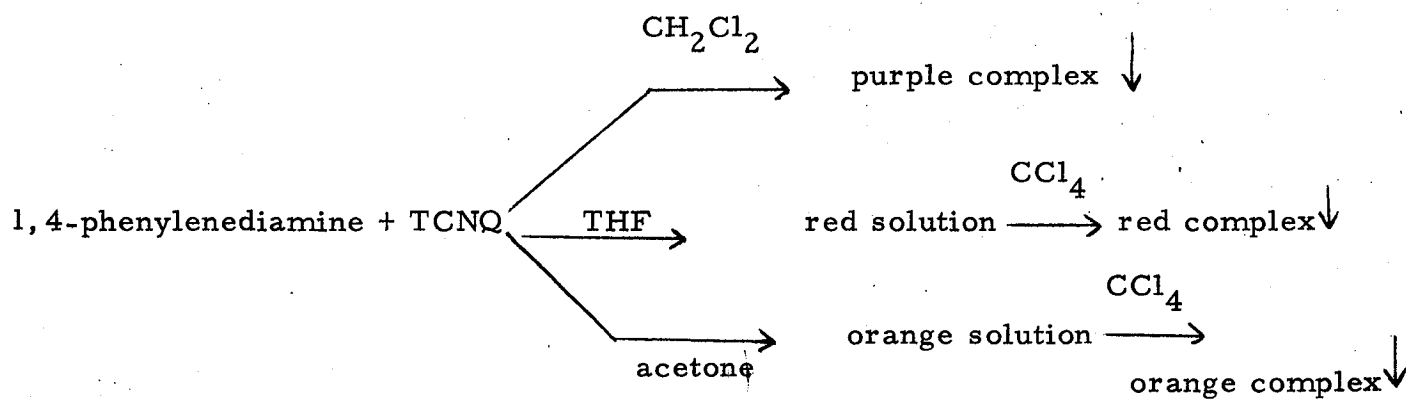


Figure I-2. Reactions of 1,4-Phenylenediamine With TCNQ in Different Solvents

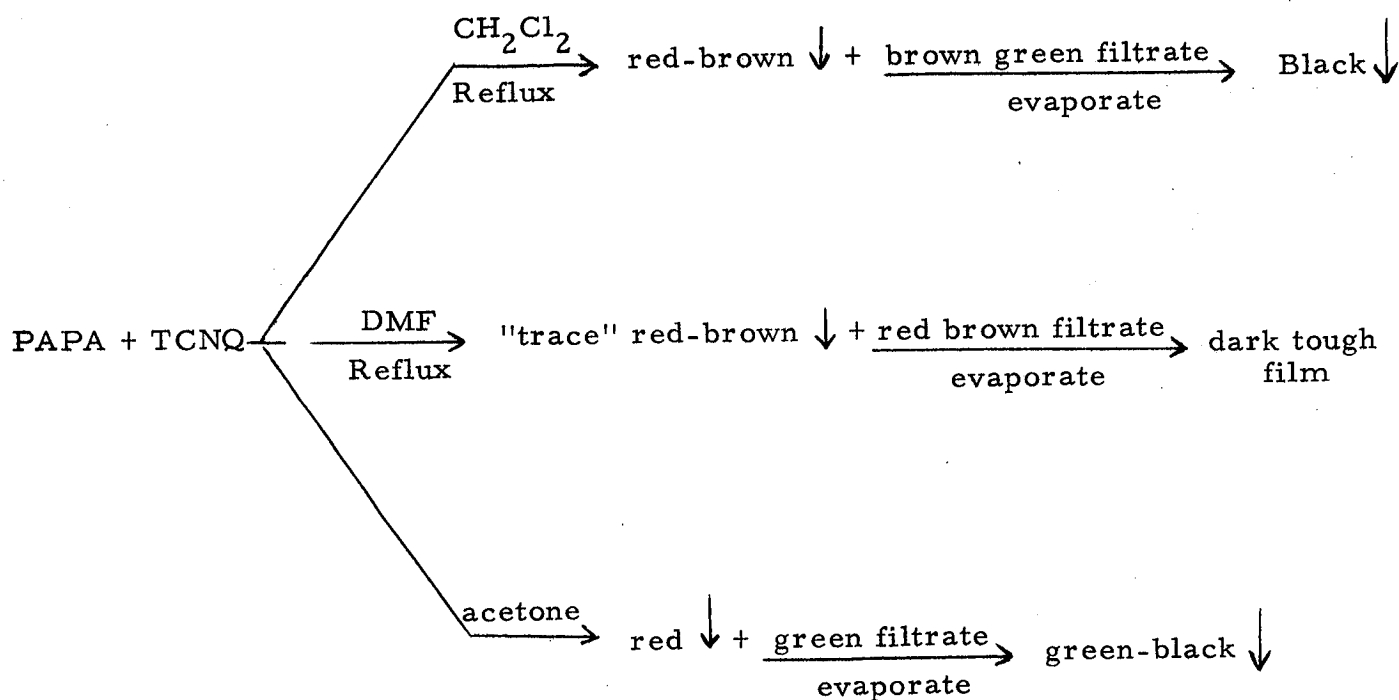


Figure I-3. Reaction of Poly(p-aminophenylacetylene) With TCNQ in Different Solvents

