Electrically conducting three-dimensional (octacyano phthalocyaninato polysiloxane) polymer

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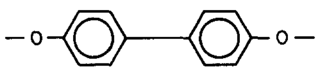
Polymeric (octacyano phthalocyaninato polysiloxane) has been prepared by reacting 1, 2, 4, 5 tetracyano benzene (TCNB) with silicon tetrachloride in refluxing quinolene and hydrolysing the resulting product with dilute alkali. The product has been characterized by infrared (i.r.), ultraviolet–visible (u.v.–vis.) spectra, elemental analysis and electron spectroscopy chemical analysis (ESCA). The polymer shows improvement in electrical conductivity by six to seven orders of magnitude ($10^{-1}\,S\,cm^{-1}$) on thermal treatment.

(Keywords: polymeric phthalocyanine; (octacyano phthalocyaninato polysiloxane) polymer; electrical conductivity; bridge-stacked structures; charge carriers; thermal treatment)

INTRODUCTION

Phthalocyanines and their polymers are known to have highly aromatic structures and excellent stability against heat, light, moisture and air. Hence they have attracted a great deal of attention in the search for environmentally stable, electrically conductive polymers[1–4]. Polymers in which neighbouring phthalocyanine rings are cofacially stacked through substituent atoms or ligands, such as F, O, C_2^-, CN^-, pyrazine, 4,4′-bipyridine and 1,4-dicyanobenzene, attached to the central metal atom (like washers threaded onto a shaft) show improved electrical conductivity on doping with electron acceptors such as I_2 (References 5–11). The conductivity of the doped polymers decreases with increasing metal-to-metal distance due to diminishing intermolecular charge transfer[12]. The improved conductivity remains only as long as the dopant molecules are retained in the polymer. Like all other one-dimensional conductive polymers, these doped polymers are predicted to undergo metal to semiconductor transition (Peierl's instability) at low temperatures[13].

The metal to semiconductor transition in most of the one-dimensional systems could be avoided by improving interchain interactions[14]. This would be possible if electron-withdrawing substituents were present in the polymer: for example, substituted phthalocyanines such as octacyano copper phthalocyanine exhibit large electrical conductivity due to intermolecular charge transfer[15]. Polymeric phthalocyanines possessing substituents like —CN, —COOH



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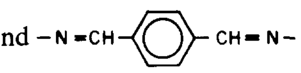

have been prepared and shown to exhibit stable electrical conductivities by thermal treatment[16–19].

This paper is concerned with the preparation of (octacyano phthalocyaninato polysiloxane) polymer (*Figure 1*), in which adjacent phthalocyanine moieties are laterally connected through conjugated $-\overset{|}{C}=N-\overset{|}{C}=N-$ type structures and neighbouring phthalocyanine rings are cofacially assembled through Si—O—Si linkages. Hence it is expected to have both lateral and longitudinal overlap of phthalocyanine π orbitals, which could make

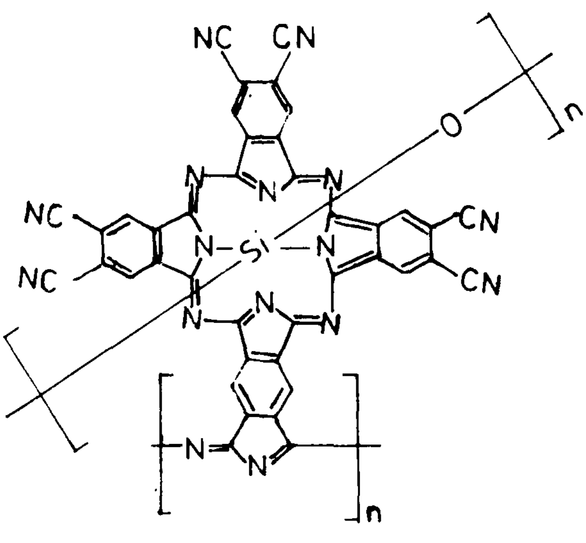

Figure 1 (Octacyano phthalocyaninato polysiloxane) polymer $(C_{40}H_8N_{16}\,SiO)_n$

