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THE ELECTRICAL AND OPTICAL PROPERTIES OF POLY (4-ETHYLIDENE-1, 3-CYCLOPENTYLENE VINYLENE)

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ABSTRACT

The intrinsic viscosity, electrical conductivity and IR absorbance were measured for the sample of poly (4—ethylidene—1, 3—cyclopentylene vinylene). The sample is strongly oxidized in air. Under vacuum the activation energy is 1.38 eV at T > 377°K. The electrical conductivity of the annealed samples increases at low temperature and decreases at high temperature. The electrical conductivity of the samples which were exposed to air shows the metallic behaviour.

INTRODUCTION

Electrical conduction in organic molecular solids (Gutmann *et al.* 1967) differs in several important ways from that in metals and typical semiconductors like silicon and germanium. Really, there is no satisfactory theory of organic conduction that has yet emerged, but the molecular nature of organic solids dictates their electrical properties.

There are four principal types of organic conductors, namely, conjugated chains, free radicals, charge transfer complexes and oroganometallic compounds. Charge carriers are most readily formed by the activation of non-bonding or n-bonded electrons which then delocalized in a conjugated system form as internal conduction path of high mobility.

The aim of this work is to study the effect of annealing on the electrical conductivity of poly (4-ethylidene-1, 3-cyclopentylene vinylene) and also to study the IR absorbance spectra at room temperature.

EXPERIMENTAL

Poly (4-ethylidene-1, 3-cyclopentylene vinylene) was prepared in the same way previously described in case of polymerizing 5-ethylidene-2-norbornene using $WCL_6/(CH_3)_4Sn$ as catalyst. (Feast and Harper 1985).

The viscosity measurements of the title polymer were made at 25°C ± 0.05°C using ASTM Standard equipment with chlorobenzene as standard.

The electrical conductivity was measured in a continuous regime at a rate of about 0.5°C/min. The conduction current was measured using an electrometer type 610C-Keithly instrument (Mounir *et al*, 1987). Compressed pellets of 1 cm^2 area and 0.1-0.15 cm thickness were moulded at 25°C and at pressure of 10 tons/cm^2. The samples were changed from white powder to transparent plastic sheets at pressure 10 tons/cm^2.

The samples must be under vacuum during the electrical measurements to avoid any oxidations.

The IR spectra was studied using a PYE UNICAM Sp 2000 infrared spectrophotometer.

RESULTS AND DISCUSSIONS

The intrinsic viscosity of poly (4-ethylidene-1, 3-cyclopentylen vinylene) was estimated as 8.1 x 10^{-3} deciliters/gram from plotting the ratio η sp/C against C (Fig.1), and extrapolate to infinite dilution, where sp is the specific viscosity of the polymer and C its concentration in grams per 100ml of solution (Flory, 1981).

Fig. 2 shows that the electrical conductivity decreases with temperature at temperature range 377 - 300°K, this decrease in conductivity may be due to humidity or surface impurities.

At temperature > 377°K, the conductivity increases with temperature, i.e. there are two slopes or two mechanisms of condution. At this range of temperature the activation energy is 1.38 eV which is calculated from Arrhenious Eq.

$$\sigma_o = \sigma \exp^{-E/KT}$$

This value of activation energy shows that this sample has the semiconducting character.

Fig.1 shows the temperature dependence of the electrical conductivity of the annealed samples. As the time of annealing increases the transition temperature is shifted towards higher temperature.

