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FURTHER INVESTIGATIONS ON THE THERMOELECTRICAL AND PHOTOCHEMICAL PROPERTIES OF 2,5-DISTYRYLPYRAZINE (DSP) AND AZODIISOBUTYRONITRILE (AIBN) SINGLE CRYSTALS

M.M. ABOU-SEKKINA

Chemistry Department, Faculty of Science, Tanta University, Tanta (Egypt)

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ABSTRACT

DC-electrical conductivity has been studied for fresh and partially photopolymerized 2,5-distyryl-pyrazine (DSP) single crystals of the α-modification. α-DSP crystals show semiconductivity with a positive activation energy for DC-electrical conduction, $E_a = 0.86$ eV. The specific conductivity, σ, falls and E_a increases as photopolymerization proceeds due to the consumption of delocalized π-electrons in the formation of cyclobutane rings and also the shrinkage accompanying photopolymerization.

This behavior has been contrasted to that of azodiisobutyronitrile (AIBN) crystals. AIBN crystals show semiconductivity for fresh samples that changes to semi-metallic conductivity upon irradiation ($\lambda_{ex} = 365$ or 337 nm).

INTRODUCTION

The four-center type photopolymerization of many diolefins has been extensively studied using a variety of techniques including spectroscopic [1–3], structural [4,5] thermal [6] and colligative methods [4]. The electrical conductivity of diolefinic crystals has not been reported and it would be of interest to study the semiconducting behavior of the prototype diolefinic material 2,5-distyrylpyrazine (DSP) and its photopolymer. The crystal structure of DSP has previously been studied [7,8]. In the photopolymerizable α-modification, the crystals are in the form of plates with the c-unit cell in the same direction as the long crystal axis. The molecules are spaced by the c-translation forming an almost parallel plane-to-plane stack. In this stack the ethylenic double bonds approach each other at the shortest intermolecular distances of 3.939 Å. Upon UV-irradiation ($\lambda_{ex} = 365$ nm), these olefinic double bonds add together giving a high molecular weight and a highly crystalline polymer with cyclobutane rings in the backbone [4]. Organic semiconductors are well known [8] and polymeric semiconducting crystals attract much attention due to their chemical stability and expected technological applications [8].

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The electrical conductivity behavior of DSP has been contrasted to another molecular crystal system, namely azodiisobutyronitrile [9,10] (AIBN), that is one of the earliest and most extensively studied free radical initiator. It undergoes thermal or photochemical homolysis to yield nitrogen molecule and a pair of cyanoisopropyl free radicals. There is a reported phase transformation from monoclinic needles to triclinic plates of AIBN at 65–80°C prior to melting and decomposition at 100–104°C. Phase transformation in the reported temperature range has been studied using differential scanning calorimetry (DSC) [9] and X-ray diffraction [10].

EXPERIMENTAL

DSP was prepared according to the method of Hasegawa et al. [11] and purified by chromatography and vacuum sublimation as described earlier [12]. Crystals of the α-modification plates of dimensions $4 \times 2 \times 1$ mm were grown by vacuum sublimation in the dark [2].

AIBN crystals were grown by slowly cooling a benzene solution down to ca. 3°C. Plate-like crystals of dimensions $10 \times 2 \times 1$ mm were used for electrical conductivity measurements.

Irradiations were carried out either by using the excitation light of a Shimadzu RF 510 spectrofluorophotometer or a nitrogen laser system ($\lambda_{ex} =$ 337.1 nm), as described elsewhere [13].

DSC measurements were taken using a DuPont 990 thermal analyzer as a function of temperature.

The apparatus used to measure the temperature dependence of the DC-electrical conductivity has been described earlier [14]. A silver paste was used as the electrode materials to attach the crystals to the needle points of the electrodes and also as the guard ring to eliminate the effects of surface conduction in all single crystal measurements. Measurements of the DC-electrical conductivity for DSP was continued up to 150°C due to its thermal stability in this temperature range, but for AIBN measurements were taken only upto ca. 70°C due to its early sublimation and thermal decomposition of the residual material at 100–104°C [9].

