Doping-Induced Absorption in Polyphenylacetylene Films

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Abstract

The processes of donor and acceptor doping of polyphenylacetylene (PPA) films electrochemically obtained on transparent electrodes have been studied. It has been shown that donor *n*-doping of the PPA by lithium leads to formation of free charge carriers in the conjugated polymer chain, which cause a doping-induced absorption in the long-wave region. Under acceptor *p*-doping of the PPA films by iodine, the doping-induced optical absorption is observed in the short-wave region. It results from the complexes of charge transfer between the PPA and iodine.

Key words: polyphenylacetylene, electrochemical preparation, optical spectra, donor and acceptor doping, absorption bands.

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Introduction

Polyphenylacetylene (PPA) is a known organic molecular semiconductor with a significant photoconductivity [1-3]. It belongs to a family of π-conjugated polymers and has attracted a close attention of researchers because of its interesting electric and optical properties (e.g., photoconductivity, third-order nonlinear optical response and high sensitivity to relative humidity variations [4]). The energy of π-π* transition for the PPA gets into the range of 2.3–2.5 eV [3], thus providing a possibility of use in various optical devices operating in the visible spectral range, e.g., electrophotographic photoreceptor devices [2] and solar cells based on photosensitive organic-inorganic heterostructures [5].

Most of studies for the electronic properties of the PPA films have been so far concerned with the polymer obtained by chemical polymerisation of phenylacetylene (PA) in the presence of metal-complex catalysts [6,7]. As a result, a stereo-regular *cis*-polymer with a low electric conductivity (10^{-10}–10^{-9} Sm/cm [1]) is formed. Under appropriate thermal treatment (403 K), it transfers to a *trans*-isomer suitable for chemical doping. Preparation of *trans*-PPA layer on the solid surface is usually carried out by film casting from polymer solution in the organic solvent. Such films have a high resistance, are uneven and characterised by a poor adhesion to the surface [1,3]. Owing to doping by electron acceptor (J_2, AsF_5) or donor (Na, Li) and under illumination, the PPA conductivity may rise by 2–4 orders of magnitude [1,3,6]. Recently a possibility for direct formation of *trans*-PPA films with significant conductivity has been demonstrated, based on using some electrodes (Pt, Cu, ITO) and electrochemical polymerisation [8,9]. It has been found that electrochemically obtained PPA films are characterised by polycrystalline, globular or fibrous structures, depending on the current density and the electrode material used in the process. The location of absorption bands in the optical spectra of the PPA films depends on the conditions of polymer preparation [1–3]. For more wide applications of electrochemically obtained PPA films, it would be necessary to investigate the optical properties of these films and, in particular, the effect of doping on the optical spectra of the PPA.

In the present work the processes of doping-induced absorption in the optical spectra of electrochemically obtained PPA films have been studied under both the donor and acceptor doping.

Experimental

The PPA films were obtained by the electrochemical polymerisation of the PA in acetonitrile solution and in the presence of lithium salts as a supporting electrolyte [8,9]. The films obtained on the ITO electrodes were washed with methanol and dried in vacuum at $T = 323$ K. The films were doped electrochemically in 0.1 M $LiClO_4$ acetonitrile solution at the current density $i = 5$ mA/cm^2 in argon atmosphere. The acceptor doping was provided by the iodine vapour and iodine solution in the chloroform. The IR spectra of the PPA film were obtained with “Specord M-80” spectrophotometer in the range of $\upsilon = 400–4000$ cm^{-1}. The optical absorption spectra were recorded for the PPA films deposited on the ITO electrodes by means of SP-26 spectrophotometer in the range of $\lambda = 320…1000$ nm. The elemental analysis of the lithium content in the PPA films was performed with the atomic absorption method on the basis of flame photometer PFM-30-MZ. The specific conductivity of the PPA was measured on the sandwich-like ITO-PPA-Au structure at the room temperature. Finally, the PPA film structure was studied with scanning electron microscope ISI-DS-130.

