

Thermal Conductivity of Some Electron Transfer Polymers

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Synopsis

A number of electron transfer polymers were prepared by reacting various α , ω -alkanediamines with benzoquinone. The resulting polymers, through the formation of inter and intramolecular complexes, displayed high thermal conductivity with a strong temperature dependency. The mechanism contributing to the increased thermal conductivity was attributed to strong interchain complexing.

INTRODUCTION

Thermal conductivity of high polymers has been studied by a number of investigators to elucidate the mechanism of heat flow in both the crystalline and amorphous regions.¹⁻⁴ The crystalline contribution at "low" temperatures is dependent upon the transfer of energy by coupling of the lattice vibrations, thus creating traveling waves whose energy and momentum are quantized. These quantized waves are called phonons. The amorphous regions at "higher" temperatures have been described by Eiermann² as three dimensional networks of elementary thermal resistances consisting of van der Waals and main valence bonds. The resistance to heat flow of the main valence bonds is about ten times smaller than that of the van der Waals bonds so that the thermal conductivity of the amorphous polymer is, therefore, determined principally by the behavior of the van der Waals bonds. Similarly, Hansen and Ho² treat the conduction of heat in the amorphous regions as an energy transfer between bonded and non-bonded molecular segments; the energy transfer being much easier between the bonded segments. These theories suggest that increased thermal conductivity of amorphous polymers may be achieved by (1) increasing the molecular weight; (2) increasing the crosslink density; and (3) polymer coupling through molecular charge transfer complex formation.

We have prepared and evaluated a series of polymers for thermal conductivity in which preferred molecular orientations exist by the formation of inter and intramolecular charge transfer complexes. The polymer

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complex appears to promote increased thermal conductivity presumably by phonon conduction in the pseudo crystalline region through main chain coupling, and possibly some electronic contribution. The polymers are described as electron transfer polymers following the nomenclature developed by Cassidy.⁵

EXPERIMENTAL

Preparation of 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 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 condenser, 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 min. The mixture was filtered yielding a red-brown precipitate and a blood red filtrate. The precipitated polymer was slurred several times in cold THF, filtered, washed with hot THF, and vacuum dried at 40° overnight.

Elementary Analysis

	%C	%H	%N	%O
Found	66.86	6.89	9.13	16.62
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.

TABLE I
Reaction Conditions and Properties of Some Poly (Alkane Diaminoquinones)*

Diamine	Pressed disk	Specific heat Cal/ g-°C 120°C	Fisher-Johns Melting Point Apparatus		Density g/cm ³
			Color change—Temp	Melting point	
1,2-Ethane	Hard & brittle	—	Red brown→dark brown 230°	>300°	1.45
1,3-Propane	Hard & brittle	0.430	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	Semiflexible		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

* Solvent = THF; atmosphere = N₂; temperature = 30°C; mole ratio of amine/benzoquinone = 1:3.

Measurement of Thermal Conductivity

The apparatus consists of an evacuated chamber (capable of 10⁻⁶ torr), an electrical heater, and suitable radiation shields. Thermal conductivity of the test sample is measured relative to that of copper. One-half inch diameter cylindrical copper thermodes are employed with iron-constantan thermocouples permanently attached for temperature measurements. Thin foils of indium, 0.010 in., are positioned between the copper thermodes and the organic polymer specimens and a small compressive force maintained by use of a compressed spring on the upper thermode to ensure good thermal contact.

The thermal conductivity values are computed as the simple inverse ratio of the temperature gradients from the following expression:⁶

$$k_s = \frac{k_{Cu} t_{Cu} d_s}{t_s d_{Cu}}$$

where k_s and k_{Cu} are the thermal conductivities of the sample and copper thermode, t_{Cu} is the temperature difference between thermocouples on the

lower copper thermode, and t_s is the extrapolated temperature difference across the specimen. d_s is the thickness of the sample and d_{Cu} is the distance between thermocouples on the lower copper thermode.