In all cases, measurements of the DC-electrical conductivity as a function of temperature were undertaken in the direction parallel to the *c*-axis, that is in the same direction of the long crystallographic axes of DSP [15] and AIBN [10].

The relatively small cross-sectional areas of crystals prevented measurements of the conductivity perpendicular to the long axes. For DSP single crystals, the readings were recorded automatically in the range of 20 mV cm^{-1} in air up to 150°C, but for AIBN readings were undertaken in the range of 20 or 50 mV cm^{-1} in air up to 70°C.

RESULTS AND DISCUSSION

Figures 1 and 2 show the variation of the logarithm of DC-electrical conductivity (log σ) as a function of reciprocal absolute temperature for DSP and AIBN single crystals before and after irradiations. The concentration of current carriers and hence the semiconductivity increase with increasing temperature according to a Boltzmann-type distribution with the activation energy, E_a, for the conduction process given by [16]

$$\sigma = \sigma_0 \, e^{-E_a/kT} \tag{1}$$

where σ is the specific conductivity, σ_0 is the pre-exponential factor, which is a constant independent of temperature, and E_a is the activation energy for conduction. Thus, semiconductivity with a positive activation energy is distinguished from metallic conductivity which falls as the temperature rises. DSP and AIBN are typical molecular crystals that are bonded via weak Van der Waals' forces.

The energy gap, $E_g = 2E_a$, is the energy separating the highest filled or valence band from the conduction band. The energy gap measured for DSP

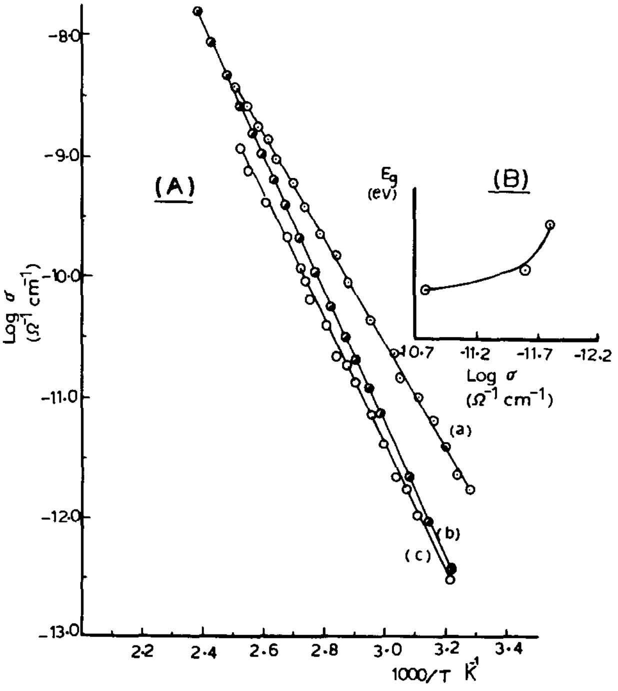

Fig. 1. (A) Temperature dependence of DC-electrical conductivity of DSP single crystals: (a) fresh sample (before irradiation); (b) after UV-irradiation (3 h); (c) after laser-irradiation (1000 pulses). (B) Variation of E_g (eV) of DSP single crystals as a function of log σ_{50} before and after different irradiations.

