TITLE: Correlation Between Electrical and Optical Properties of Polymer Nanostructures Based on Polydiacetylene

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Correlation between electrical and optical properties of polymer nanostructures based on polydiacetylene

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Abstract. A change in optical properties of conducting polydiacetylene THD (poly-1,1,6,6-tetraphenylhexadiinediamine) under doping has been investigated for the first time. Spectral dependencies of extinction coefficient were studied in the range 400-25000 cm^{-1} either for non-doped PDA THD (with d.c. conductivity $\sigma < 10^{-9}$ S/cm) or for doped polymer at various doping levels (the ultimate value of conductivity is about 5×10^{-3} S/cm). The obtained data allow to suggest that in PDA with conductivity $\sigma > 10^{-4}$ S/cm a high concentration of the charge carriers takes place. The observed sufficiently low macroscopic conductivity is attributed to the complicated hierarchy of structural units which is typical of polymeric materials. The results are compared to the corresponding data obtained for conducting polyacetylene.

Introduction

At the previous symposium (Nanostructures: Physics and Technology-97) we reported for the first time the electrical and noise properties of doped polydiacetylene–the only class of conjugated polymers capable of solid state polymerization. The conductivity of any conductive polymer has its origin in transport of a free carrier (soliton or bipolaron) along a conjugated sequences in polymer molecules. These sequences can be considered as quasi-one-dimensional wires of 1.5–15 nm length (10–100 C=C bonds). The macroscopic conductivity of polymers depends on concentration and mobility of the carriers along the wires, as well as on the probability of the carrier "jumps" from one wire to another one inside of a separate fibril and from one fibril to another fibril. The experience in investigation of other doped polymers evidences that the only study of electrical behaviour of the doped polymer does not allow to estimate the relative contribution of the different processes to macroscopis polymer conductivity.

In the present work for the first time the optical properties of a doped conducting PDA THD are investigated both in the vicinity of the edge of the intrinsic absorption and in IR region. Studying the extinction in the vicinity of the edge of the intrinsic absorption may give the independent information on the concentration of the charge carriers as a function of the doping conditions and doping level.

The analysis of IR absorption spectra in a region up to 5000 cm^{-1} and the comparison the obtained data with known spectra for conducting PA (see, for instance, [1]) also allows to get some additional information on the concentration of free carriers. Besides, these investigations enable one to follow the changes in a vibration spectra of initial polymer upon doping.

1 Results and discussions

In Fig. 1(a) the spectral dependencies of extinction coefficient are shown for PDA THD doped to various doping levels in a region of 5000–25000 cm^{-1}. Solid line 1

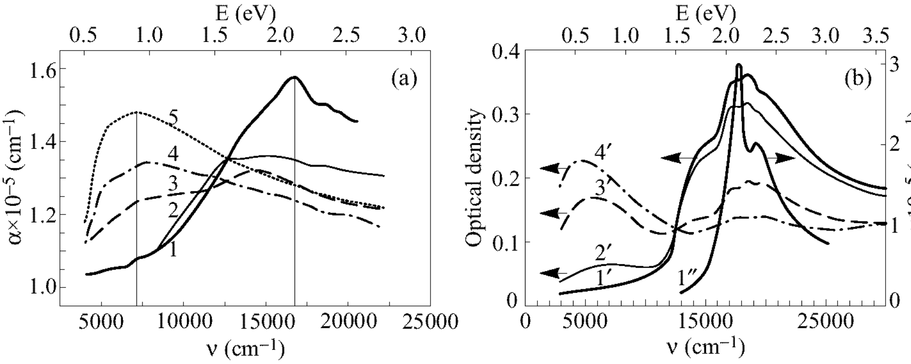

Fig 1. Spectral dependencies at various doping levels: (a) for doped PDA THD and (b) for doped PA. (a): 1—the undoped PDA sample ($\sigma < 10^{-9}$ S/cm), 2—$\sigma \sim 10^{-6}$ S/cm, 3—$\sigma \sim 10^{-5}$ S/cm, 4—$\sigma \sim 10^{-4}$ S/cm, 5—$\sigma \sim 10^{-3}$ S/cm. (b): 1′—the undoped PA sample, 2′—$\sigma = 20$ S/cm, 3′—$\sigma = 50$ S/cm, 4′—$\sigma = 100$ S/cm. [1], 1″— the dependence for PDA dispersed in PMMA matrix.

