

An unusual doping mechanism in polyarylenphthalides

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The results of our study of a doping mechanism in the nonconjugate polymer polydiphenylenphthalide, which leads to the appearance of a metal-like conductivity, are reported. A special feature of this process is the three-stage transformation of the electronic subsystem of the polymer and the appearance of a polaron lattice in the final stage.

The increase of the conductivity upon doping in the nonconjugate polymer polydiphenylenphthalide was reported in Ref. 1. However, there is no information on a possible molecular mechanism for doping. This question has become more interesting because of the discovery in thin films of such polymers of a high spontaneous conductivity, and because of the anomalously high sensitivity of the latter to the pressure.^{2,3}

Thin polymer films of thickness 5–20 μm were doped in iodine vapors using the traditional technique. In Fig. 1 we show the results of measuring the temperature dependence of the conductivity of polymer films for various dopant concentrations. The conductivity grows with increasing dopant concentration in the entire temperature range. The dependence clearly has two different regions: a low-temperature region with weak dependence $\sigma(T)$ and a high-temperature one with strong dependence. At low temperatures $\sigma(T)$ obeys the Mott law and is described by a function of the form $\sigma = \sigma_0 \exp(-W/kT)^n$, where $n < 1$. Here W varies weakly with concentration, by ≈ 0.5 eV. It should immediately be stated that the narrow temperature range does not permit a sufficiently accurate determination of the argument of the exponential functions. In this range of the dependence there is apparently a sort of hopping mechanism of charge transfer in the polymer sample. At temperatures above 250 K the conductivity is observed to increase sharply, which has earlier been attributed to temperature excitation of bipolarons.¹

The most significant changes in the nature of the conductivity occur when the dopant concentration exceeds 50% by mass, i.e., concentrations for which the number of dopant ions approaches the number of elementary links in the molecular chain. The electrical conductivity becomes like that in a metal and is virtually independent of the temperature, weakly increasing as the temperature is lowered. This is an unexpected result, since a metal-like temperature dependence of the conductivity is rarely observed in conjugate doped polymers even such as polyacetylene.⁴ In the present case such a dependence is obtained in a nonconjugate polymer doped with iodine, and the specific electrical conductivity is low, amounting to only $10^{-3} \Omega^{-1} \cdot \text{cm}^{-1}$.

To understand the details of the doping mechanism, we studied the optical absorption spectra. In Fig. 2 we show the optical spectra of polymer films in the visible and UV ranges. Here the variation can be split into three stages. In the first stage

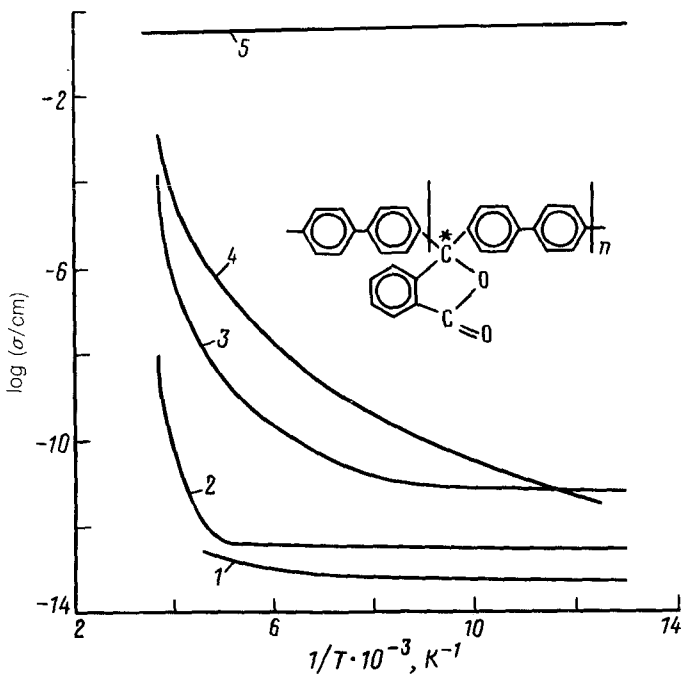


FIG. 1. Temperature dependence of the conductivity of polydiphenylphthalide for various dopant concentrations I_2 : (1) 15%, (2) 30%, (3) 50%, (4) 68%. The inset shows the structural formula of the polymer; the star denotes the quaternary carbon.

(curve 2) an impurity band with maximum at 3.3 eV begins to be formed in the absorption spectrum. A 15–20% increase in the dopant concentration leads to growth of the impurity and intrinsic absorption bands. In the second stage $C > 20\%$ (curve 3) there is significant broadening and a shift of this absorption band to the near IR part of the spectrum. For further increase of the dopant concentration to 50–60% the shift reaches 2.5 eV. The absorption edge is formed near 0.8 eV. This stage is accompanied by a significant “smearing” of the intrinsic polymer absorption bands.