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the interactions three-dimensional. Thermal treatment of this polymer is expected to result in formation of extended conjugated structures through opening of peripheral cyano groups, so that any discontinuity in the conduction path in a particular direction could be compensated by the availability of extended conjugated structures in other directions. In addition to this, unreacted silanol moieties in the polymer could undergo further condensation to give more Si—O—Si bridge-stacked linkages, leading to very large conductivity. In the light of the recent interest in electrically conductive polymers for various applications[20–23], we have undertaken a detailed study of the structure and the effect of thermal treatment on the electrical conductivity of the polymer.

EXPERIMENTAL

Tetracyanobenzene (TCNB) was prepared from pyromelliticdianhydride (PMDA) by the procedure of Norrell *et al.*[16]. It was recrystallized from dioxane. $SiCl_4$ (BDH) was distilled and used. Quinolene was vacuum distilled over KOH and used fresh. Only distilled solvents were used for washing and purification of the polymer.

Preparation of poly(octacyano phthalocyaninato polysiloxane)

TCNB (1.78 g; 10 mmol) was heated with $SiCl_4$ (5.99 g; 35 mmol) in refluxing quinolene (12 ml) for 5 h. The mixture was cooled to room temperature, diluted with $CHCl_3$ and filtered. The residue was extracted with chloroform for 2 h and then with acetone for 2 h in a Soxhlet apparatus. The product was dried at 80°C for 2 h in vacuum. Analysis for $C_{40}H_8N_{16}SiCl_2$ was as follows: calculated - Cl, 8.7; N, 27.62%; found - Cl, 3.2; N, 27.4%. The product (0.75 g) was treated with 3 ml pyridine and 24 ml 1% NaOH solution. The mixture was refluxed for 1 h and filtered. The residue was washed with water several times until it was free from pyridine. The product (0.5 g) was dried at 100°C in vacuum for 4 h. Analysis for $(C_{40}H_8N_{16}SiO\ 3H_2O)_n$ was as follows: calculated - C, 59.24; H, 1.73; N, 27.63; Si, 3.45%; Cl, nil; found - C, 59.74; H, 1.76; N, 26.83; Si, 3.5%; Cl, nil.

The silicon content of the polymer was determined from the residue obtained after completely burning the compound in air, by thermogravimetric analysis (t.g.a.).

Infrared (i.r.) spectra of the samples were recorded in KBr pellets with a Perkin–Elmer 283 spectrometer.

Ultraviolet-visible (u.v.-vis.) spectra of the sparingly soluble portion of the sulphuric acid solution of the polymer were recorded using a Varian Cary 2390 UV–VIS–NIR spectrophotometer.

Thermal treatment. The above polymer was pressed into pellets of diameter 13 mm and thickness approximately 1 mm under 9 tons of load in a Carver press. The pellet was heated in helium ($\approx 50\,\mathrm{ml\,min^{-1}}$) at a rate of $20°\mathrm{C\,min^{-1}}$ from 30°C to 750°C; after being held at 750°C for 20 min the pellet was cooled to room temperature in helium. The pellet was loaded into the Keithley conductivity adaptor and electrical conductivity was measured.

Measurement of electrical conductivity. The electrical conductivities were obtained by using a cell containing a guard ring and electrodes made of stainless steel discs. The special mounting devices of a Keithley 6105 resistivity adaptor were used for making measurements. The measuring circuits consisted of an HP 6144 precision power supply and a Keithley 6100 solid state electrometer. Measurements were made by maintaining a constant disc potential across the sample pellets and the current was recorded continuously. The conductivity was calculated using the formula[24] $\sigma(\mathrm{S\,cm^{-1}}) = di/AV$, where d is sample length (cm), i is current (amps), A is area of the pellet ($\mathrm{cm^2}$) and V is applied potential (volts).