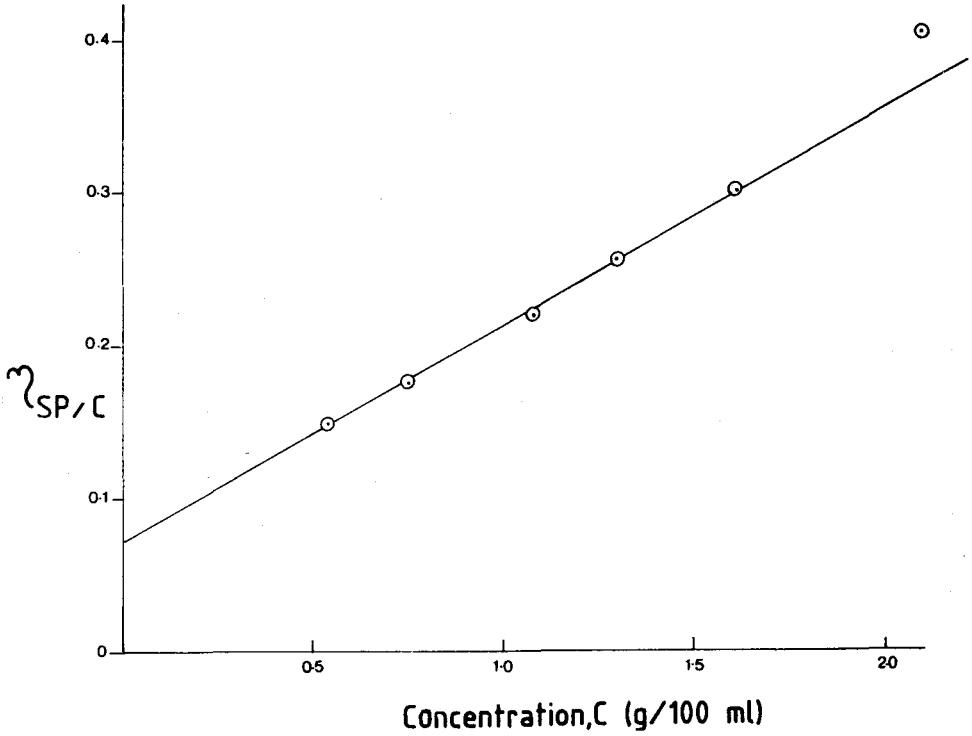

Fig. 1: Concentration dependance of η sp/C of Poly (4 - ethylidene - 1, 3 - cyclopentylene vinylene) in chlorobenzene at 25°C ± 0.05°C.

The electrical conductivity of the annealed samples increases at low temperature and decreases at high temperature. The decrease of conductivity at high temperature with increasing the time of annealing may be due to recombination mechanisms of carriers or destruction of the plastic network.

Fig. 2 inset (a) shows the increase of the conductivity at low temperature range with increasing the time of annealing.

Fig. 3 shows the temperature dependence of the electrical conductivity at different annealing temperatures in air; the time of annealing is constant (1 hr). The electrical conductivity increases with increasing the annealing temperature. As temperature increases the electrical conductivity decreases i.e. the samples are oxidized and the behaviour is metallic according to the Eq.

$$\sigma = \frac{e^2 n \lambda C}{6KT}$$

Where λ is the mean free path of the carriers between two collisions, C molecular velocity, n number of charge carriers and K is Boltzmann constant.

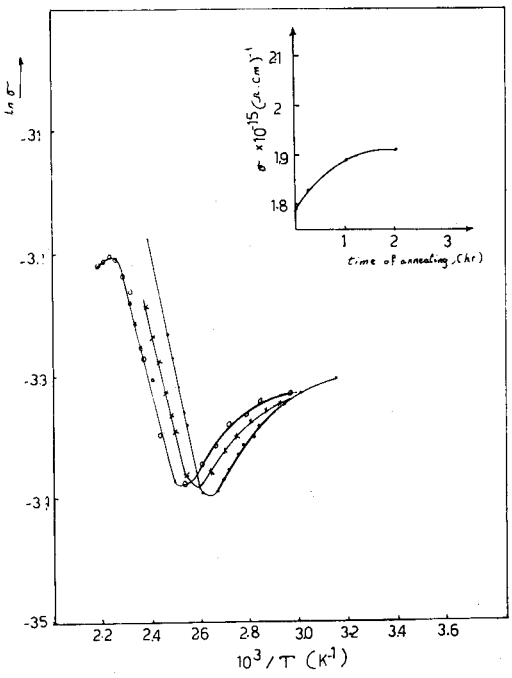

Fig. 2: The temperature dependence of the dc electrical conductivity of poly (4 - ethylidene - 1, 3 - cyclo - pentylene vinylene) before and after annealing. The temperature of annealing is 100°C.
. unannealed sample
o time of annealing is 1 hour
x time of annealing is 2 hours
Inset (a) variation of conductivity as a function of time of annealing.

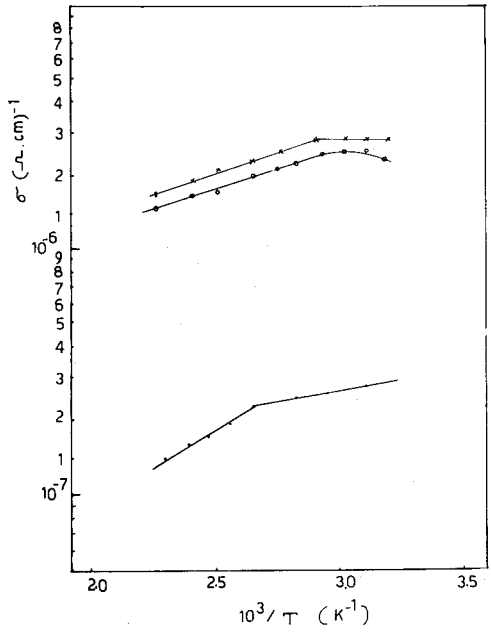

Fig. 3: The temperature dependence of the electrical conductivity of poly (4 - ethylidene - 1, 3 - cyclo - pentylene vinylene) at different annealing temperatures in air.
The time of annealing is 1 hour.
70°C., 0 86°C, x 100°C.