Results and discussion

Synthesis and characterisation of the PPA

During the process of cathode electrochemical polymerisation of the PA, a conducting polymer layer with the specific conductivity in the region of $10^{-7} – 10^{-4}$ S/cm is formed on the surface of the ITO cathode [8,9]. The process is running as an anion-radical polymerisation [8] and it yields in forming a compact uniform film with a metallic gloss. The absorption bands located at 3060, 2960, 1600, 1504, 1390, 1680, 850 and 760 cm^{-1} are observed in the IR spectrum of the obtained polymer (see Fig. 1). This confirms that the synthesised PPA is a polymer characterised with the elementary link $[\text{-}(C_6H_5)\text{-}CH{=}CH\text{-}]_n$ and the space structure of *trans*-PPA [3,6] (see Scheme 1).

According to the scanning electron microscopy (SEM) data, the obtained polymer

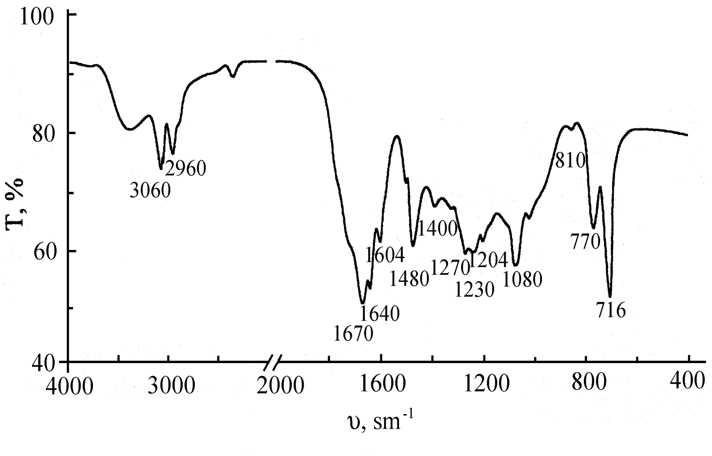
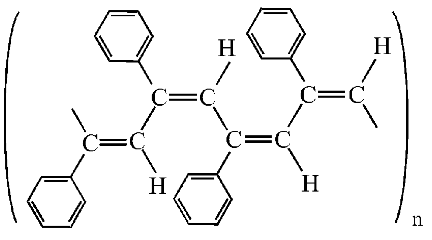


Fig. 1. IR spectrum of the PPA film.



Scheme 1. Molecular structure of the PPA.

films characterised with a polycrystalline structure (the size of crystallites being 0.01–0.03 mm – see Fig. 2) are stable in the organic solvents [1].

Electrochemical donor doping of the PPA

In the PPA obtained by the chemical synthesis under complex catalysts, dissolved in $CHCl_3$ and founded on the quartz, the absorption bands are observed only in the UV region [3,9]. The two main bands are observed in the absorption spectra of electrochemically obtained PPA in the near-UV and visible spectral ranges (Fig. 3). First of them is located at 360–380 nm. It corresponds to the π-π^* transition in the band gap, while the second, positioned in the visible region (600–700 nm), is caused by free carrier absorption [10-12]. Prolongation of the electrolysis time leads to increasing optical absorption in a wide spectral range, perhaps, due to growing film thickness and changing structure of the polymer (see Fig. 3).

It is found from the elemental analysis that the PPA film formed on the ITO cathode during electrochemical polymerisation undergoes doping by lithium. The doping level (y) of the PPA-Li films is in the range of 2–7 at. % Li, depending on the electrolysis time and the current density.

Electrochemical n-doping of the PPA by lithium under the electrochemical cathode process yields in the increasing intensity of the absorption band located near 600–700 nm and redistributing the intensity of the short-wave band at 360–380 nm (see Fig. 4) This band demonstrates a small bathochromic shift with the increasing quantity of charge carriers passed during the electrolysis, possibly, owing to increasing conjugation length [11]. The appearance of the additional band at 450 nm might be associated with formation of anion-radical (polaron) particles in the conjugated chain of the PPA [12]. A negative charge generated under the electron transfer is delocalised along the conjugated polymer chain