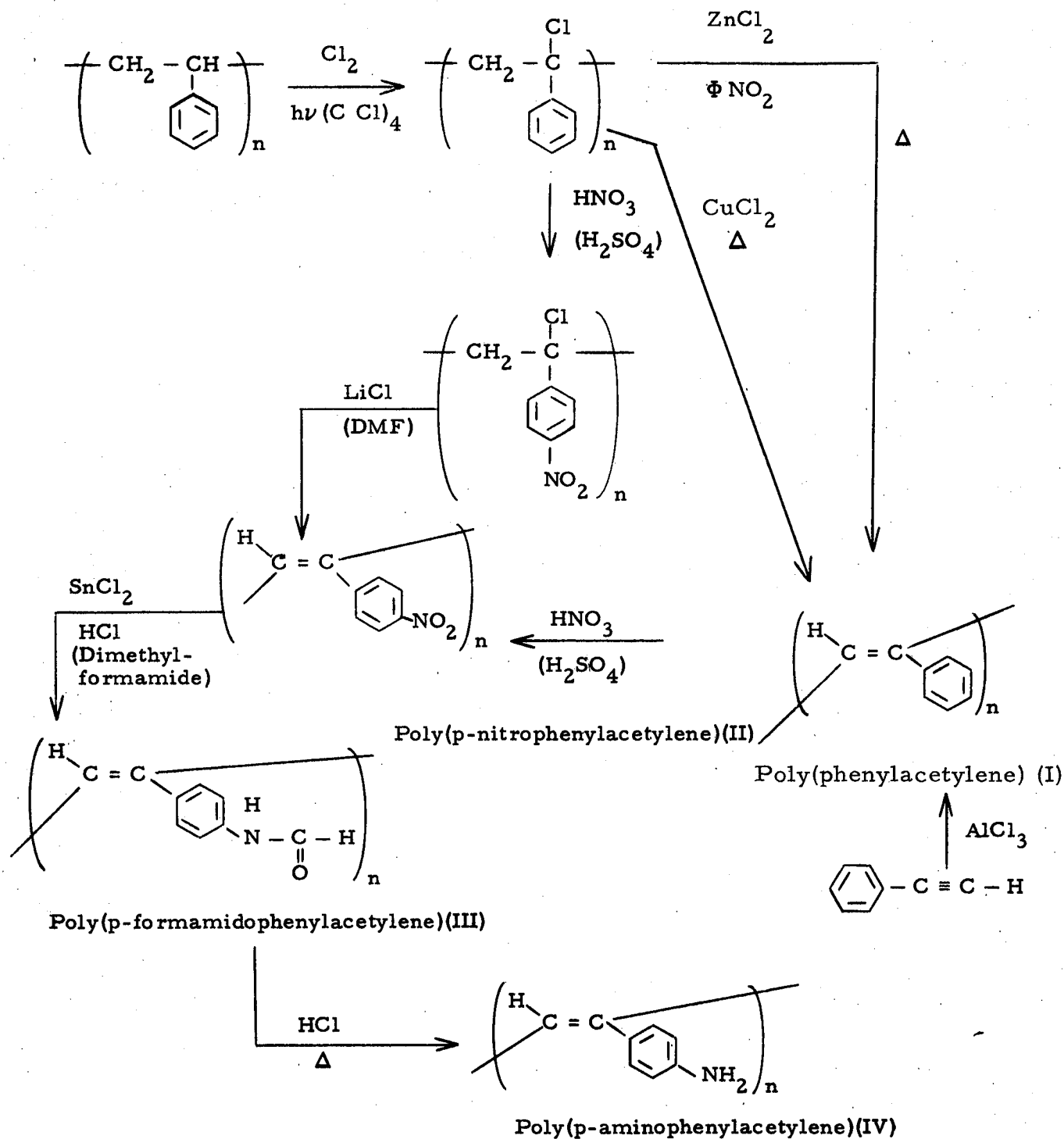