corresponds to a spectrum of undoped initial polymer. Quantitative value of extinction coefficient has been calculated with regard to the density of PDA THD single crystals.

It is known that the average length of a conjugated sequence in a polymer can be estimated from the value of the energy corresponding to extinction maximum: the energy corresponding to absorption maximum reduces with increasing of a conjugated length and reaches the ultimate value $\simeq 2$ eV at sufficiently large conjugated length. For polyacetylene, for instance, $E_0 \simeq 2.1$ eV has been observed [1] (Fig. 1(b)). Analising the curve 1 in Fig. 1(a) one can conclude that in the investigated PDA THD exposed to intensive mechanical disintegration an average conjugated length remains practically intact.

From Fig. 1(a) it is seen that with the increase of a doping level a longwave maximum is generated in a near IR region at $E_1 \simeq E_0/2$, and the amplitude of this maximum grows with increasing doping. On the contrary, an amplitude of the maximum at $E = E_0$ corresponding to the maximum for undoped material monotonically decreases with increasing of doping level. A picture is qualitatively resembles a change in optical absorption spectra repeatedly observed for polyacetylene upon doping (Fig. 1(b)). The comparison of these spectra allows to draw a conclusion that the doping mechanism of polydiacetylene and polyacetylene are qualitatively analogous. One should, however, pay an attention to a very important fact: in polyacetylene, a large scatter in the values of macroscopic conductivity (over several order of magnitude) is observed at relatively low conductivity, when the absorption at $E = E_0$ remains significantly higher than that at $E = E_1$. At the same time, at high level of doping, when the absorption at $E = E_1$ exceeds that at $E = E_0$ the macroscopic conductivity is always appears to be highly enough ($\sigma \sim 10$–100 S/cm). The absorption at $E = E_1$ for curve 5 (Fig. 1(a)) is equal practically to the initial absorption at $E = E_0$ in undoped PDA THD and the absorption peak at $E = E_0$ is suppressed at the great extent. Nevertheless, the macroscopic conductivity in PDA appears to be lower by a factor of 4–5 orders of magnitude than that in polyacetylene. Of course, even for one and the same material (polyacetylene)

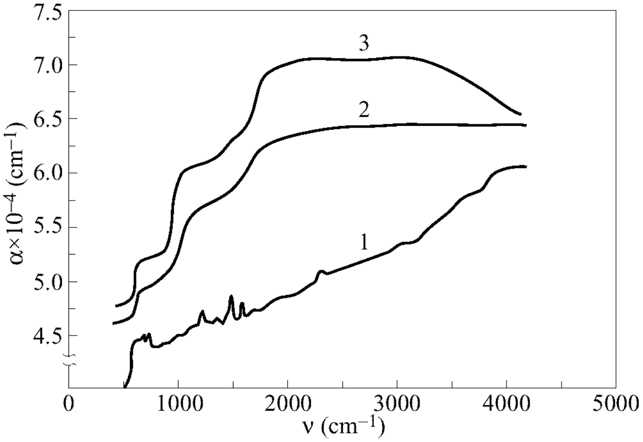

Fig 2. Spectral dependence of extinction coefficient of doped PDA THD for various doping levels. 1—the undoped sample, 2—$\sigma \sim 10^{-4}$ S/cm, 3—$\sigma \sim 10^{-3}$ S/cm.

the scatter in conductivity may be of several order of magnitude for the same values of $\alpha(E_1)/\alpha(E_0)$. Relative quantity of free carriers taking part in macroscopic conductivity may strongly (exponentially) vary depending on orientation of fibrils in a polymer, density of "fibrillar net", mutual disposition of polymer molecules and dopant chains. All things being equal, various portions of the carriers can be concentrated (in dependence on polymer structure) in the isolated clusters and "dead ends", or in conducting chains of an infinite cluster providing macroscopic conductivity.