Pellets were prepared for thermal conductivity measurements by pressing in a die at 190° for 15 min. The die was cooled to 50° prior to removal of pressure. During the preparation of the pellets the polymer changed color from red-brown to blue-black. The pressed pellets ranged in properties from strong and flexible to extremely brittle depending on the number of methylene groups in the diamine.

Measurement of Specific Heat

The specific heat of three selected polymers was determined (Table I) by use of a Perkin Elmer Differential Scanning calorimeter (DSC-1B) using a comparison technique in which an external standard (sapphire) was used. The DSC was programmed at $20^\circ/\text{min}$ and sensitivity of 4 mcal/sec full scale.

RESULTS AND DISCUSSION

A series of electron transfer polymers was synthesized and investigated for thermal conductance. The polymers, prepared by reacting selected α, ω -diamines with an excess of *p*-benzoquinone, contained quinone, hydroquinone and secondary amine groups. The quinone and hydroquinone

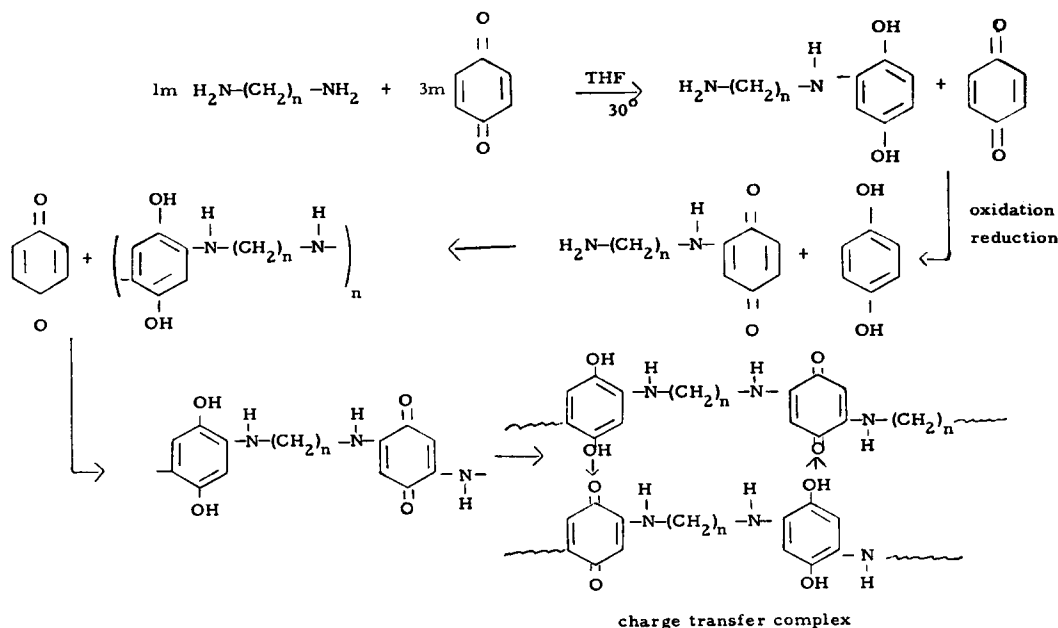


Fig. 1. Proposed reaction sequence of benzoquinone with α, ω -alkanediamines.

groups, when "oriented," as a charge transfer complex, yielded material of high thermal conductivity.

