

New conducting polymers, 3.* Doping, stability, electrical, and optical characteristics of poly-(P-phenylphosphoethynediyl)

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Abstract: Studies on direct-current electrical conductivity and optical properties of a new solution of processable conducting polymer are reported. Electrical conductivity of thin films of the polymer on glass plate at room temperature was 6×10^{-6} S/cm. Study of conductivity with variation of temperature does not provide any definite thermal activation energy, which is in accordance with the amorphous nature of polymer. Optical absorption data adopting the Bardeen equation showed that maximum 'optical gap' (E_g) is 3.30 eV. Doping with Br₂-vapor was found to be only partially effective in decreasing E_g by 0.43 eV. The polymer was found to be quite stable under normal atmospheric conditions. Environmental stability of both undoped and doped polymer has been discussed.

Key words: Conducting polymers; processability; optical gap; doping; environmental stability

Introduction

Synthesis of stable and processable conducting polymers is of current academic as well as commercial interest [1]. 3-substituted polythiophenes are now considered to be in this desirable class of polymers, because some of them are soluble in common solvents due to the presence of proper substituents [2]. Methyl group substitution to the simplest aliphatic chain conducting polymer, i.e., polyacetylene, imparts solubility to the system, but it becomes more susceptible to atmospheric degradation [3]. Using the concept of participation of non-bonded pairs of electrons to the electronic delocalization in the chain, we synthesized a simple aliphatic chain polymer with carbon and phosphorus atoms in the backbone providing phenyl pendent groups to the chain. The polymer was synthesized through condensation polymerization of diiodoacetylene and dilithium derivative of dichlorophenyl phosphine [4]. That the polymer

chain is electron delocalized with participation of non-bonded pairs of electrons of phosphorus atoms is evident from spectral responses [5]. In contrast to well-studied conducting polymers [6], this polymer is soluble in some high-boiling polar solvents. This enables us to cast thin films on glass plate. The films are not free-standing due to the low molecular weight of the polymer. The virgin polymer in the film formed shows direct-current (dc) electrical conductivity value ($\sim 6 \times 10^{-6}$ S/cm), which is comparable to the undoped *trans*-polyacetylene ($\sigma \simeq 10^{-5}$ S/cm) [6, 7]. It is also found to be thermally stable. Degradation starts at above 250 °C in air [5].

Here we discuss the electrical and optical properties, and environmental stability of both the virgin and the doped polymer.

Experimental

Film preparation

Uniform thin films on glass substrate were obtained by spin-coating technique using a specially designed apparatus [8].

*Part 2: [5]

Polymer solution in dimethyl formamide (20% w/v) was placed on a clean glass plate mounted on the rotating disc of the apparatus. The disc was rotated at high speed (~ 2000 rpm) for 30 s to obtain a thin uniform coating of the polymer on glass plate. Polymer films of various thicknesses (0.2–1.4 μm) were obtained by controlling the speed of rotation and heating the disc. Film thickness and uniformity were determined with a Surfometer SF 101 planer product (UK).

Electrical conductivity measurement

Direct-current electrical conductivity of the polymer films on glass substrate was measured by the two-probe method. The principle of this measurement was to apply certain dc potential across the sample and to measure the current passing through it. A Philips (Model PP 9004) dc micro-voltmeter was used in this measurement. Graphite paint (Acheson DAG 540) was applied by brushing it on at the two ends of the polymer film to make electrical contacts, which were tested to be ohmic.

Electrical conductivity measurement was also carried out by varying the temperature between 300–406 K.

Thermoelectric test

Carrier-type of the material was determined by using thermoelectric test. The method [9] was based on the deflection of a sensitive galvanometer connected between the hot and cold ends of the sample. The sign of deflection indicated the carrier-type.

Optical absorption study

Optical absorption study of the polymer in the film formed on glass substrate was performed using a Shimadzu UV-VIS-NIR spectrophotometer (model UV-365) with reference to glass.

Doping: i) Solution doping

Solution doping of the polymer with iodine (I_2) was carried out by treating 0.1 gm of the powdered polymer in 0.1 M solution of I_2 in *n*-hexane. Doping was carried out at the reflux temperature of the mixture for about 8 h. The treated polymer was then removed and washed thoroughly with the solvent. In an attempt to obtain perchlorate doping, polymer was treated with a concentrated perchloric acid solution in water, as described above, and washed thoroughly with water after the treatment.