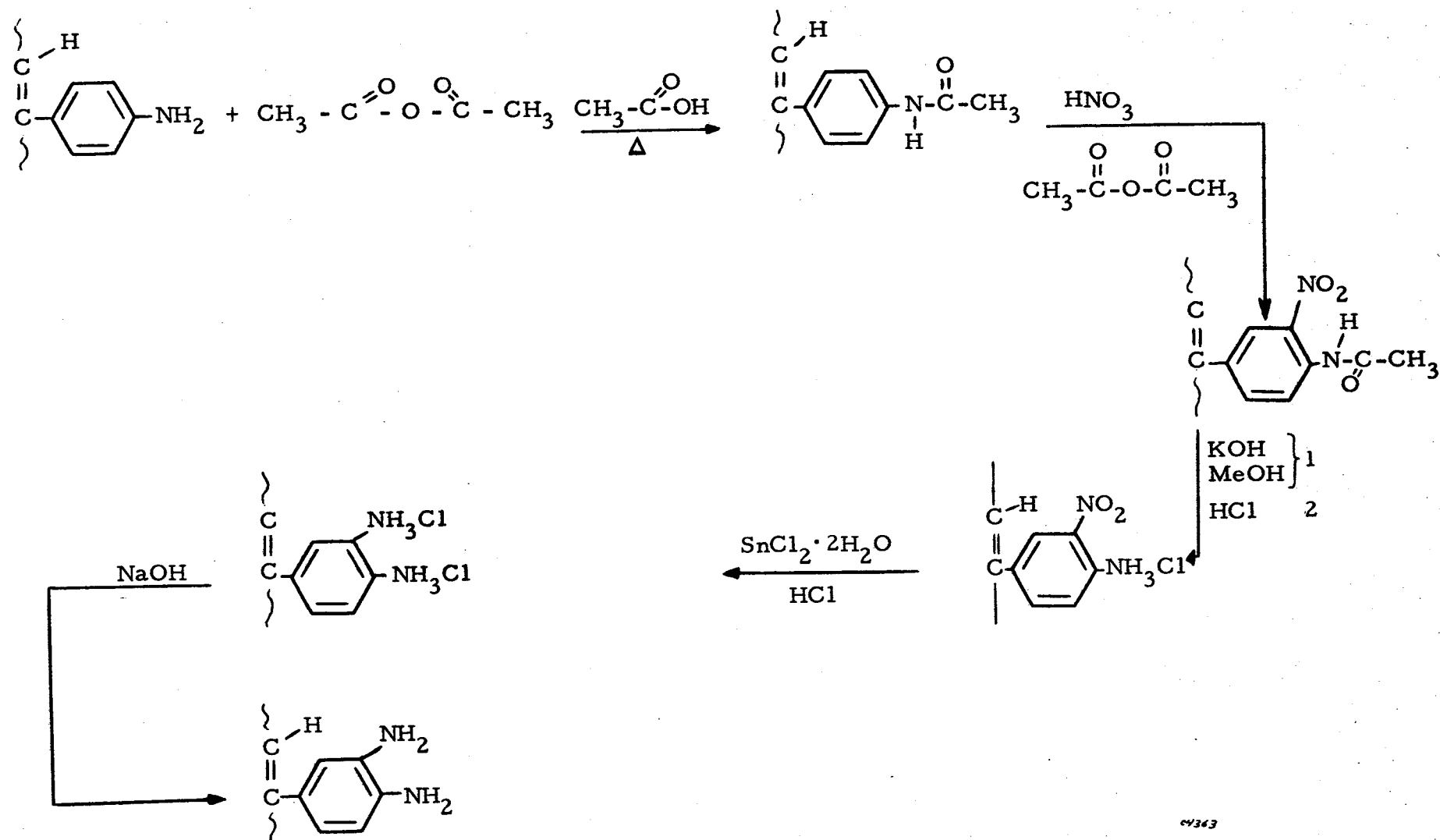