Analysis of the shape of the long-wavelength absorption edge of doped samples showed that the transition from the first to the second stage is accompanied by a significant change in its shape. In the second stage the dependence of the absorption coefficient on the frequency of the incident radiation begins to obey the Urbach law.⁵ The formation of an Urbach edge for dopant concentrations above some value indicates that there is an important contribution to optical transitions from delocalized electron states. Such behavior of $\alpha(\omega)$ at the absorption edge is typical of conjugate polymers.⁶ In our case this is possible only because of the increase of the overlap integral of the wave functions of the π electrons of neighboring arylene links as the potential barrier on the quaternary carbon atom, labeled C^* in Fig. 1, is lowered. In the third doping stage (curve 4), when the dopant concentration exceeds 50% by mass,

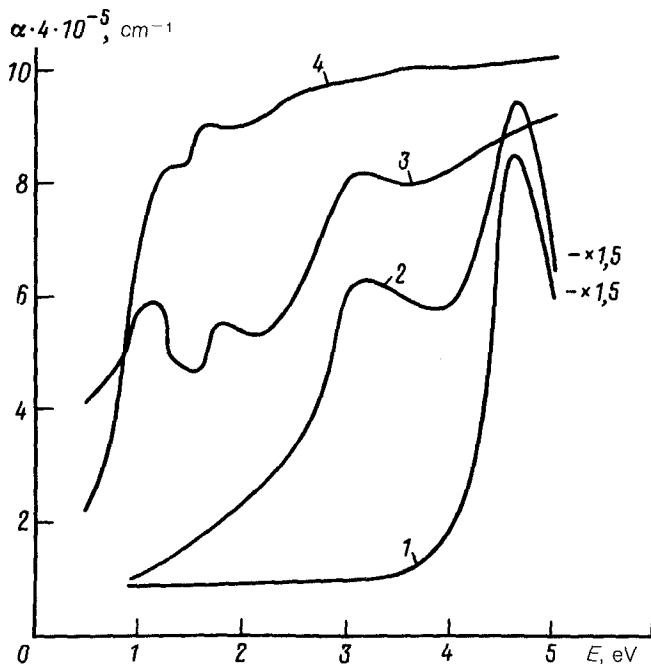


FIG. 2. Absorption spectra of iodine-doped polydiphenylphthalide: (1) $C_{I_2} = 0\%$, (2) $C_{I_2} = 20\%$, (3) $C_{I_2} = 45\%$, (4) $C_{I_2} = 58\%$.

there is an overall decrease of the absorption coefficient and the continuum splits into three bands. The first is located in the UV region at 3.3 eV, the second has maximum at 1.8 eV, and the third has maximum at 1.2 eV. The spectrum acquires a form similar to that of doped conjugate polymers. A partial analysis of the optical properties was done in Ref. 7 using the polaron model. However, we should point out one discrepancy which was not taken into account in that study. Usually, the polaron absorption and the polaron states related to it are formed at energies below that corresponding to the width of the bandgap. In our case the polaron structure of the spectrum is formed within the existing absorption band. This obviously requires independent investigation. However, in the present study we notice that the stages of optical splitting and transition to metal-like conductivity coincide. The transition to the metallic state in polymers with a nondegenerate ground state is now often attributed to the formation of a polaron lattice.^{8,9} We apparently have an example of such a transition in this case. In order to interpret the phenomena occurring in the three doping stages, we need additional information, in particular, on the nature of the interaction and the coordination of the dopant with the polymer molecule. The data of the IR and NMR ¹³C spectroscopy accordingly are of interest in this regard. They can be summarized briefly as follows. During the first two doping stages there is significant broadening and increase of the intensity of the IR line corresponding to vibrations of the carboxyl group of the side fragment (1700 cm^{-1}). During the third stage, the structureless

background grows, "smearing out" the vibrational spectrum. In the NMR spectra the largest shift of two lines—the quaternary carbon C^* and the carboxyl group—is fixed in the doping. The shifts occur in opposite directions in such a way that the negative charge increases because of the interaction with the dopant ion on the carbon of the carboxyl group, while the positive charge increases because of the quaternary carbon. These data indicate that the dopant is coordinated with the carboxyl group of the phthalide fragment. This process leads to a lowering of the potential barrier on C^* for the π electrons of the aromatic system in the basic polymer change.

In summary, the doping process in polyphenylenphthalide can be represented as follows. 1) In the first stage, there is formation of a complex with transfer of a charge of the type polymer + iodine, where the iodine is coordinated with the carboxyl group of the side fragment and the positive charge is localized on the quaternary carbon C^* . The presence of the latter lowers the potential barrier for the π electrons of the adjacent arylene chains and therefore aids their delocalization. 2) In the second stage, when the concentration of such pairwise-conjugate fragments is increased to the extent that they combine into more extended ones along the chain of the structure, the conductivity is observed to grow, the Urbach edge is formed, and an anomalously large shift of the absorption edge to the near-IR region occurs. 3) The third stage corresponds to a concentration at which at least one dopant ion occurs on nearly every chain of the macromolecule. This causes the π -electron subsystem of the polymer to undergo a transition to a delocalized state. Further increase of the concentration apparently leads to doping of the polymer by the traditional mechanism and to formation of the polaron lattice.

In polymers of the polyarylenphthalide class the doping-related high conductivity thus occurs as a result of a modification of the electronic structure of the polymer during the doping. This modification creates favorable conditions for delocalization of the π electrons.

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