A possible reaction sequence for the formation of the polymer is shown in Figure 1. In the first reaction step, the diamine adds to the benzoquinone which is simultaneously reduced to the hydroquinone. The product, in an excess of benzoquinone, is rapidly oxidized and undergoes a second amine addition thus forming the aminohydroquinone polymer.¹⁰ This polymer, in the presence of benzoquinone, is partially oxidized but becomes insoluble in THF prior to complete oxidation. Although the reaction sequence depicts the final product as alternating quinone and hydroquinone groups, the backbone structure most probably contains sequences of quinone and some hydroquinone groups. In addition, the flexibility of the

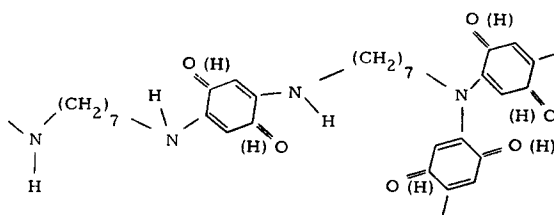


Fig. 2. Proposed structure of polyaminoquinone prepared from 1,7-heptanediamine and benzoquinone.

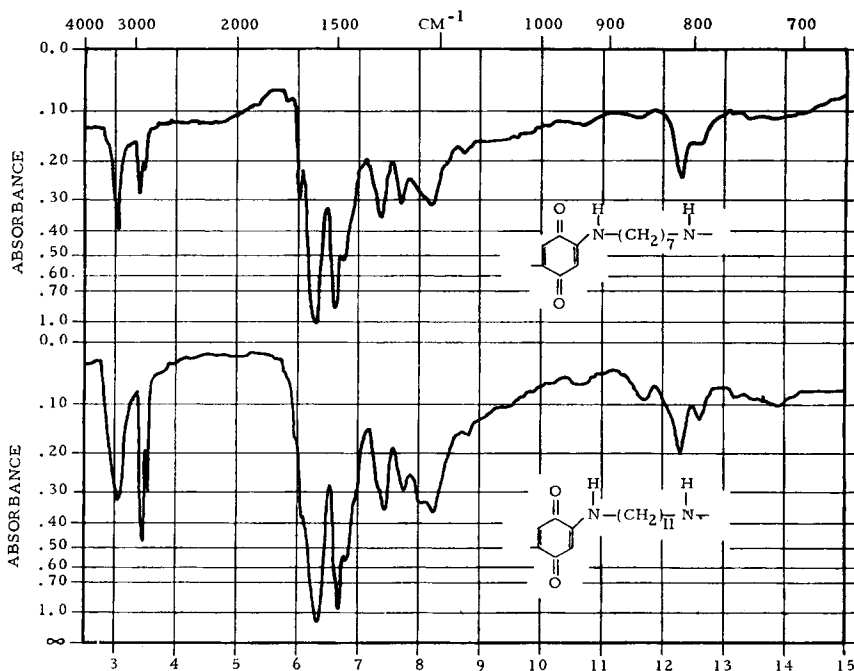


Fig. 3. Infrared spectrum of some polyaminoquinones.