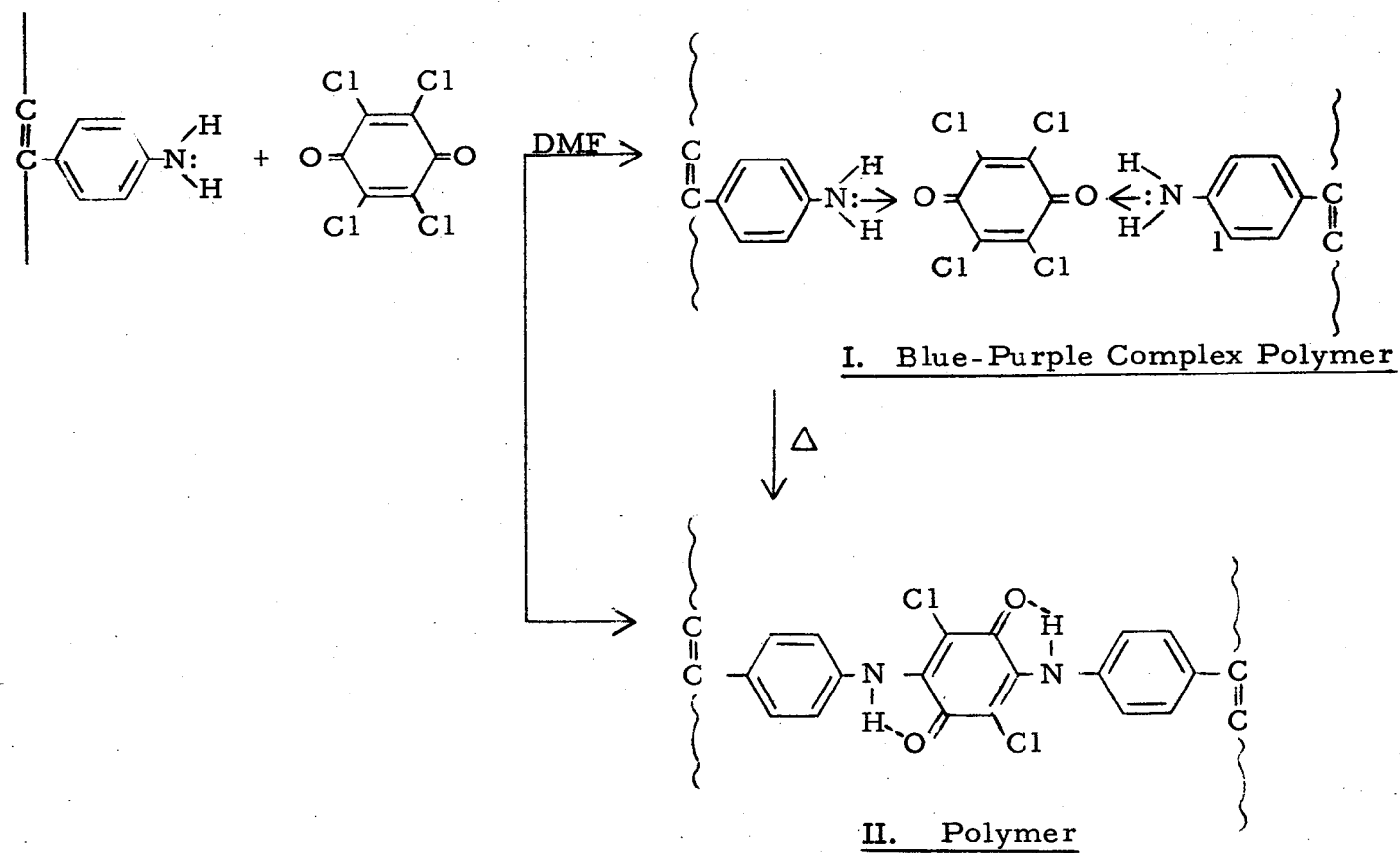