Iodine and chlorine content of the treated polymer were then estimated using the Schöniger combustion flask method.

ii) Gaseous phase doping

Gaseous or vapor-phase doping of the polymer was performed on the film cast on glass substrate using iodine, bromine, and oleum vapor.

For doping with I_2 , the film was kept inside a closed glass chamber (with stopcock arrangement) containing solid I_2 . The chamber was then slowly evacuated until violet vapor of I_2 filled the system. The film was kept for 24 h in such condition and then removed, kept in a vacuum desiccator, and evacuated for 0.5 h. Electrical conductivity of this I_2 treated film was then measured.

In Br_2 doping, liquid Br_2 was poured into a 25-ml flask, and the film was exposed to the vapor by holding it on the open mouth of the flask. The experiment was performed on a number of films with different exposure times.

The film was treated with oleum using the same procedure as that of bromine, but this doping was carried out under reduced pressure (~ 100 torr) with an arrangement similar to that of I_2 above. The doping duration was 0.5 h.

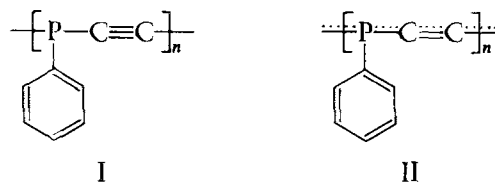
Environmental stability

Environmental stability was studied by keeping the polymer (both powder and film) in a normal environment for a certain period of time and then measuring electrical conductivity in the film form (i.e., the film was cast in the case of powdered material before measurement) to note any effect.

Results and discussion

Electrical and optical properties of undoped polymer

The chemical structure of the polymer, which has been reported elsewhere [4, 5], may be represented by structures I and II:



Electrical conductivity data of the polymer films of various thicknesses at room temperature are shown in Table 1. The average electrical conductivity of

Table 1. Electrical conductivity vs film thickness

Film thickness (in μm)	Conductivity (in S/cm) $\times 10^6$
0.21	6.1
0.57	5.8
0.75	7.2
0.96	4.9
1.32	6.4

the virgin polymer is 6×10^{-6} S/cm. The polymer was scrupulously purified by reprecipitation and thorough washing with distilled and purified solvent to free it from any ionic contaminants. Variation of electrical conductivity (σ) with rise in temperature is shown in Fig. 1. Moderate increase

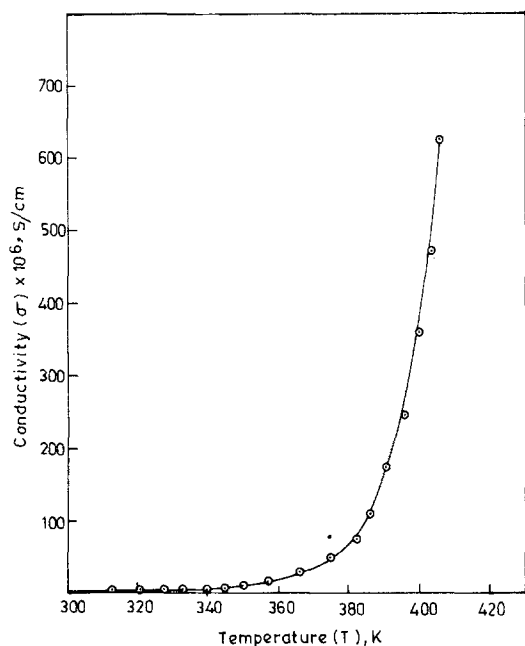


Fig. 1. Variation of the polymer film's conductivity with temperature

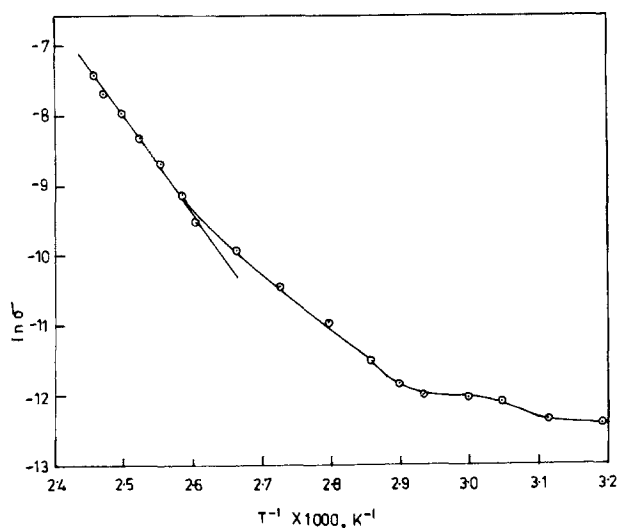


Fig. 2. Plot of conductivity vs T^{-1}

in conductivity was observed within the range 330–385 K, but beyond that, increase in conductivity was very sharp with rise in temperature. Plot of $\ln \sigma$ against T^{-1} is shown in Fig. 2. The slope of the curve is found to vary with temperature and, hence, no definite thermal activation energy is calculated. This behavior may be due to the amorphous nature [10] of the polymer. That the polymer is amorphous is also observed in x-ray diffractogram of the material [4].