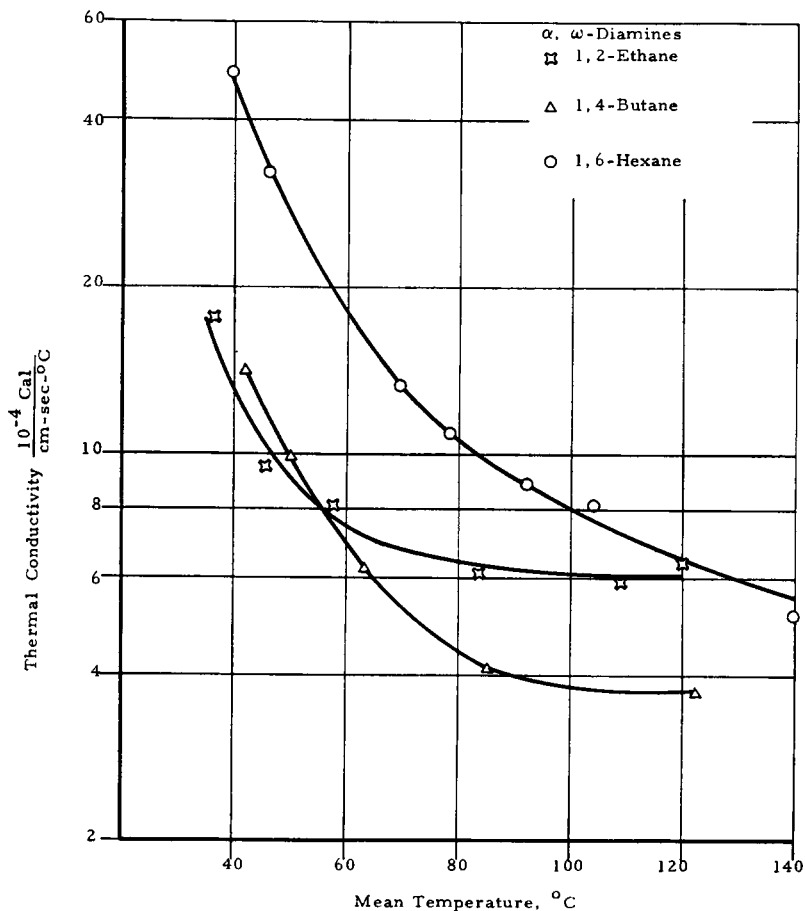


Fig. 4. Thermal conductivity-temperature plot.

alkane chain permits the formation of strong inter and intramolecular complexes of quinhydrone.^{5,7,8} Figure 2 depicts a possible structure of the crosslinked 1,7-aminoquinone polymer based on infrared, thermal stability and elementary analysis. The elementary analysis of the polymer is given below:

	%C	%H	%N	%O
Found	66.86	6.89	9.13	16.62
Theory	66.80	6.94	9.72	16.65

Figure 3 depicts two typical infrared 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

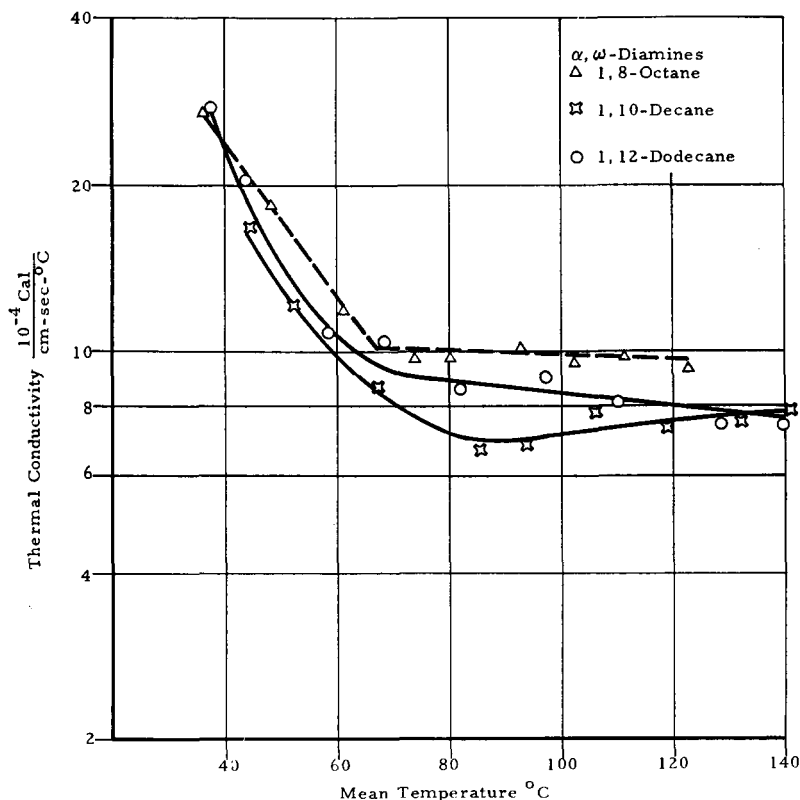


Fig. 5. Thermal conductivity-temperature plot.