Figure I-4. Reaction Sequence Used in Preparation of Some Poly(phenylacetylenes)



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



C3070

Figure I-6. Reaction of PAPA and Chloranil

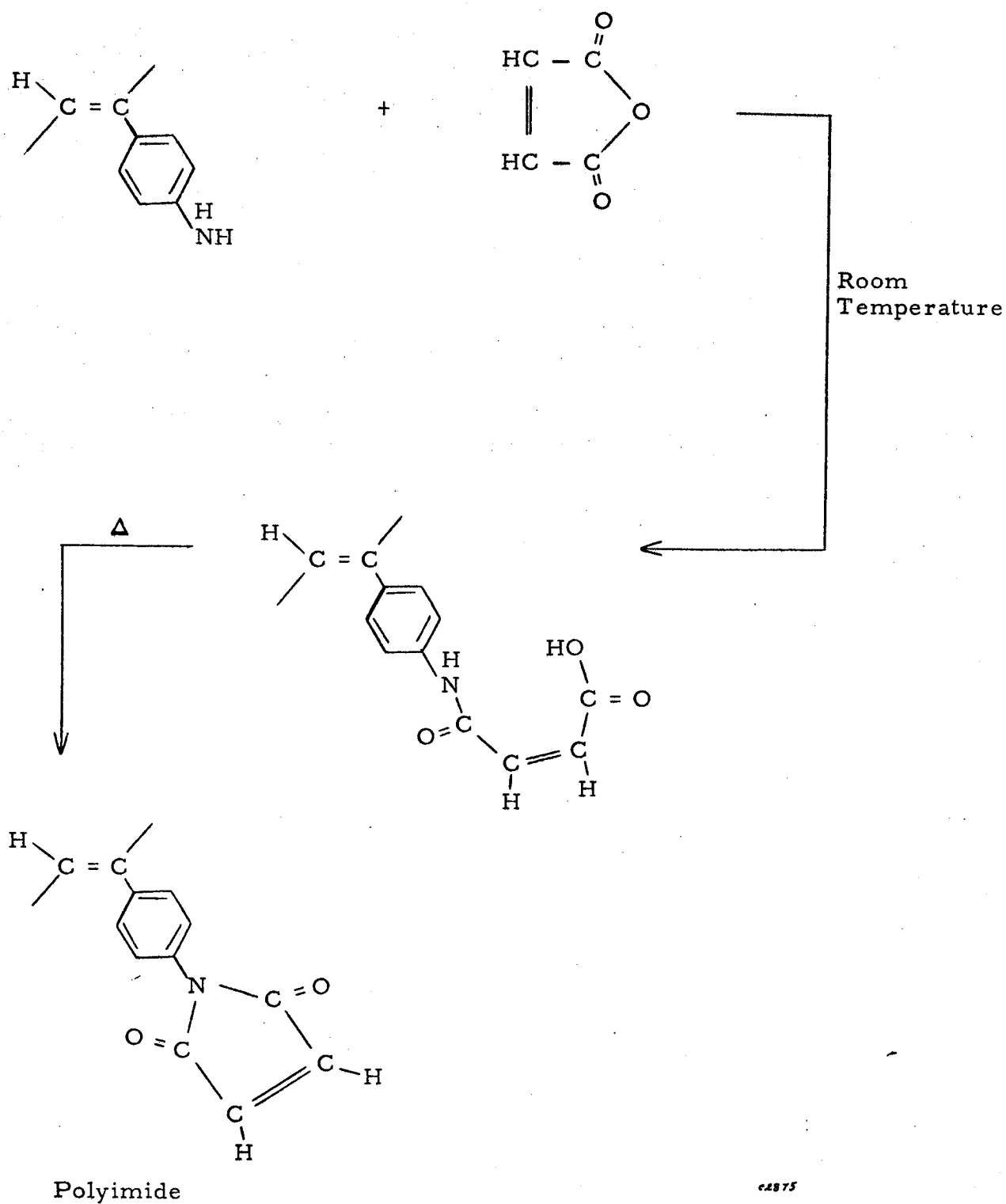


Figure I-7. Preparation of Poly(p-N-maleiimidephenylacetylene) from Poly(p-aminophenylacetylene) and Maleic Anhydride

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)

	<u>% C</u>	<u>% H</u>	<u>% Cl</u>
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(alpha-chlorostyrene) 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 ground 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

	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% Cl</u>
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

	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% Cl</u>
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 H₂O. 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

	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% Cl</u>
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 H₂O made basic with concentrated NH₄OH. 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

	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% Cl</u>
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.

<u>Elementary Analysis</u>				
	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% Cl</u>
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.

<u>Elementary Analysis</u>					
	<u>% C</u>	<u>% H</u>	<u>% Cl</u>	<u>% O</u>	<u>% Ash</u>
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 ($\sim 250^\circ\text{C}$) 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)

	<u>% C</u>	<u>% H</u>	<u>% Cl</u>
Found	51.9	3.8	43.9
Theoretical	55.8	3.5	40.7

(B) Poly(β -chlorophenylacetylene)

	<u>% C</u>	<u>% H</u>	<u>% Cl</u>
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% HNO₃ - 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 - H₂O 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-nitro-phenylacetylene derivative had been formed.