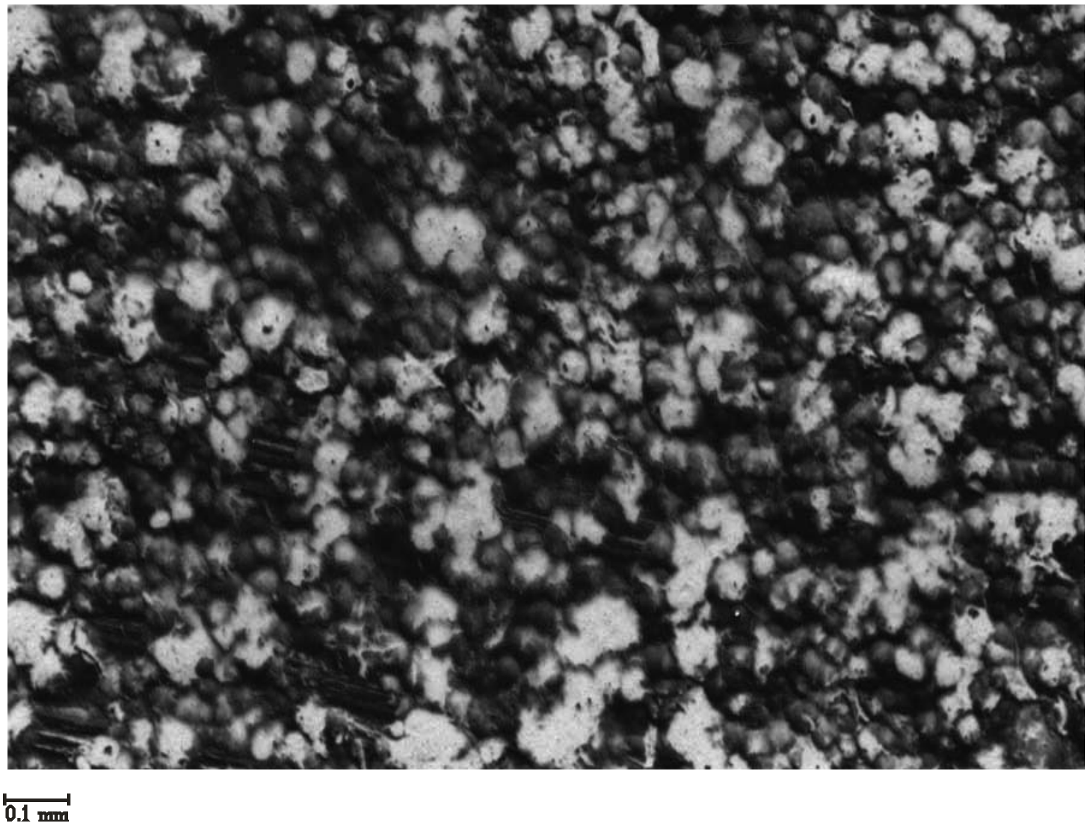


Fig. 2. Scanning electron microscope image of the PPA film deposited onto the ITO electrode (x100).

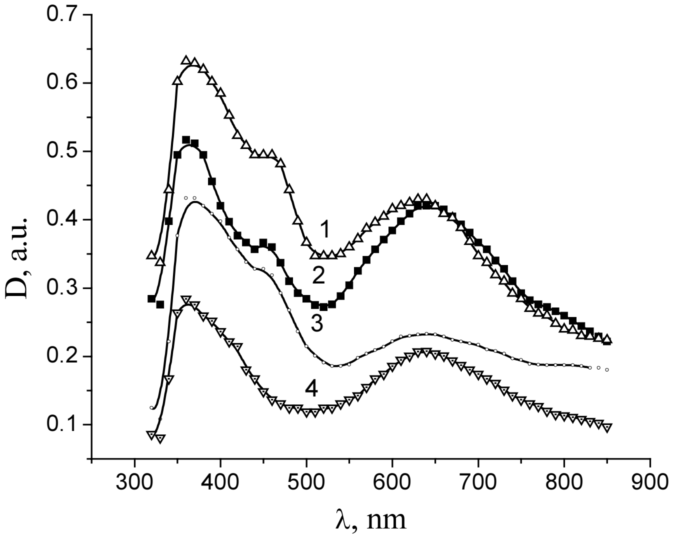


Fig. 3. Effect of electropolymerisation time on the optical spectra of the PPA films deposited onto the ITO cathode. The times of electrolysis are 40 (1), 30 (2), 20 (3) and 10 min. (4) and the current density is equal to *i* = 3.2 mA/cm^2.