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} . This absorption band is also present in the polymer prepared by reacting benzoquinone with N,N' -dimethyl-1,6-hexane-diamine and therefore excludes the possibility of absorption due to oxime formation. Additional, tentative, absorption band assignments are given in Table II.

The thermal conductivity-temperature (k - T) behaviors of the polymers prepared from benzoquinone and the α, ω -alkanediamine series are shown in

TABLE II
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

Figures 4 through 7. In all cases, except for the polymer prepared from the 1,9-nonanediamine, 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

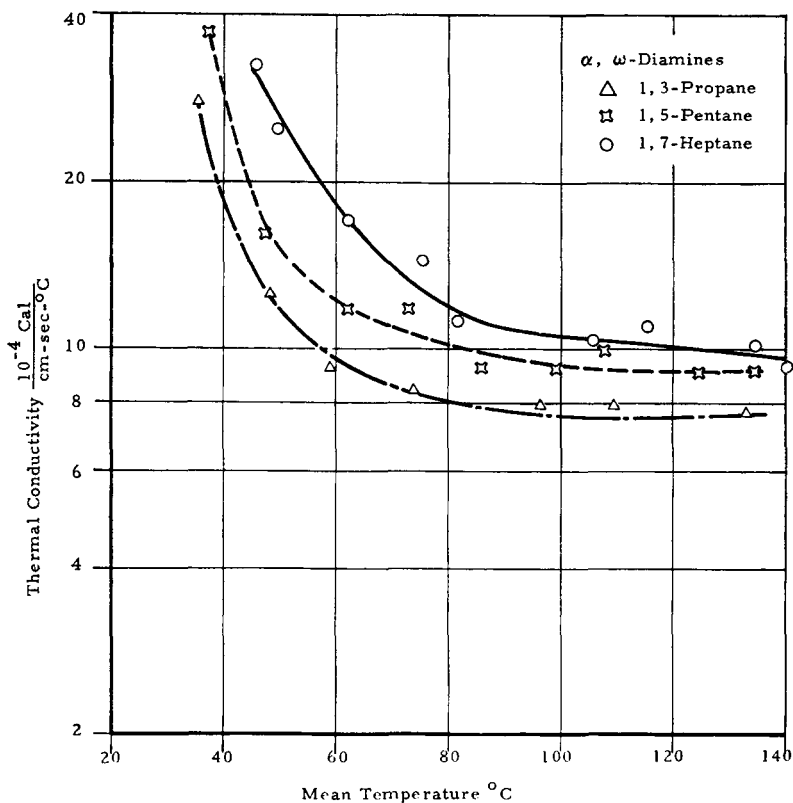


Fig. 6. Thermal conductivity-temperature plot.

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 6. The similarities of the (k - T) curves of quinhydrone and the amino-quinone 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

methylene 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 8. In addition, the polymers prepared from the odd numbered α,ω -diamines display increased thermal conductivity as compared to neighboring even numbered diamines.

At present, the mechanical properties of the polymers have not been studied in any detail; however, we have observed, as expected, an increase of flexibility as the number of methylenic groups were increased from 2 to