Thermoelectric test showed that the hot point acted like the positive terminal of a battery and, hence, it is an *n*-type material [9].

Optical absorption spectrum of polymer films of different thicknesses (0.18, 0.75, and 1.29 μm) showed similar behavior, i.e., absorption starts from wavelength of radiation ~ 500 nm. No sharp absorption edge is observed, which is in accordance with the nature of the amorphous material. One such spectrum is shown in Fig. 3. Maximum "optical gap" (E_g) is determined by using the expression given by Bardeen *et al.* [11]:

$$\alpha \propto (h\nu - E_g)^2/h\nu$$

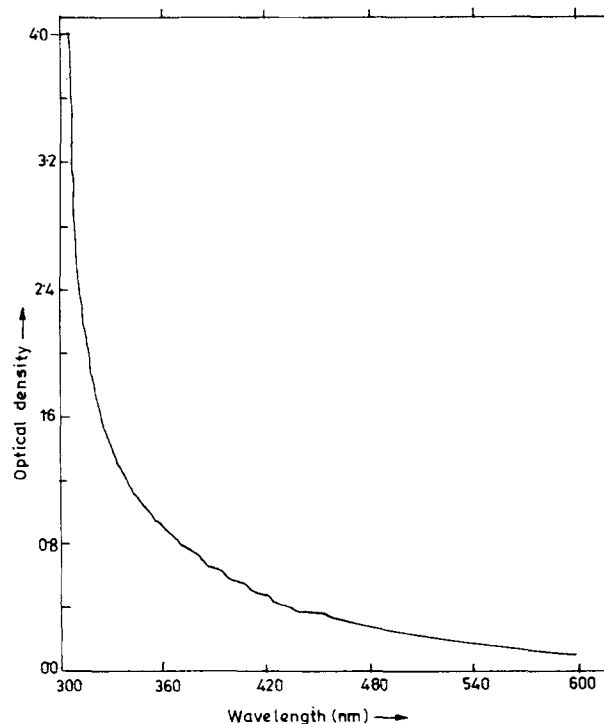


Fig. 3. Optical absorption spectrum of the polymer film on glass substrate (thickness 1.29 μm)

where $\alpha[(2.303 \times \text{optical density})/\text{thickness}]$ is the absorption coefficient at energy of absorbed radiation $h\nu$. Plot of $(\alpha h\nu)^{1/2}$ vs $h\nu$ is shown in Fig. 4. The intercept of the curve on energy axis gives the value of E_g , which is 3.30 eV.

Electrical conductivity value, increase of conductivity with rise in temperature, and thermoelectric test show that the polymer is *n*-type material with conductivity in the semiconductor region.

Because our material is amorphous in nature, having electrical conductivity in the semiconductor range, we attempted to treat optical absorption data in the same way as the data are treated in the cases of inorganic amorphous semiconductors, such as As_2Te_3 [12], GeTe [13], and As_2Se_3 [14, 15]. Optical gap, estimated using the same Bardeen equation, is applicable for indirect transition. Energy for maximum absorption (E_{max}) is usually considered as a measure for the optical