Norbornene - derived polymers (El Saffin *et. al.* 1982) and bicyclo - fulvenes - derives polymers (Feast *et. al.* 1985) are easily susceptible to air oxidation. These polymers were found to be oxidized through tertiary C - H bond which are also allylic. The polymer collected from 5 - ethylidene - 2 - norbornene have the same characters; it was found to be oxidized easily.

The IR absorbance spectra of the oxidized sample was made in the range 4000 / 600 cm^{-1}. The observed bands are 3400, 2900, 1700, 1600, 1430 and 1350 cm^{-1} which refer to hydrated H_20, CH, C = 0, C = C, CH_2 and CH_3 respectively (Fig. 4).

Under pressure the sample is changed from white powder into colourless plastic sheet. The plastic sheet is strongly oxidized after few hours in air, and its conduction mechanism shows the metallic behaviour.

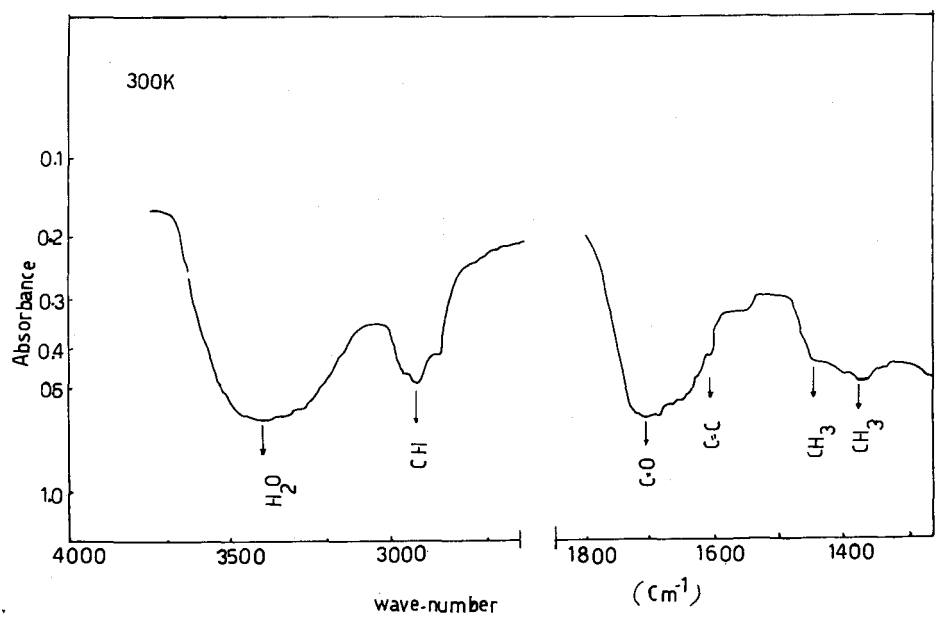

Fig. 4: The IR absorbance spectra of the oxidized sample.

Under vacuum the electrical conductivity shows two conduction mechanisms. At T > 377°K the activation energy is 1.38 eV, i.e., the sample has the semiconducting behaviour. The presence of ν (C = 0) in the IR spectra may be due to oxidation.

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التوصـــيل الكهـربي والخـــواص البصريـــة للبولي (٤ ـ إيثلدين ـ ١ ، ٣ ـ سيكلوبنتلين فيتايلين)

لميـــس شحـــاده ـ عـــلي الشـــكيل
و محمـــد مـــنير

يعني هذا البحث بقياس التوصيل الكهربائي وكذلك دراسة الإمتصاص بالأشعة تحت الحمراء واللزوجة الفعلية لعينة بولي (٤ ـ إيثلدين ـ ١ ، ٣ ـ سيكلوبنتيلين فينايلين) وقد تم حساب قيمة طاقة التنشيط في غياب الهواء (under vacuum) وتساوي 1.38ev إلكترون فولت عند حوالي T 377K وقد وجد أن التوصيل الكهربي للعينات المستخدمة يزداد عند درجات حرارة منخفضة ويقل عند درجات حرارة مرتفعة . وقد وجد أن التوصيل الكهربي للعينات المعرضة للهواء توضح خاصية معدنية .