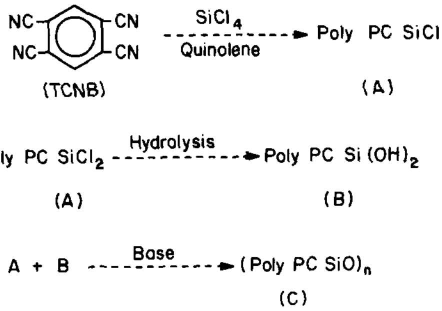
RESULTS AND DISCUSSION

1,2,3,4-Tetracyano benzene was heated with silicon tetrachloride in refluxing quinolene. This procedure is adapted from the methodology used by Kenney *et al.*[25], for the preparation of monomeric phthalocyaninato silicon analogues from 1,2-dicyano benzene. The i.r., u.v.-vis. ESCA (electron spectroscopy chemical analysis) and elemental analysis data agree with the following results.

Polymeric (octacyanophthalocyaninato polysiloxane) of the structure shown in *Figure 1* is formed by the reaction Scheme 1. The mechanism for the reaction producing the network polymer is probably similar to that of formation of polymeric (octacyano copper phthalocyanine) from TCNB and copper salts[26].

The dichloro compound A undergoes partial hydrolysis to the corresponding dihydroxy compound B through the adventitious moisture impurity present during work-up of the system. This is inferred by the observation that the chlorine content of the intermediate isolated before the alkali treatment step was 3.2% instead of the calculated value of 8.7% from the molecular formula $C_{40}H_8N_{16}SiCl_2$ of the compound A (*Scheme 1*), the nitrogen content agreeing with the calculated value of 27.6%. The compounds A and B undergo self-condensation to give the bridge-stacked polymer C (*Scheme 1*), in presence of alkali. Since the reaction is carried out at lower temperature (refluxing NaOH solution) and for 1 h, the number of bridge-stacked units formed is believed to be small[27].

It is known[26,28] that heating of 1,2,4,5-tetracyano benzene with metal or metal salts may lead to different reaction products, namely polymeric (octacyano metallophthalocyanine) (*Figure 1*), polyisoindolenines (polynitriles), *Figure 2a*, polytriazine (*Figure 2b*), polymeric phthalocyanine, in which benzene rings of the adjacent macrocycles are shared in common (*Figure 2c*), and their copolymers. Polynitriles from benzonitrile, succinonitrile



Scheme 1 Formation of polymeric octacyano phthalocyaninato polysiloxane. The structure of polymer C is shown in *Figure 1*

or oligoisoindolene from 1:2 dicyano benzene show broad absorption between 1700 and 1600 cm^{-1} without any fine structure[28–30]. The polymer C (*Scheme 1*) obtained in the present case, gives a good resolved i.r. spectrum (*Figure 3*) without any such broad absorption in the above region, indicating the absence of polynitrile (*Figure 2a*) type structures. The absence of peaks at 1360 and 1520 cm^{-1} in the i.r. indicates absence of polytriazine structures (*Figure 2b*) also[31,32]. The extremely fused structure shown in *Figure 2c* should have very little or no cyano peak in the i.r. But the polymer C (*Scheme 1*) shows a clear-cut peak at 2220 cm^{-1}, indicating absence of such structures. Moreover, the elemental analysis for the fused structure (*Figure 2c*), should correspond to $C_{20}H_4N_8SiO$ $3H_2O$ with C, 52.86; H, 1.56; N, 24.67; and Si, 6.67%; whereas the observed values are C, 59.74; H, 1.86; N, 26.8; Si, 3.5%, which agree with the molecular formula $C_{40}H_8N_{16}SiO$ $3H_2O$, corresponding to the structure shown in *Figure 1*. Hence the exclusive formation fused ring structure (*Figure 2c*) is ruled out. The formation of copolymer of the above is also ruled out on similar grounds. The i.r. spectrum (*Figure 3*) shows the characteristic peaks assignable to phthalocyanine skeleton at 750–770, 890–910, 1010–1020, 1080, 1140–1150 and 1300 cm^{-1}, which indicates the presence of phthalocyanine moieties[33–35].