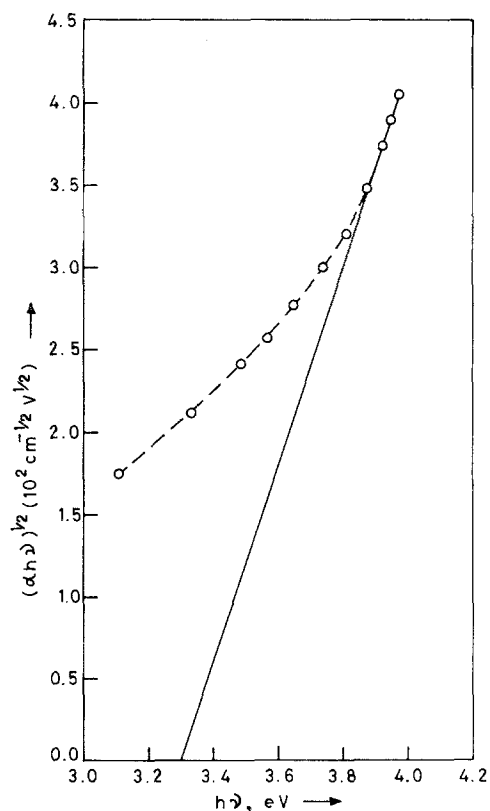


Fig. 4. Plot of the square roots of the product of optical absorption coefficient and photon energy against photon energy for the polymer film

energy gap in conducting polymers. Fincher *et al.* [16], of course, mentioned that the precise value for the energy gap required a detailed theoretical model. Using the conventional definition of the onset of absorption, they estimated the value of E_g for polyacetylene (PA) in the range 1.4–1.6 eV (in contrast to $E_{\text{max}} = 1.9$ eV, for *trans*-PA). These authors, however, have not referred to any definition or equation in this case. However, we followed the method used for estimating the optical gap in amorphous inorganic semiconductors for the treatment of optical absorption data of our polymer. A similar procedure was followed recently by Ikeda and coworkers [17].

Doping and properties of doped polymer

Results of elemental analyses (Cl, I) for perchlorate and iodine doped materials by the Schöniger method [18] showed that no dopant was incorporated in any one of the solution doping processes.

Electrical conductivity measurement was performed to learn the result of doping in the gaseous-phase doping process. Because the amount of the material in the film is very small, no attempt was made to know the amount of dopant incorporated by elemental analysis, as was the case for powder material. In the case of I_2 or oleum doping, the resulting film was very much similar to that of untreated one. There also was practically no change in the electrical conductivity value. However, in case of Br_2 -doping, the appearance of the film was changed. It became visibly less transparent than the undoped one. Electrical conductivity data of the Br_2 -treated film with exposure times are presented in Table 2. These results show that conductivity increases about 200 times on exposing the

Table 2. Electrical conductivity of bromine-doped polymer film with different exposure times

Exposure time (in s)	Conductivity (in S/cm) $\times 10^3$
0	6×10^{-3}
10	1.2
20	1.9
40	2.8
60	3.1
120	3.2
300	2.7

film for about 40 s. Increase in exposure time does not have much effect on the conductivity value, rather it decreases slightly with longer exposure time.

Results of electrical conductivity measurements of the vapor-phase doped polymer films reveal that both I_2 and oleum are not as effective as dopant for our polymer. I_2 was also found to be ineffective as dopant in the cases of poly-para-phenylene (PPP) or poly-phenylene sulfide (PPS) [6] due to its poor oxidizing power. Stability of our virgin polymer is as good as undoped PPP or PPS, which is an indication that it cannot be oxidized by such a poor oxidizing agent as I_2 .

Vapor-phase doping of the polymer with Br_2 was found to be partially successful. Br_2 , being a stronger oxidizing agent than I_2 , might have resulted in oxidation of the polymer chain. Due to high reactivity of Br_2 , an additional type of reaction might have taken place upon longer exposure. This may be the cause for a slight decrease in conductivity value with longer exposure to bromine (Table 2). Similar observation was noted in the

case of doping PA with Br_2 . Decrease in conductivity was observed above 5 mol% doping level. Reactive Br_2 added to the C-C multiple bond ultimately lead to an insulator on higher exposure [19].

Carrier-type determination by thermoelectric test showed that the Br_2 -doped polymer was a *p*-type system. Hence, Br_2 acts as an acceptor dopant.

The optical absorption spectrum of the Br_2 -doped polymer (with exposure time 10 s) is shown in Fig. 5. The estimated value for maximum E_g in this case is 2.87 eV (Fig. 6), which is only 0.43 eV less than in the case of virgin polymer. Hence, Br_2 doping is not as effective in decreasing the polymer's optical energy barrier.