To a solution of 20 g SnCl₂·2H₂O 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 H₂O and reprecipitated by adding 100 ml of conc. HCl. The dihydrochloride salt was dissolved in 40 ml of H₂O and added to a cold solution (10°C) of 10 g NaOH in 25 ml H₂O. 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 NH₄OH to 3 parts H₂O. 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-chloro⁴-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, SnCl₂, (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 NH₄OH. 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 stirring 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 Crosslinking of Poly(p-aminophenylacetylene)

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

*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, $-\text{NH}-\text{CO}-\text{NH}-$.

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 dimethylformamide 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 9.1 μ ; 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

<u>Mole Percent of TDI</u>	<u>Wt of Polymer Used (gms)</u>	<u>Volume of 20% Solution of TDI in Benzene (ml)</u>	<u>Wt of TDI Used (gms)</u>	<u>Yield (Wt)</u>
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 NH₂ 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 N₂ 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)

<u>Mole Ratio</u> <u>PAPA/Terephthalaldehyde</u>	<u>Mole of PAPA</u>	<u>Mole of TPA</u>	<u>Ml of DMSO</u>		<u>Ml</u> <u>HCl</u> <u>Conc.</u>
			<u>PAPA</u>	<u>TPA</u>	
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

<u>Moles/Wt. of Acceptor</u>	<u>Moles/Wt. PAPA Donor</u>	<u>Total Vol. Acetone</u>	<u>Precipitates Acetone Sol</u>	<u>Acetone Insol</u>
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 ELECTRON TRANSFER POLYMERS

2.4.1 Preparation of Poly(alkylaminoquinone) Polymers

The reaction sequence for the formation of the polymers 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 30° . 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, a red, solvent-swollen polymer is isolated, washed several times with warm THF, and vacuum dried. Table I-I lists the various polymers prepared under these reaction conditions and a few selected physical properties.

A specific reaction of 1,7-heptanediamine-benzoquinone is as follows. Para-benzoquinone (30 mmoles) was dissolved in enough tetrahydrofuran (THF) to make up a 10 wt % solution. This solution was added to a 150 ml reaction vessel equipped with a reflux condensor, mechanical stirrer, a nitrogen inlet, and dropping funnel. A nitrogen stream was used to purge and blanket the benzoquinone solution and with adequate cooling (30°) 10 mmoles of a

1,7-heptanediamine solution prepared at 10 wt %, was added dropwise with vigorous stirring. Following the addition of the diamine solution, the reaction was allowed to continue for about 60 minutes. The mixture was filtered yielding a red-brown precipitate and a blood red filtrate. The precipitated polymer was slurried several times in cold THF, filtered, washed with hot THF, and vacuum dried at 40° overnight.

<u>Elementary Analysis</u>				
	<u>%C</u>	<u>%H</u>	<u>%N</u>	<u>%O</u>
Found	66.86	6.89	9.13	16.32
Theory	66.7	7.7	12.0	13.7

Elementary analysis of the polymer indicates a high content of quinone or hydroquinone and a corresponding decrease in the diamine. These results may be due to low molecular weight of the polymer in which the end groups are terminated with the quinone or hydroquinone, and/or the polymer may be crosslinked by quinone.

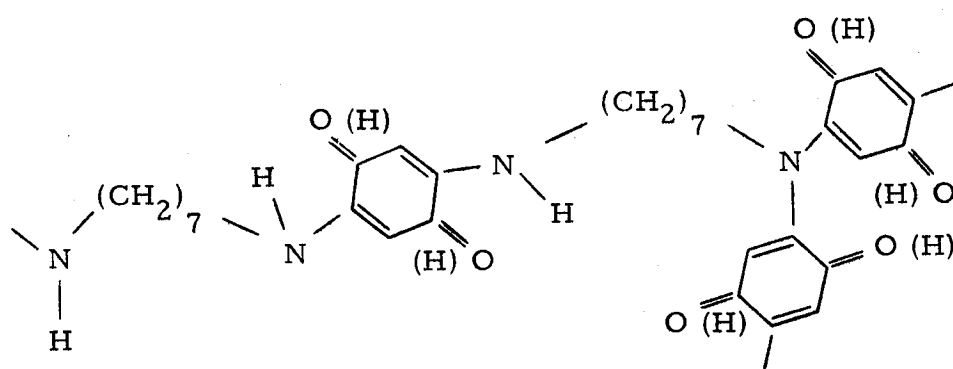
The most probably structure and calculated elementary analysis is given in Figure I-8.