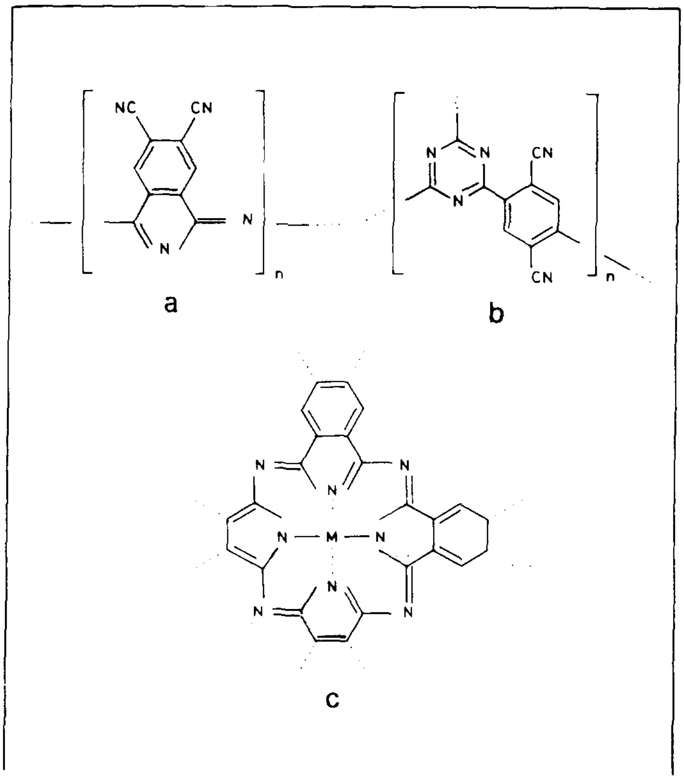


Figure 2 (a) Polyisoindolenines (polynitriles). (b) Polytriazines. (c) Polymeric phthalocyanines (M = $\{$Si—O$\}_n$

The u.v.–vis. spectrum of the limited soluble portion of the polymer in concentrated H_2SO_4 (*Figure 4*) shows the absorption peaks characteristic of the substituted phthalocyanine structures at 740, 690 and 630 nm and the soret band at 348 nm. Their absorption coefficients are comparable with the values reported for substituted metallophthalocyanines[33–35] (*Table 1*). The ratio of the intensity of the peaks at $\lambda = 215$–230 nm to that at λ_{max} (≈ 740 nm) is 0.801, indicating that the polymer is structurally uniform[33–35].

The ESCA binding energies of C(1s), indolene N(1s) and aza N(1s) occur at 285.2, 400.3 and 401.3 eV, respectively. These values agree with the reported values for phthalocyanine structures[17].

The presence of bridge-stacked Si—O—Si links in the polymer is proved by the presence of an i.r. absorption peak at 987 cm^{-1} (Reference 36). This is further confirmed by ESCA. The observed binding energies for Si(2s) and Si(2p) for the polymer occur at 156.0 and 103.2 eV, respectively. The corresponding values for SiO_2 and polydimethyl siloxane, where Si is tetra coordinated are 152.7 and 102.0 eV, respectively[37,38]. Thus there is an increase of ≈ 3.5 eV in the Si(2s) values and ≈ 1.2 eV in the Si(2p) values for the present polymer, which has the bridge-stacked structures shown below:

$$\begin{array}{c} \mathrm{N}\quad\mathrm{N}\quad\mathrm{N}\quad\mathrm{N} \\ \backslash\quad/\quad\backslash\quad/ \\ -\mathrm{Si}-\mathrm{O}-\mathrm{Si}- \\ /\quad\backslash\quad/\quad\backslash \\ \mathrm{N}\quad\mathrm{N}\quad\mathrm{N}\quad\mathrm{N} \end{array}$$

In this structure the silicon atoms are hexacoordinated and the presence of phthalocyanine ligand on the silicon atom probably causes a positive shift in the binding energy values of Si(2s) and Si(2p).

