

Bipolaron conductivity of polymers stimulated by an anomalous thermal polarizability of side fragments of the molecules

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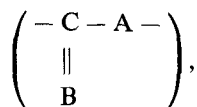
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The electrical properties of polyarylenephthalides—conducting polymers of a new class—have been studied. The experimental results show that the transition to a conducting state as the temperature is changed results from the formation of bipolarons in the polymer chain.

Studies of bipolaron states in conducting polymers have recently attracted considerable interest because of the possible occurrence of a superconducting state in these materials.¹ The conditions for the appearance of bipolarons and also their dynamics depend on the particular structure of the polymer. In polyphenylene, for example, a bipolaron forms in a region between two defects of the polymer chain at a corresponding defect concentration, as was shown in Refs. 2 and 3. Experimentally, a bipolaron state can be monitored by observing the changes in the optical and electrical properties of the polymers.

In this letter we report an experimental study of the electrical conductivity and optical properties of conducting polymers of a new class, in which the charge transport is determined by the properties and structure of side fragments of the molecules. Some typical representatives of this class are the polyarylenephthalides⁴:



where A is diphenylene, B is a phthalide group, and C is carbon. They contain a C–O–C atomic group, which has some strong acceptor properties. The overall structural formula of the polymers which were studied in the present experiments is shown in Fig. 1. The polymer samples are uniform films 10–150 μm thick, in which the molecules are oriented preferentially in the direction perpendicular to the surface. This orientation is monitored by a polarized-optics method involving conoscopic patterns.⁵ The dc electrical conductivity of the samples is measured in the direction perpendicular to the surface of the film. Platinum electrodes provide ohmic contact. A guard ring around one of the electrodes eliminates surface currents. For the ac measurements we use an R589 ac bridge. The polymers were doped with iodine, with the result that the conductivity increased from 10^{-15} to 10^{-5} Ω/cm at an iodine concentration $\sim 40\%$ and a temperature of 300 K. The measurements were carried out over the temperature range 4.2–350 K.

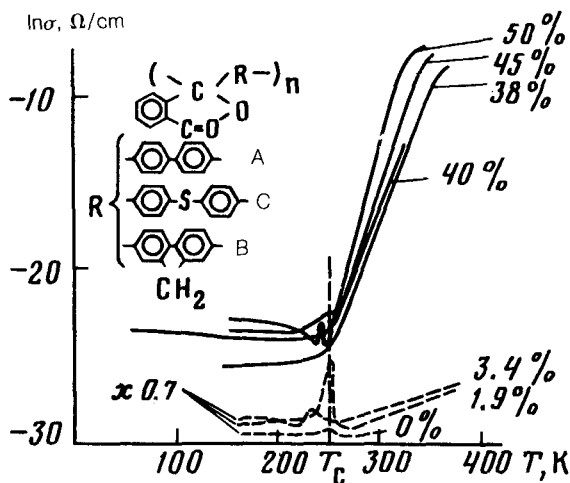


FIG. 1. Temperature dependence of the conductivity of polydiphenylenephthalide. Solid lines—Direct current; dashed lines—alternating current, $\omega = 1$ kHz. A) Polydiphenylenephthalide; B) polyfluorenylphthalide; C) polydiphenylenesulfidephthalide.

Figure 1 shows the temperature dependence of the dc conductivity of polydiphenylenephthalide for samples with various degrees of doping. Over the range 4.2–260 K, the conductivity σ is at a minimum and is independent of the temperature; above 260 K, in contrast, we find $\ln \sigma \propto T$. Over an interval of 30 K, the absolute change is 10^5 ; the critical temperature (T_c) does not depend on the dopant concentration. Figure 1 shows the changes in the ac conductivity at a frequency of 1 kHz as the temperature is varied; these results agree well with the results of the dc measurements. The only differences are in the absolute values of the surge in the conductivity near T_c ; in the dc case, this surge can be seen while only at low concentrations of I_2 .

For amorphous systems the existence of a critical temperature, above which there are sharp changes in the magnitude and nature of the conductivity is linked with the possibility of a localization-delocalization transition involving the electron subsystem.⁶ In this class of polymers, however, the conductivity cannot be described by the microscopic model of Ref. 7, since x-ray structural studies have not revealed a temperature-induced change in the structure of the polymer above T_c . An answer to this question is provided by an experimental study of optical absorption in the vicinity of the corresponding electronic transitions and also of the fluorescence spectra.

