

Doping of a Nonconjugated Polymer by an Organic Compound with Two Stable Energy States

D. D. Karamov^{a,*}, A. N. Lachinov^{a,b}, S. A. Pshenichnyuk^a, A. A. Lachinov^a,
A. F. Galiev^a, A. R. Yusupov^b, and S. N. Salazkin^c

^a Institute of Physics of Molecules and Crystals, Ufa Federal Research Center, Russian Academy of Sciences, Ufa, 450075 Russia

^b Akmulla Bashkir State Pedagogical University, Ufa, 450008 Russia

^c Nesmeyanov Institute of Organoelement Compounds, Moscow, 119991 Russia

*e-mail: karamov_danf@bk.ru

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Abstract—We investigate the effect of doping by a small-molecular-weight organic compound phenolphthalein of a non-conjugated polymer polydiphenyleneophthalide. Phenolphthalein is known to possess two energy stable states—neutral and charged, as a result of the capture of an excess electron. The morphology of polymer films surfaces observed by atomic force microscopy. The analysis of current–voltage characteristics showed that an increase in the concentration of the dopant leads to an increase in the conductivity. A non-trivial relationship between the increase in the conductivity and charge carrier mobility and the increase in the dopant concentration was found. At the same time, the presence of the dopant does not result in a significant change in the charge carrier concentration.

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INTRODUCTION

In electrically conductive polymers, the conductivity level is often governed by the addition of a dopant and its concentration [1–7]. The doping agents are usually both inorganic and organic compounds. In recent years, low-molecular-weight organic dopants are often used to tune the electronic states of the polymer matrix, which allows one to increase the efficiency of transport of various charge carriers in organic heterostructures [1–17]. This is especially typical in the search for ways to increase the efficiency of radiative recombination of excitons in multilayer electroluminescent devices including a great number of interfaces between different materials [9, 10]. Typically, in the above-described cases, modification is performed on organic materials with delocalized outer-shell π -electrons based on conjugated compounds [1–7, 9, 10]. However, no less interest is presented by organic compounds with a broad bandgap, which include nonconjugated polymers [8, 11–18]. Such polymers have no delocalization of π -electrons along the polymer chain, and such delocalization is restricted by the limits of the monomer unit. Nevertheless, such organic materials are of great interest, since a large energy gap between the highest occupied and lowest unoccupied orbitals allows one to change the electronic properties of the material in a wide range and, in the case of electroluminescence, to pro-

vide, for example, a difficult-to-obtain blue light source [4, 11]. Nonconjugated polymers, the thin sub-micron films of which can change their conductivity in a wide range, are known [15, 17]. The choice of organic dopants is also of interest. Generally, the main objective of a dopant is to create a stable electronic state resulting in a change in the electronic properties of a material [1]. At the same time, molecular dopants with several energy stable states, the transitions between which occur depending on the conditions of interaction with the matrix molecules, are also of concern to control the charge generation and transfer in an organic medium [7, 18]. In particular, phenolphthalein-type compounds which can exist in two stable states, neutral and charged, resulting from the interaction with excess charge of the medium, are known [19].

The aim of the present work was to study how doping of submicron poly(diphenyleneophthalide) films by phenolphthalein molecules influence their conductivity.

MATERIALS AND METHODS

The polymer material was poly(diphenyleneophthalide) (PDP), a nonconjugated polymer thin films of which show charge instability phenomena [15, 20], and the doping agent was phenolphthalein (PP) pro-

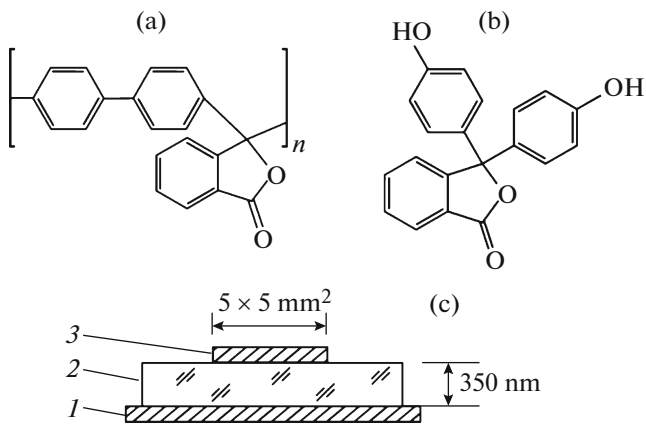


Fig. 1. Structural formulas of (a) poly(diphenyleneophthalide) and (b) phenolphthalein and (c) a schematic diagram of the sample structure: (1) metal 1, (2) polymer, and (3) metal 2.