Thus the polymer is believed to have the structure shown in *Figure 1*. The presence of bound water molecules was confirmed by isothermal heating of a known weight of the polymer sample at 250°C for 5 h in

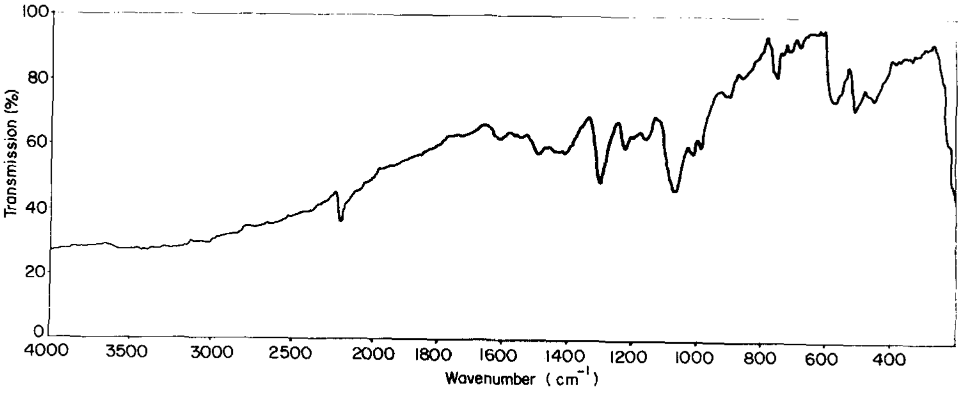


Figure 3 I.r. spectrum of (octacyano phthalocyaninato polysiloxane) polymer

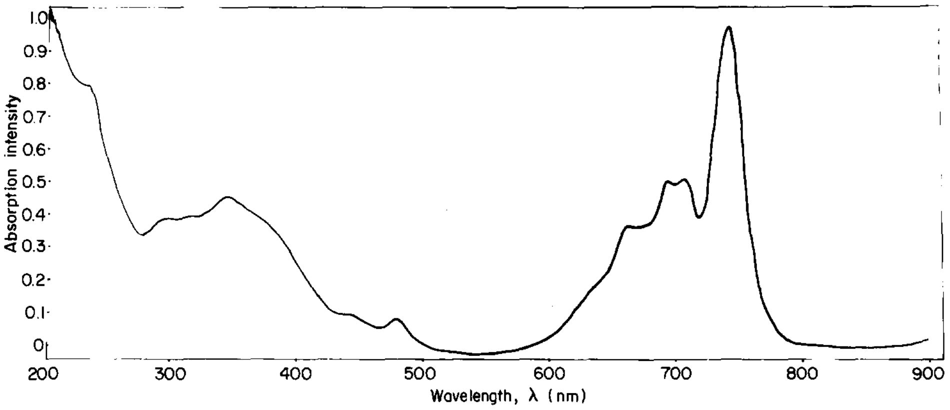


Figure 4 U.v.–vis. spectrum of (octacyano phthalocyaninato polysiloxane) polymer

Table 1 Absorption coefficients at different wavelengths in the u.v.–vis. spectrum of the polymer (concentration: 9.6 mg/1000 ml in 97% sulphuric acid)

Wavelength (nm)	Absorption coefficient[a] (l g^{-1} cm^{-1})
740	104.00
720	57.29
692	54.16
660	41.67
630	20.80
476	10.41
346	47.91
290	41.66
233	83.33

[a] Since the molecular weight of the polymer is not known absorption coefficients are expressed in l g^{-1} cm^{-1}