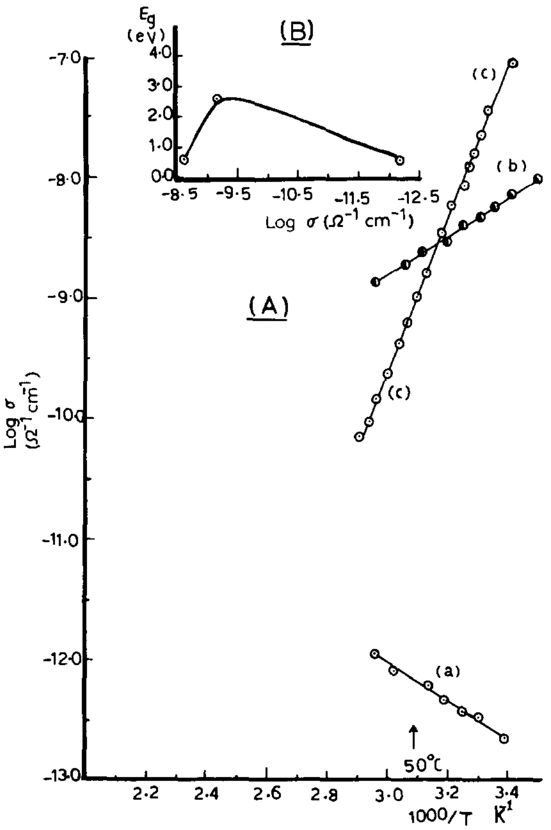

Fig. 2. (A) Temperature dependence of DC-electrical conductivity of AIBN single crystals: (a) fresh sample (before irradiation); (b) after UV-irradiation (3 h); (c) after laser-irradiation (1000 pulses). (B) Variation of E_g (eV) of AIBN single crystals as a function of log σ_{50} before and after different irradiations.

single crystals is relatively low compared with other molecular crystals, e.g., polynuclear hydrocarbons [8]. It is suggested that the orbitals of the π-electrons of the olefinic double bonds in DSP molecules overlap to give a nonlocalized orbital stretching throughout the crystal parallel to the *c*-axis which is also the measurement axis.

As clearly shown from Table 1, $2E_a$ is thus the energy gap between the highest filled band or the valence band and the conduction band. In this respect, its value is discussed in terms of a single electron transition in the isolated molecule and overlap of π-orbitals between neighboring molecules. This investigation was originally stimulated by the suggestions of Gyorgi [17] and Vartanian [18] in earlier publications on the possible role of mobile electrons in protein molecules.

Upon irradiation, the electrical conductivity of DSP single crystals decreases and the activation energy of conduction, and consequently the

TABLE 1

Activation parameters for fresh and irradiated DSP and AIBN crystals

Material	Treatment	E_a (eV)	E_g (eV)	η (eV)
DSP	Fresh	0.80	1.60	–
	Laser irradiated (λ_{ex} = 337.1 nm)	1.60	3.20	0.80
	UV-irradiated (λ_{ex} = 365 nm)	1.00	2.00	0.20
AIBN	Fresh	0.30	0.60	–
	Laser irradiated (λ_{ex} = 337.1 nm)	1.30	2.60	1.60
	UV-irradiated (λ_{ex} = 365 nm)	0.36	0.72	0.66

energy gap, increases. This is attributed to the π–π addition accompanying photopolymerization of DSP resulting in cyclobutane rings along the backbone of the polymer chains. This forms a barrier energy opposing current flow and thus decreasing electrical conductivity. There is another important factor that prevails at the latter stages of photopolymerization, that there are slight differences between the unit cells of DSP monomer and its polymer crystals. The *c*-axis contracts by 1.5% upon photopolymerization [4]. As photopolymerization proceeds, contacts between the reaction front and the rest of the reacting monomer decrease and these created voids obviously lower electrical conductivity and elevate its attendant activation energy for conduction and energy gap. This is in agreement with earlier observations that conductivity increases in long range order and is highest in single crystals [19].

It has been possible to study the temperature dependence of electrical conductivity since the DSP polymer is thermally stable up to ca. 300°C and no structural changes are reported in the investigated temperature range (30–150°C) [6].

The effects of oligomerization or polymerization of DSP on the decrease of its electrical conductivity and increase of its activation energy for conduction (see Fig. 1) could be ascribed to the alteration of the DSP monomer single crystals as a result of DSP oligomerization and polymerization. This was in accordance with the previous results of Stockman [19] deducing that mobility increases with long range order and is highest in single crystals.