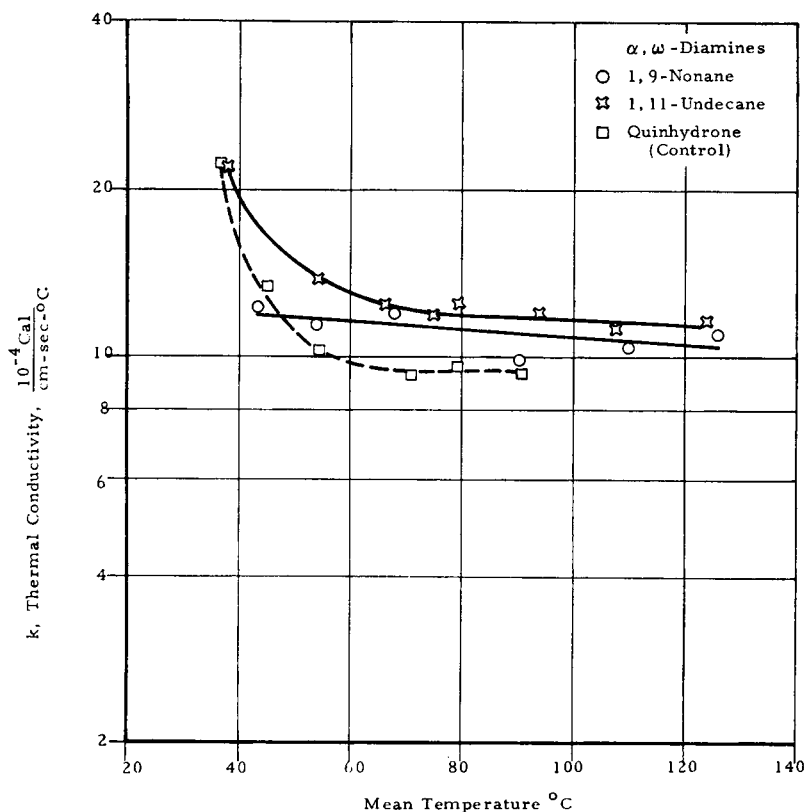


Fig. 7. Thermal conductivity-temperature plot.

12. The polymer prepared from the benzoquinone-1,2-ethanediamine reaction was brittle and glassy, compared to the tough flexible polymers prepared from diamines containing at least 5 methylenic groups. During the preparation of the thermal conductivity pellets, using elevated temperature and pressure, a brief flow of the polymer occurs. The briefness of the flow, which is followed by a dimensional stability to further heat and pressure, indicates the formation of a three-dimensional crosslinked network. This

conclusion was substantiated by recent work in which the dynamic modulus of elasticity was monitored as a function of temperature utilizing the vibrating reed.⁹ These results will be published at a later date. Infrared analysis of the polymer before and after thermal and pressure treatment are

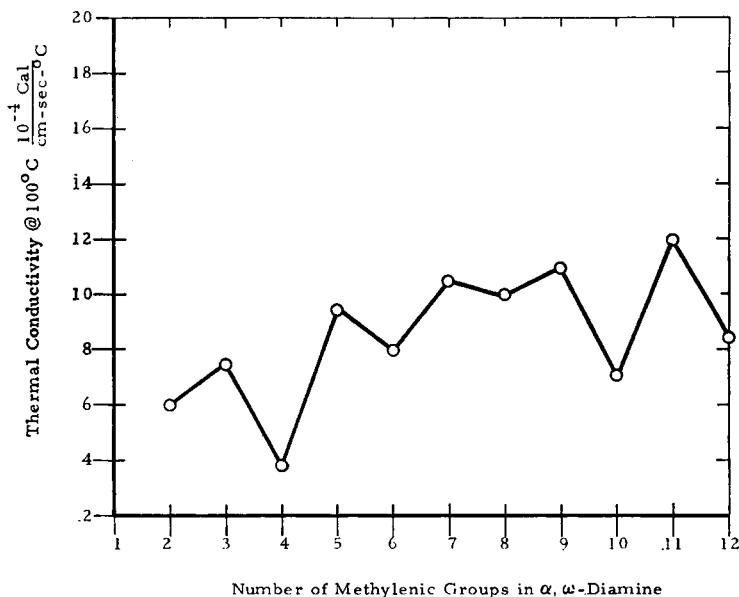


Fig. 8. Thermal conductivity as a function of methylenic groups in the α, ω -diamines.

identical thus indicating no major chemical changes due to pressure and temperature.

CONCLUSIONS

A series of electron transfer polymers have been prepared by reacting a number of α, ω -alkanediamines with benzoquinone. The polymers display high thermal conductivity with a strong temperature dependency presumably through the formation of molecular charge transfer complexes.

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