Table 2 Room temperature electrical conductivity of the polymeric (octacyano phthalocyaninato polysiloxane) after heating at various temperatures and the corresponding weight losses

Temperature[a] (°C)	Weight loss (%)	Electrical conductivity (S cm^{-1})
Before heat treatment	—	2.6×10^{-7}
450	6.0	3.2×10^{-5}
750	14.0	4.0×10^{-1}

[a] Polymer pellets are heated in helium atmosphere from room temperature (30°C) to the noted temperature at a rate of 20°C min^{-1} and held at that temperature for 20 min

vacuum (1 mm Hg $\approx 10^{-2}$ Pa). The weight loss was 7%, which agrees with the presence of three molecules of water per repeat unit.

Electrical conductivity studies

Table 2 shows the electrical conductivity of the polymer before and after heat treatment at various temperatures and the corresponding weight losses during the heat treatment. It is obvious from the table that the electrical conductivity increases by two orders of magnitude on heating the polymer to 450°C and by six orders of magnitude on heating to 750°C. It is also seen that the weight loss was 6% when the polymer was heated to 450°C. This corresponds to elimination of three molecules of water from the starting polymer and formation of more bridge-stacked linkages, namely Si—O—Si bond formation. It is reported that bridge-stacked structures are easily formed on heating the corresponding silanols[15]. Heating to 750°C has resulted in a weight loss of 14%, of which 6% accounts for the loss of water molecules and the excess 8% loss is probably due to the formation of pre-graphite polycondensed ring structures.

For most organic compounds possessing cyclizable terminal groups, in general, heating to 700–800°C is followed by a large increase in conductivity due to formation of polycondensed ring structures leading to carbonaceous residues[39]. It is observed that the nitrogen content of the present polymer after heating has become 24.5%. This indicates that carbonization has occurred only to a very small extent, probably through the elimination of some of the terminal cyano groups.

The increase in electrical conductivity may be explained via the formation of extended conjugated structures which promote charge carrier mobilities and also through formation of radicals which cause increase in their numbers[14]. The formation of extended conjugated structures is proved by the i.r. spectrum of the heat-treated polymer, whch shows a large decrease in —CN absorption (at 2220 cm^{-1}) and a broad band at 1600–1620 cm^{-1}, indicating the formation of —C=N—C=N— structures through cyclization of terminal cyano groups[26]. In addition to this, the i.r. spectrum contains the characteristic absorption bands assignable to phthalocyanine skeleton. The spectrum, however, shows bands with loss of fine structure and lower intensities than the parent compound. The ESCA of the heat treated polymer shows characteristic core binding energies of C(1s), N(1s), Si(1s), Si(2p) and O(1s). These observations indicate that thermal treatment has not affected the phthalocyanine skeleton.

The formation of free radical defects in the heat treated polymer is proved by the presence of a broad electron spin resonance (e.s.r.) signal of line width 40 mT. Radical defects in the form of solitons (bond alternation defects) as in *trans* polyacetylene could be expected in the phthalocyanine polymer due to the presence of energetically identical mesomeric structures of iso-indolene and phthalocyanine moieties, as shown in *Figures 5a* and *b*. When transition occurs between phases A and B or A′ and B′, the system passes through soliton bound states[40,41,17]. The electronic conduction in the polymer could be explained via hopping of these bound states from one chain to another, as in lightly doped polyacetylenes or pyrolysed polyimides[42,43].