For AIBN single crystals, the DC-conductivity after irradiation is $\sim 10^4$ times greater than that before irradiation (see Fig. 2). This could be explained as being caused by electron delocalization [20] and/or increased mean-free-path resulting in an increased mobility of current carriers in the AIBN polymer. Further, the entirely different behavior of the conductivity of photo-irradiated AIBN crystals is explained in terms of the role played by free radicals in electrical conduction. Free radicals are obtained upon photolysis of AIBN [9,10]. For fresh AIBN crystals, the temperature dependence reveals semiconducting behavior (see Fig. 2, curve a). Upon UV or

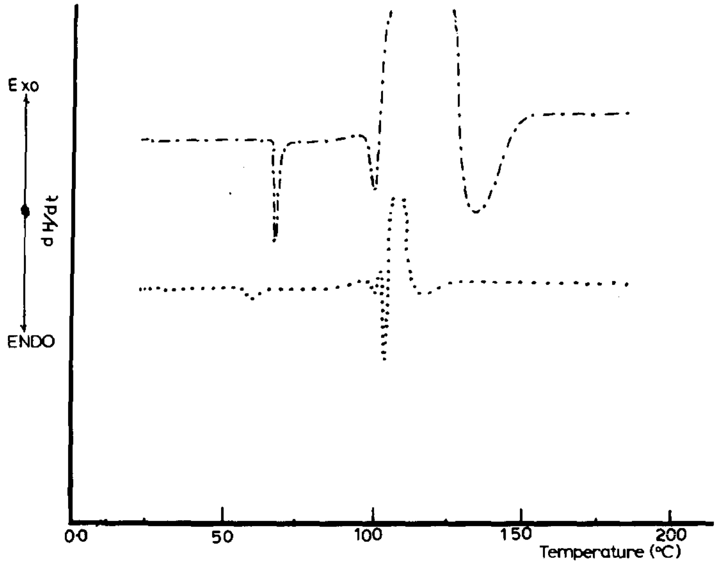

Fig. 3. DSC curves of AIBN single crystals. (–·–·–) Fresh crystals, (······) crystals UV-irradiated for 3 h ($\lambda_{ex} = 365$ nm).

laser irradiation, the material shows a negative temperature coefficient of electrical conductivity (see Fig. 2, curves b and c), i.e, metallic conduction mechanism. In this respect, the photo-generated free radicals might act as current carriers similar to free electrons in metals. Table 1 summarizes the activation parameters for the materials investigated.

Consequently, Figs. 1B and 2B show the variation of energy gap, E_g (eV), with the logarithm of electrical conductivity at definite temperatures (log σ_{50}) for DSP and AIBN single crystals, respectively. From these correlations, the behavior of DSP and AIBN single crystals is different.

Accordingly, the activation energy for either UV or laser induced carrier liberations could be calculated herein for the first time using the following expression developed by the author

$$\eta = \eta_2 - \eta_1 \tag{2}$$

where η_2 is the activation energy for conduction after UV or laser irradiation and η_1 is the activation energy for conduction before irradiation. Results obtained for both DSP and AIBN single crystals are recorded in Table 1.

Figure 3 shows DSC curves for AIBN crystals before and after photo-irradiation. For fresh samples, there is a sharp endothermic peak at 64°C that is in the same temperature range as reported earlier for phase transformation [9,10]. This is followed by overlapping of the endothermic and exothermic peaks which are assigned to melting, sublimation and subsequent decomposition of the material. Similar behavior is displayed by photo-irradiated AIBN samples with a clear broadening of the phase transformation peak at 64°C. Such broadening is attributed to the slight lattice damage caused by photolysis of AIBN single crystals. There is also a deviation from the baseline starting at ca. 80°C in the DSC calorigrams of photo-irradiated AIBN crystals that is attributed to the role of photo-generated radicals in enhancing further material decomposition. For the above reasons, the electrical conductivity was monitored at temperatures less than 70°C.

Accordingly, a probable explanation is that the primary radiation damage caused during irradiation is the product of point defects and free radicals or free electrons by irradiation. The defects so formed are quite mobile, especially at high temperatures. The most universal and most important microstructural changes caused by irradiation are the expansion and/or melting of the individual grains or crystallites of the materials investigated. This may induce a number of point defects in the normal crystal lattices.

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