Figure 2 shows the absorption spectra of a polymer at various iodine concentrations. The addition of I_2 gives rise to two new absorption bands, at 3.2 and 1.05 eV, whose presence is evidence of the formation of levels of the polaron or bipolaron type in the band gap.³ The low concentration of spin carriers, $< 10^{14} \text{ cm}^{-3}$, determined by an ESR method, suggests that the levels are of a bipolaron nature. Figure 3 shows the absorption coefficient of an I_2 -doped polymer as a function of the temperature at a fixed wavelength corresponding to the bipolaron absorption band. In the temperature interval 260–230 K, there is sharp decrease in the optical absorption, which is evidence

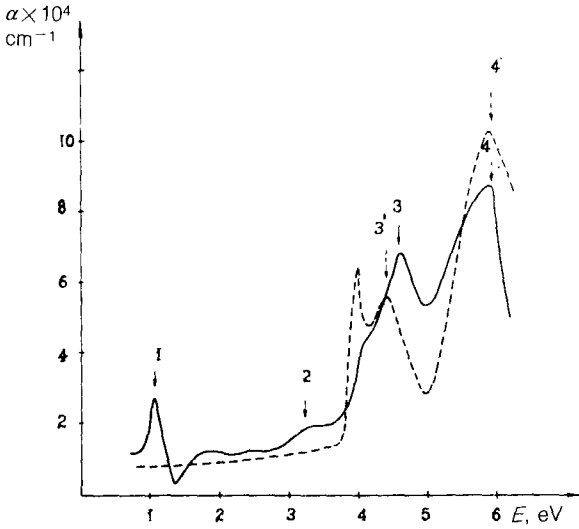


FIG. 2. Absorption spectrum of polyfluorenylphthalide. Solid line—doped with iodine (30%); dashed line—undoped. 1,2) Bipolaron absorption bands; 3,3',4,4') aromatic absorption bands.

of a decrease in the density of the corresponding states in the band gap. Curve 2 shows the absorption coefficient versus the temperature for a model compound, a monomer unit of a polymer molecule: phenolphthalein dissolved in an alkali solution. The nature of the coloring of phenolphthalein in an alkali medium is known⁸; it results from scission of the phthalide ring and the appearance of a positive charge at the central carbon atom. The decrease in the optical absorption as the temperature is lowered below a certain critical value apparently occurs because of the inverse process—the restoration of the C—O—C bond—in the phthalide fragment. Phenolphthalein behaves in a similar way when subjected to uniaxial pressure.⁹ Further evidence that the changes in the optical properties of the polymer result from changes in the state of the

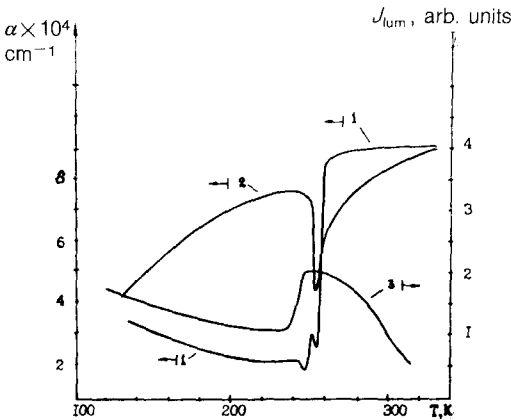


FIG. 3. Optical absorption coefficient versus the sample temperature at $\lambda_{\text{const}} = 400$ nm. 1—0.1% solution of phenolphthalein in a 2% solution of KOH in $\text{C}_2\text{H}_5\text{OH}$; 2—film of polyfluorenylphthalide with 15% I_2 ; 3—temperature dependence of the luminescence of the polymer. $\lambda_{\text{excit}} = 336$ nm; $\lambda_{\text{emiss}} = 550$ nm.

electron subsystem in the phthalide fragment of the macromolecule is the sharp decrease in the fluorescence intensity in the temperature interval 260–230 K when the fluorescence is excited in the absorption band of the side phthalide grouping (curve 2 in Fig. 3).

Summarizing these experimental results, we can conclude that a generation of charge carriers occurs in the doped polymer above T_c because of the thermal excitation of the C–O–C bond in a phthalide fragment of the molecule. The presence of an acceptor such as iodine leads to a partial or complete bond scission which in turn induces a positive charge at the central carbon atom in the polymer chain. The role played by iodine here is analogous to the role played by alkali in the case of phenolphthalein. The bipolaron in this case consists of two positive charges which are localized at carbon atoms that are bound to each other by a quinoid structure.

In this class of polymers the presence of atomic groupings with a low energy for the thermal excitation of electron bonds, ~ 0.05 eV, in the side fragments apparently sets the stage for the generation of polaron and bipolaron states as a result of the change in the temperature of the sample. This situation stands in contrast with the existing possibility in known polymers—through a change in the dopant concentration.

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