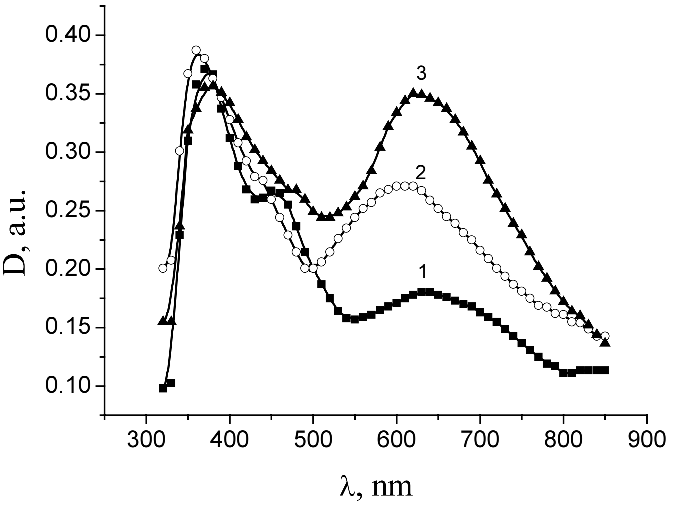


Fig. 4. Evolution of absorption spectra of the PPA films deposited onto the ITO surface in the process of electrochemical *n*-doping in 0.1 M LiClO$_4$ acetonitrile solution. The current density is 5 mA/cm^2, the doping times 0 (1), 10 (2) and 20 min. (3). The film is obtained at the current *i* = 3.2 mA/cm^2 acting during 20 min.

and compensated by the lithium cations, in accordance with Scheme 2.

$$[\text{-}(C_6H_5)\text{-}CH{=}CH\text{-}]_n + ye + y\text{Li}^+ \rightarrow$$
$$\rightarrow [\text{-}(C_6H_5)\text{-}CH{=}CH\text{-}]_n^- y\text{Li}$$

Scheme 2. Process of electrochemical *n*-doping of the PPA film.

Such the mechanism may be assigned to the donor or *n*-type doping of the PPA. As a result of electron injection from the electrode to the polymer chain, negative polarons (anion-radicals) are formed [10,12]. At higher doping levels, polarons associated with bipolarons appear. They cause a doping-induced absorption, which is especially expressed in the long-wave region (see Fig. 4). The process of *n*-doping of the PPA induces increasing electric conductivity (up to 10^{-4} S/cm), but the polymer tends to the native form through reoxidation. Notice also that the *p*-doped PPA exhibits a higher stability to the environment [3].

Acceptor p-doping of the PPA

The PPA reacts readily with organic and inorganic electron-accepting compounds, such as J_2, Br_2 and AsF_5, giving rise to a more highly conducting material [3,6]. Several forms of the acceptor-doped PPA have been shown to represent charge-transfer (CT) complexes, whose solutions show a broad CT band extended to the near-IR range [3]. The nature of the PPA-J_2 complex has been examined in the studies [3,6]. However, the effect of acceptor doping on the optical spectra of electrochemically obtained PPA films still remains unknown. We have established that a different behaviour of the absorption bands is observed under the doping of electrochemically prepared PPA films by iodine. Namely, this reduces to a large growth of the first maximum at 360–380 nm, while the band at 600–700 nm almost disappears (see Fig. 5).

The optical spectra presented in Fig. 5 allow one to suggest that the process of dedoping-doping occurs in the PPA films, which is caused by iodine. The process of dedoping in electrochemically obtained PPA films may proceed in the way illustrated by Scheme 3.

$$[\text{-}(C_6H_5)\text{-}CH{=}CH\text{-}]_n yLi + 1/2yJ_2 \rightarrow$$
$$\rightarrow [\text{-}(C_6H_5)\text{-}CH{=}CH\text{-}]_n + yLiJ\ \ldots$$

Scheme 3. Process of dedoping of the PPA-Li film by iodine.

The undoped PPA film exhibits one absorption band at 360–380 nm that corresponds to electron transition in the band gap of organic semiconductor [3,10]. The process of acceptor *p*-doping of the PPA causes significantly increased optical absorption and broadening of the band.