duced by Alfa Aesar (Figs. 1a, 1b). PP was chosen because it has been observed earlier that this compound, when present in a polymer matrix, has an effect on the electronic switching threshold characteristics of a thin-film material. This observation has yet to obtain a necessary explanation. At the same time, it is known that, upon interaction with an excess electron, the structure of PP can pass into a π -conjugated state. It was assumed that the concentration of excess electrons can be controlled by changing the level of charge carrier injection into the polymer matrix and, thereby, initiating such transition within the polymer matrix so as to have an effect on its conductivity.

The structure of the sample appears as a metal/polymer/metal system (Fig. 1c). The metal electrode was made of copper and indium. Copper was deposited by thermomdiffusion vacuum coating onto the surface of a glass plate. The indium electrode was of clamp type and formed by knurling the indium foil onto the polymer film surface.

Polymer film samples were prepared from a 5 wt % solution of the polymer in cyclohexanone by its centrifugation on the copper electrode surface. After deposition, the film was subjected to drying: first, for 30 min in air at room temperature and, then, for 40 min at 150°C to remove the residual solvent. Phenolphthalein was added to a solution of the polymer at an amount of 1, 2.5, 5, 10, 15, and 20 wt % of the total dry weight.

The current–voltage characteristics (CVCs) of thin films were studied using a Keithley 2400 sourcemeter under normal conditions. The voltage range (0–2 V) was chosen taking into account injection processes occurring in film samples. Preliminary measurements showed that it is this voltage range where the functional dependence of current I on applied voltage U , $I \propto kU^n$, changes. That is, this dependence passes into a

superlinear mode at $n > 1$ and an injection mechanism begins to be manifested.

The resulting polymer films were preliminarily studied by atomic force microscopy (AFM). The contact force method of AFM and approaches earlier described in [21] were used. The study of the film morphology showed that they are not homogeneous in thickness and inclusion defects are absent, which suggests that there are good film-forming properties of solutions of the polymer and polymer with the molecular dopant.

A more detailed study of how the small-molecular-weight dopant influences the morphology of thin films was performed on silicon plates with a characteristic local surface roughness of about 0.1–0.2 nm. Figure 2 shows the data of the AFM study of the polymer film surface. Figures 2a and 2b show AFM images of the surface of the starting film and the doped film containing 20 wt % of PP, respectively. The dependences of the thickness and arithmetic mean roughness of films on the dopant concentration are shown in Fig. 2c. It was found that the thickness of the polymer film remains unchanged with an increase in the concentration of PP (within the AFM measurement error) to be in a range of 330–350 nm and the surface roughness increases by more than fivefold from 0.3 to 2 nm.

It seems that the roughness change is likely due to the surface modification of the polymer film upon an increase in the concentration of PP molecules. This is well seen on the AFM image shown in Fig. 2b.

A decrease in the film thickness upon a decrease in the concentration of PP by 20 wt % is likely due to a decrease in the viscosity of the starting solution of PDP + PP because of the increase in the concentration of the small molecular-weight component.

RESULTS AND DISCUSSION

Typical CVCs of experimental structures are shown in Fig. 3. Analysis of the measurement data showed that the CVCs have a nonlinear shape for all considered concentrations of PP. The highest conductivity of films is observed at an impurity content of 20 wt %, and the lowest conductivity was observed for pure PDP.