2.4.2 Reaction of Mixed Diamines with p-Benzoquinone

Benzoquinone (60 mmoles) was dissolved in tetrahydrofuran (THF). Ethylenediamine (10 mmoles) and 1,6-hexanediamine (10 mmoles), both dissolved in 50 ml of THF, were added to this solution. The solution was stirred in air with development of a strong exotherm that brought the temperature to 65°C. The reaction was continued for ten minutes, then filtered. The precipitate was washed with THF and extracted with ethyl alcohol. A pellet prepared from the material was hard and brittle. Not tested for thermal conductivity.

2.4.3 Reaction of p-Benzoquinone with 1,12-Dodecanediamine and 3,3'-Diaminobenzidine

1,12-dodecanediamine and 3,3'-diaminobenzidine (10 mmoles each) were dissolved in 50 ml of THF and 50 ml of dimethylacetamide (DMA). This solution was added, under nitrogen and with good stirring, to 60 mmoles of p-benzoquinone in 50 ml of DMA. The reaction was continued for three hours at reflux. There was no visible precipitate. Air was bubbled into the reaction vessel without causing a precipitate. The polymer was precipitated in hot ethyl alcohol, filtered and dried in a vacuum oven at ambient temperature. After drying, a pellet was prepared at 200°C under 10,000 psi (gage). When cool, the pellet was very flexible. Infra-red indicates majority of the polymer consists of quinone and 1,12-dodecanediamine.



<u>Elementary Analysis</u>				
	%C	%H	%N	%O
Found	66.86	6.89	9.13	16.62
Theory	66.80	6.94	9.72	16.65

Figure I-8. Probable Structure and Elementary Analysis of
1,7-Heptanediamine-benzoquinone Reaction
Product

2.4.4 Reaction of N,N'-Dimethyl-1,6-Hexanediamine with 2,5-Dimethyl-p-Benzoquinone

Equal molar amounts of N,N'-dimethyl-1,6-hexanediamine and 2,5-dimethyl-p-benzoquinone were dissolved in 100 ml of dimethylformamide (DMF). The solution was refluxed in air for 30 hours, then evaporated to dryness on a hot plate. The resultant polymer was slurried in a 1:1 alcohol - H₂O mixture, filtered and dried in a vacuum oven.

2.4.5 Reaction of Phenol with Formaldehyde (1:1.5 Mole Ratio, Respectively)

A solution of 0.5 moles of phenol and 0.75 moles of 37% aqueous formaldehyde was added to a one liter resin flask equipped with a mechanical stirrer, reflux condensor, nitrogen inlet and vacuum connections. To this solution was added 3.5 ml of KOH at 50% concentration. The solution was taken to reflux (90°C) using a partial vacuum. At this time an additional 3.5 ml of KOH was added. The refluxing was continued for 30 minutes followed by concentration to approximately 50% solids. A film was cast and cured from this resin which yielded a reference thermal conductivity of 7.5×10^{-4} cal/cm-sec-°C at 80°C.

2.4.6 Reaction of Hydroquinone with Formaldehyde (1:1 Mole Ratio)

Hydroquinone, 1/2 mole, and 1/2 mole of 37% formaldehyde in 90 ml of H₂O were added to a one liter reaction flask. To this solution was added 7 ml of 45% KOH. The solution was taken to reflux and held for 3 hours followed by concentration to about 50% solids. One half the product was precipitated in THF, filtered and bottled; the other half was stored at 40°F. A film of this resin yielded a thermal conductivity of about 1.3×10^{-3} cal/cm-sec-°C at 80°C.

2.4.7 Reaction of Phenol with Formaldehyde Followed by Hydroquinone (1:2:1 Mole Ratio)

One mole of phenol, 2 moles of 37% formaldehyde and 4 ml of 50% NaOH were added to a one liter reaction flask previously described. The solution was taken to reflux (90°C) and allowed to react for 2 hours. The solution was a rich amber color. One mole of hydroquinone in 50 ml of H₂O was added to the refluxing solution; the addition caused a darkening of the solution. After reacting one hour, the resin was concentrated and stored. The resin solution did not develop the jet black color previously noticed and it is believed that the late addition of the hydroquinone prevented the formation of the oxidized quinone groups.