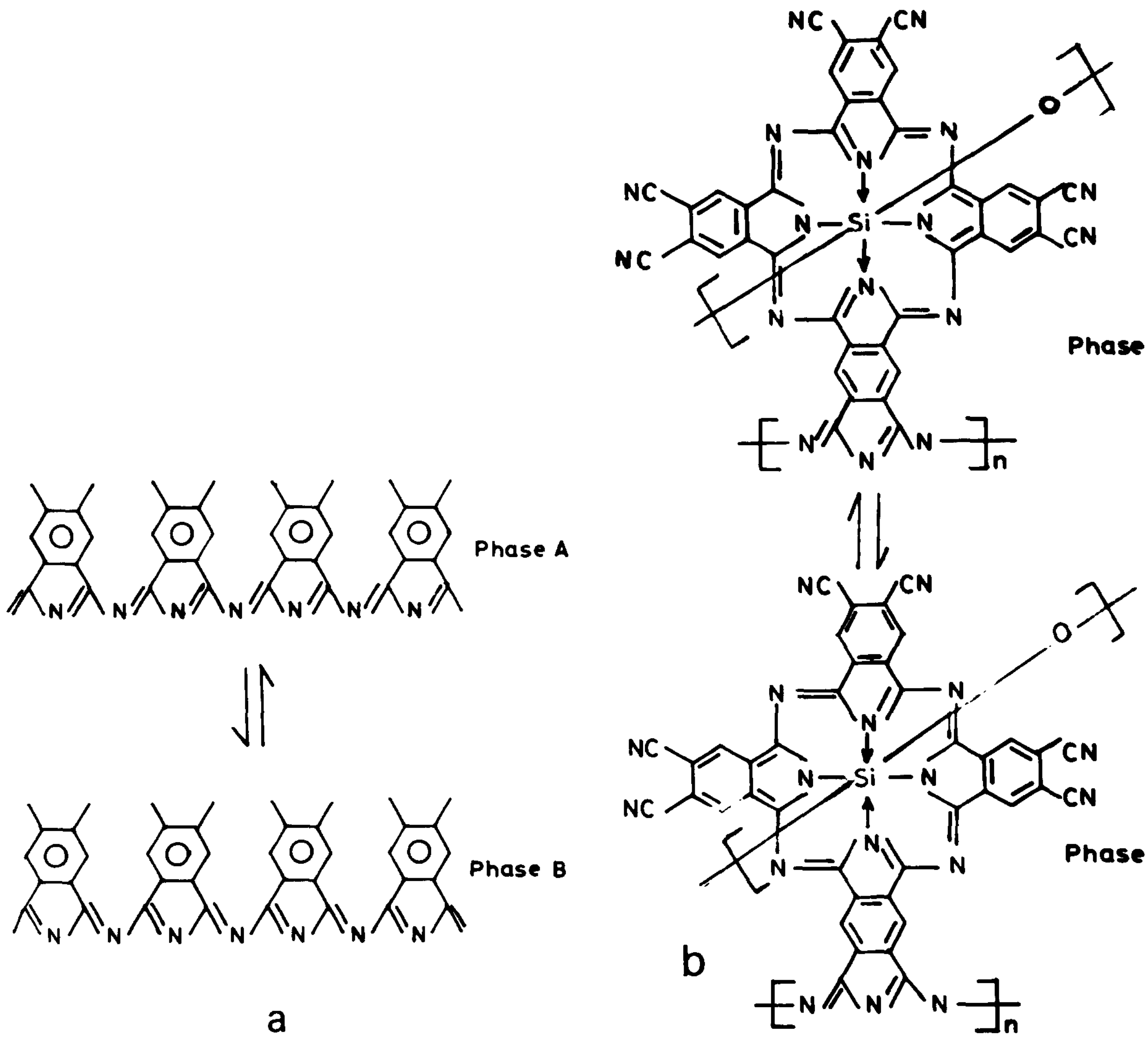


Figure 5 Ground state bond alternation patterns of the polymer poly(phthalocyaninato polysiloxane): (a) indolene moieties; (b) phthalocyanine moieties