The similar changes occur in the case of iodine doping of the PPA film kept in the solutions with different iodine concentrations (see Fig. 6). The process of *p*-doping of the PPA film may be presented by Scheme 4.

$$[\text{-}(C_6H_5)\text{-}CH{=}CH\text{-}]_n + 3/2xJ_2 \rightarrow$$
$$\rightarrow [\text{-}(C_6H_5)\text{-}CH{=}CH\text{-}]xJ_3$$

Scheme 4. Process of doping of the PPA-film by iodine.

The detailed spectra for the solution of *trans*-PPA with a variety of electron acceptors have been reported in the literature, including

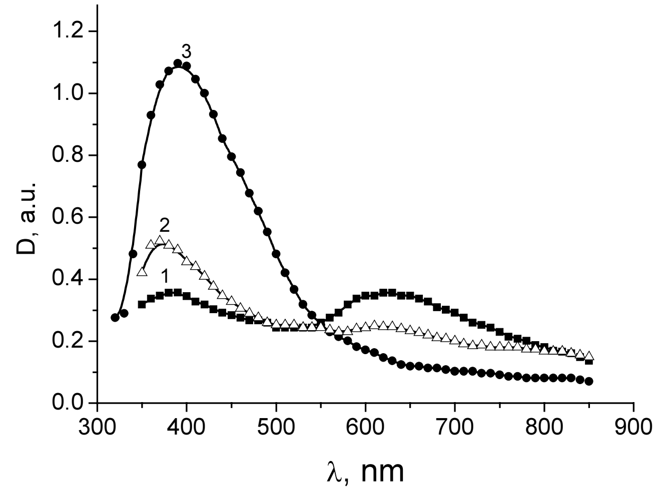


Fig. 5. Effect of acceptor doping on the electron spectra of the PPA film at different times of exposition in iodine vapours: 1 - 0, 2 – 5 and 3 – 30 s.

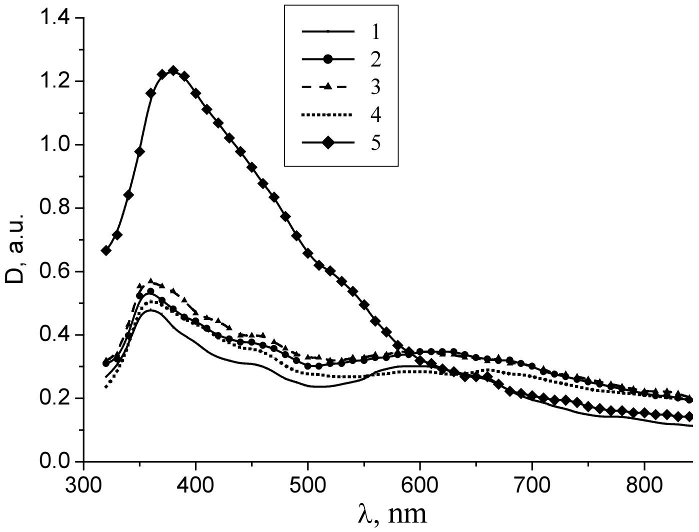


Fig. 6. Doping-induced absorption of the PPA films (1), which are doped during 120 s by the iodine in chloroform solution (the concentrations are 0.01 (2), 0.10 (3), 0.25 (4) and 1.00% (5)).

the entire spread of the CT band [1,3,6]. The absorption edge of the *π-π** transition characteristic of the polymer has been located at 670 nm. The changes in the optical spectra of the PPA films depicted in Fig. 5 and 6 are similar to those observed for the PPA-J_2 solution [3], where the existence of 1:1 complexes at low doping levels has been demonstrated [3,6]. This suggests that a process of formation of the CT complexes between the PPA and iodine takes place. The detailed nature of the complex depends upon microstructure of the polymer [3].

Conclusion

The doping-induced absorption has been observed in the PPA films electrochemically obtained on the ITO electrodes. Electrochemical doping of the PPA has been shown to cause formation of free charge carriers in the conjugated chain. It can be assigned to donor or *n*-type doping of the PPA. As a consequence, negative polaron is formed in the polymer chain. At higher levels of doping, the polarons transform to bipolarons, thus producing a doping-induced absorption, which is especially expressed in the long-wave spectral region. Under doping of the PPA films by iodine, increasingly pronounced absorption band is observed that corresponds to the *π-π** transition. Increasing iodine concentration leads to doping-induced optical absorption inside of this band, owing to formation of the CT complexes in the PPA doped with iodine.

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