2.4.8 Reaction of Phenol, Formaldehyde and Hydroquinone (1:2:1 Mole Ratio)

A one liter resin kettle equipped with a dropping funnel, reflux condenser and stirrer was charged with one mole of phenol, 2 moles of formaldehyde and one mole of hydroquinone in 100 ml of H₂O. Four ml of 50% NaOH was added. The solution was taken to reflux temperature and a color change occurred, amber → red → brown. The reaction was allowed to continue for three hours, then concentrated. A film was cast, cured and measured for thermal conductivity. A value of 1.1×10^{-3} at an average temperature of 80°C was obtained. The excellent quality of the cast film coupled with the good thermal conductivity makes this composition attractive for further investigation.

2.4.9 Reaction of Phenol, Formaldehyde and Hydroquinone (1:3:2 Mole Ratio, Respectively)

One mole of phenol was dissolved in 3 moles of formaldehyde and 2 moles of hydroquinone in 100 ml of H₂O was added. Four ml of 50% NaOH was added and the solution taken to reflux temperature. The reaction was allowed to continue for three hours, followed by concentration to 66.0% solids. A film was cast, cured and measured for thermal conductivity. A value of 9.7×10^{-4} at an average temperature of 80°C was obtained.

2.4.10 Reaction of Phenol, Formaldehyde and Hydroquinone (2:3:1 Mole Ratio)

Two moles of phenol was dissolved in 3 moles of formaldehyde and one mole of hydroquinone was added with vigorous stirring. Seven-and-one-half ml of a 50% NaOH solution was added. The reaction was taken to the reflux temperature and was held at this temperature for three hours. The solution was concentrated to 67% solids and films were cast, cured and measured for thermal conductivity. The value obtained was 6.8×10^{-4} at an average temperature of 80°C.

2.5 Miscellaneous Reactions

2.5.1 Reaction of Sulfur Monochloride with Hydroquinone

Sulfur monochloride (0.5 moles) and hydroquinone (0.5 moles) were each dissolved in 200 ml of THF. The sulfur monochloride solution was added to the hydroquinone solution and after approximately five minutes an exotherm developed, increasing the temperature to 65°C. Following the exotherm, the solution was taken to reflux. The solution slowly turned from a red to a yellow color with large amounts of HCl given off.

The reaction was continued for six hours, then the solution was evaporated to dryness. When near dryness, the mass developed a second exotherm with further release of HCl. The brown mass was dissolved in 100 ml of ethyl alcohol plus 150 ml of dioxane and refluxed overnight.

The solvent was stripped off at about 60°C under vacuum, and the solid polymer was ground and dried in vacuum oven. Recovered approximately 100 grams.

The molecular weight, as determined by vapor pressure osmometer, was about 400.

2.5.2 Reaction of Sulfur Monochloride with p-Benzoquinone

Sulfur monochloride (100 mmoles) and p-benzoquinone (100 mmoles) were both dissolved in 100 ml of THF. These solutions were mixed and taken to reflux temperature. After about one hour and 30 minutes the solution began to darken and in another 15 minutes was a dark red. Continued the reaction for another three hours then filtered with recovery of an orange precipitate. Evaporated filtrate to dryness, dissolved residue in ethyl alcohol and again evaporated to dryness. During reaction, there was no evidence of HCl being given off.

2.5.3 Reaction of Thionyl Chloride with p-Benzoquinone

Ten mmoles each of thionyl chloride and p-benzoquinone were dissolved in 100 ml in THF. This solution was taken to reflux and held overnight with apparently no reaction. Replaced THF with dioxane and refluxed this solution overnight with resulting dark coloration of solution. Evaporated the solution to dryness, dissolved residue in 50 ml of acetone then precipitated into 500 ml of water. The precipitate was air dried over the weekend.

2.5.4 Reaction of N-Oleyl - 1,3-Propanediamine with p-Benzoquinone

N-oleyl - 1,3-propanediamine (300 mmoles) was dissolved in 200 ml of THF and added very rapidly to a 200 ml solution of p-benzoquinone (300 mmoles) in THF. A strong exotherm occurred with the solution turning red. This solution was refluxed for two hours, then steam distilled. The polymer was picked up in diethyl ether, washed with water and evaporated to dryness. The polymer was again dissolved in THF, precipitated in water and dried in a vacuum oven overnight.

A major difficulty resulting with these soluble polymers is their low molecular weight. It is necessary to increase the molecular weight to a satisfactory level either by modification of reaction conditions or by the introduction of crosslinking agents. Probably some type of crosslinking agent will be required to develop mechanical stability.