Environmental stability

Storage of the powdered material for about 10 months did not affect the conductivity value (Table 3). In film form, it is also stable for 15 days. IR

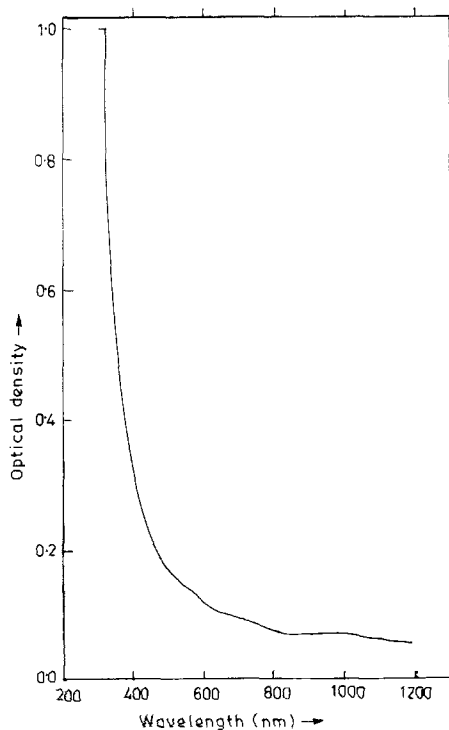


Fig. 5. Optical absorption spectrum of the bromine-doped polymer film (film thickness 0.82 μm)

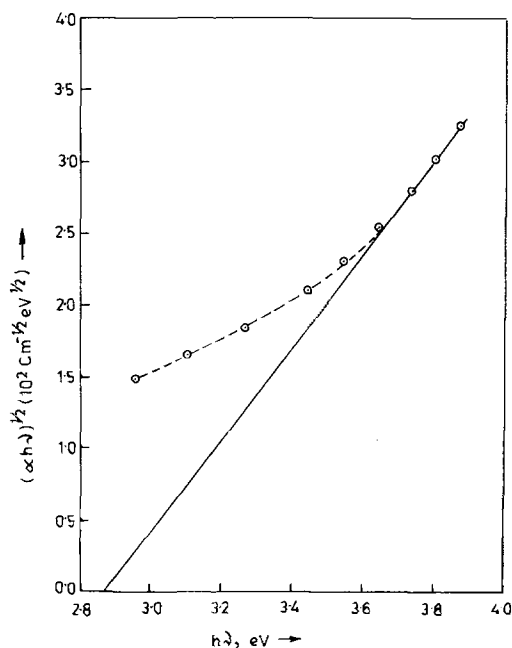


Fig. 6. Plot of the square roots of the product of optical absorption coefficient and photon energy against photon energy for the bromine-doped polymer film

spectra were recorded from time to time during storage and no change was observed in their results. This indicates that the polymer is fairly stable under normal environmental conditions.

Results regarding the change of electrical conductivity value with time for Br₂-doped polymer in normal environment are presented in Table 4. These data show that the doped polymer is not very stable. Rather, it loses its doped conductivity value almost completely within 7 days. This is probably due to the relatively high chemical reactivity of the doped specimen, which reacts with atmospheric moisture and O₂ under normal environmental condition. The stability data may be compared to those of I₂- or AsF₅-doped polyacetylene [7] (Table 5). The results indicate that the

stability of our Br₂-doped polymer is comparable to that of I₂-doped PA, but AsF₅-doped PA is much less stable. AsF₅, being a stronger oxidizing agent than I₂, probably produces a more reactive system after doping. On the contrary, Br₂ (red. pot. 1.065 V) being a stronger oxidizing agent than I₂ (red. pot. 0.53 V) [20] renders our polymer with stability comparable to that of I₂-doped PA.

Acknowledgement

M. S. Rahman is thankful to the Council of Scientific and Industrial Research, New Delhi, for financial assistance in the form of a fellowship.

Table 3. Effect of normal environment on the electrical conductivity of the virgin polymer

State of the polymer	Duration (in months)	Electrical conductivity (in S/cm) × 10 ⁶	
		Initial	Final
Powder	10	6	6
Film on glass plate	0.5	7	7

Table 4. Electrical conductivity of Br₂-doped film (exposure time 60 s) with variation of time in normal environment

Duration of time	Conductivity (in S/cm)
2 h	2.5×10^{-3}
24 h	1.6×10^{-4}
7 days	7.0×10^{-6}

Table 5. Effect on conductivity of doped polymers after 2 h exposure in air

Polymer system	Decrease in conductivity in %
I ₂ -doped polyacetylene ^a)	20
AsF ₅ -doped polyacetylene ^a)	40
Br ₂ -doped PC ^b)	19.3

^a) Data obtained from [18];

^b) Poly (P-phenylphosphoethynediyl); exposure time 60 s

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Received March 1, 1990;
accepted July 13, 1990

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