The reported electrical conductivities of simple phthalocyanines and various types of polymeric phthalocyanine are compared with the electrical conductivity of polymeric (octacyano phthalocyaninato polysiloxane) in *Table 3*. From the table it is obvious that the electrical conductivity of polymeric phthalocyanines is higher than unsubstituted monomeric phthalocyanines. This is probably due to an increase in the extent of conjugation in polymeric phthalocyanines, which causes intermolecular charge transfer[15]. The conductivity of cofacially stacked phthalocyanine polymer, in which phthalocyanine moieties are joined through Si—O—Si linkages with metal-to-metal distance 3.33 Å* is 10^{-7} S cm^{-1}. This is due to intramolecular charge transfer between phthalocyanine π orbitals[15]. This improves to large values (≈ 1 S cm^{-1}) on partial oxidation with iodine, due to formation of segregated stacks of metallomacrocycle radical cations and parallel arrays of polyhalide anions[13]. Poly(copper octacyanophthalocyanine)[26], in which phthalocyanine moieties are connected through conjugated $-\overset{|}{C}=N-\overset{|}{C}=N-$ linkages, has conductivity of the order of 10^{-7} S cm^{-1}. This is shown to improve by eight orders of magnitude (10 S cm^{-1}) on thermal treatment due to formation of conjugated network structures through the opening of peripheral cyano groups. It may, therefore, be inferred that the electrical conductivity of polymeric phthalocyanines improves to large values whether the overlap of π orbitals occurs along the plane of the phthalocyanine ring or perpendicular to it.

Table 3 Electrical conductivities of monomeric and various polymeric phthalocyanines

Compound	Room temperature electrical conductivity (S cm^{-1})
Monomeric phthalocyaninato silicon dihydroxide (Pc Si(OH)$_2$)[15]	6.0×10^{-9}
Cofacially stacked phthalocyaninato polysiloxanes (Pc SiO)$_n$[15]	3.0×10^{-7}
Polymeric copper[a] (octacyano phthalocyanine)[26]	6.7×10^{-7}
Polymeric (octacyano phthalocyaninato polysiloxane)[b]	2.6×10^{-7}

[a] The conductivity of the sample heated to 203°C in helium is reported
[b] This work

In the polymer of the present work, on the other hand, both intra- and intermolecular charge transfers could be

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* 1 Å = 10^{-1} nm

expected through lateral overlap of π orbitals via formation of conjugated $-\overset{|}{C}=N-\overset{|}{C}=N-$linkages and through longitudinal overlap of phthalocyanine π orbitals due to formation of more Si—O—Si links, on thermal treatment. The observed electrical conductivity for the unheated polymer is comparable with that of longitudinally stacked $(PcSiO)_n$ polymer[15] and laterally stacked (octacyano copper phthalocyanine) polymer[26]. The (octacyano phthalocyaninato polysiloxane) shows a lower electrical conductivity, probably due to the presence of fewer bridge stacked linkages in the unheated polymer. The electrical conductivity of the heat-treated polymer, however, is less than that of heat-treated (octacyano copper phthalocyanine) polymer. This is probably due to the steric hindrance caused by the PcSiO moieties, which prevent formation of network structures via opening of cyano groups or vice versa. The steric factor hinders inter- and intramolecular charge transfers. This effect is probably overcome at higher temperatures. This inference is supported by the observation that an increase of heating temperature from 450 to 750°C causes an increase in electrical conductivity by four orders of magnitude, i.e. 3.2×10^{-5} to $4\times10^{-1}\,S\,cm^{-1}$ (*Table 2*). Thus the temperature of heat treatment seems to play a vital role in the enhancement of electrical conductivity, which depends on the geometry of the structures formed that controls the movement of charge carriers within the chain and from one chain to the other.

CONCLUSIONS

(Octacyano phthalocyaninato polysiloxane) polymer has been prepared and characterized. The polymer, on heating to 750°C in inert atmosphere, shows an increase in electrical conductivity by six orders of magnitude. The improved electrical conductivity of the heated polymer is attributed to lateral overlap of π orbitals through formation of polycondensed ring structures via opening of terminal cyano groups and to longitudinal overlap of phthalocyanine π orbitals due to formation of more Si—O—Si linkages.

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