The data given above show that the common concentration of the carriers in PDA THD with the reached level of conductivity is, probably, not less than that in polyacetylene with conductivity $\sigma \sim 10-100$ S/cm (which corresponds already to "metallic" conductivity. Nevertheless, the ultimately reached value of conductivity for doped PDA THD is 3×10^{-2} S/cm, i.e. significantly less than that for polyacetylene.

The question arises which structural peculiarities of PDA is responsible for the large difference in conductivity. The analysis of SEM micrographs of needle-like PDA THD single crystals shows that the fibrils are perfectly aligned inside each single crystal. The order in fibril arrangement is much higher than that in "unoriented" polyacetylene. However, one should take into account two facts; first, the single crystals in a macroscopic sample have been chaotically oriented; second, it looks from our preliminary experiments that a single crystal surface comprises the potential barrier hindering exchange the free carriers between the neighbouring fibrils belonging to different single crystals.

Thus, to the transport mechanisms (which is characteristic of polyacetylene), in PDA operates an additional one-intercrystalline transport between the fibrils belonging to different single crystals. There is a hope that more perfect disposition of microcrystals and "suitable damage" of intercrystalline boundaries will allow in the future to increase significantly the conductivity of PDA THD using the same doping technique.

The spectral dependencies of extinction coefficient of PDA THD in IR region (400–4000 cm^{-1}) are shown in Fig. 2.

A curve 1 is the absorption of original undoped polymer. As distinct to the spectrum of undoped polyacetylene [1], a spectrum of PDA THD demonstrates relatively small number of typical maxima of low enough intensity: a lot of types of vibration transitions permitted in polyacetylene, in PDA are forbidden by the selection rules.

In the doped material (Fig. 2, the curves 2 and 3) the absorption bands typical of the original PDA THD are not observed. As distinct to polyacetylene, the doping does not lead to the appearance in a spectrum the new absorption bands.

In a spectrum of doped PDA THD the "steps" in the region $\nu \sim 625$ cm^{-1}, ~ 1000 cm^{-1} and ~ 1800 cm^{-1} are well pronounced. A sharp growth of extinction coefficient is also observed in a spectrum of undoped PDA THD with increasing ν higher than $\nu \sim 625$ cm^{-1} (Fig. 2, curve 1). There are not analogous peculiarities in a spectrum of undoped material at $\nu \sim 1000$ cm^{-1} and $\nu \sim$ 1800 cm^{-1}. The nature of these peculiarities are not fully clear by now.

The increase of extinction coefficient in a longwave region is usually associated with the absorption on the free carriers. Actually, with increasing of conductivity of a polymer the absorption in a longwave region grows monotonically both for PA and PDA THD. Absorption in "classical" semiconductors differs, however, from conjugated polymers in that, the absorption α in conventional semiconductors (Si, Ge, GaAs a.o.) grows with increasing wave length λ ($\alpha \sim \lambda^2$). This is caused by a fundamental reason: lower the energy of photon, lower impulse has to get a "free carrier" from the lattice (phonons) or from the impurities in order to absorb the quantum of light. An opposite situation takes place for the polymers: for the majority of bands, the absorption drops with increasing wave length. For PDA THD this tendency is more distinctly pronounced than for PA. This also confirms the assumption that the majority of carriers generating upon doping is concentrated in isolated clusters and "dead ends".

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References

[1] Tanaka J. And Tanaka M. in *Handbook of conducting polymers*, ed. T. A. Scotheim, N.Y.-Basel: Marcel Dekker, 1986, v. 2.