In all CVCs, one can distinguish an ohmic region $I \propto U^n$ ($n = 1$) and a superlinear region $I \propto U^n$ ($n > 1$). Such behavior of CVCs agrees well with the injection model [22–24]. According to the theory of space-charge-limited currents [24], the slope of the current–voltage curve changes when the concentration of injected charge carriers starts to exceed the concentration of intrinsic ones. By the position of this point on the CVC, one can estimate the equilibrium concentration of intrinsic main charge carriers, as well as their mobility. The equilibrium concentration was determined from the condition that the current values for

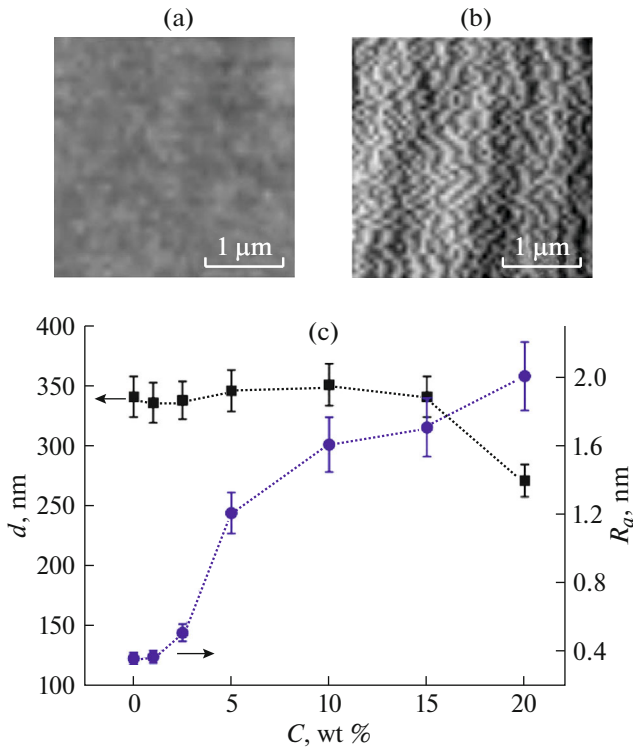


Fig. 2. Results of the analysis of AFM images of polymer film surfaces. AFM image of the polymer film (a) surface free of PP and (b) containing 20 wt % of PP. (c) Thickness and arithmetic mean roughness of the thin polymer film as a function of the weight concentration of PP in the polymer matrix.

the linear and quadratic sections of the current–voltage curve are equal at the point of inflection:

$$j_1 = \frac{en_0\mu U_n}{L}, \tag{1}$$

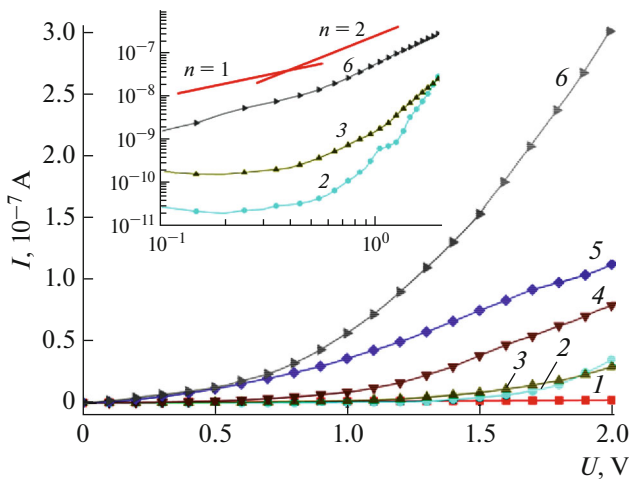


Fig. 3. CVCs of thin PDP films with different content of phenolphthalein: (1) 0, (2) 1, (3) 2.5, (4) 5, (5) 10, and (6) 20 wt %. The insert shows CVCs in logarithmical coordinates.

$$j_2 = \frac{\epsilon\epsilon_0\mu U_n^2}{L^3}, \tag{2}$$

where j is the current density, L is the distance between electrodes, U_n is the voltage corresponding to the transition point, n_0 is the equilibrium concentration of charge carriers, μ is the highest mobility of charge carriers, and e is elementary electric charge. Hence, equating Eqs. (1) and (2), we obtain the formula for concentration:

$$n_0 = \frac{\epsilon\epsilon_0\mu U_n}{eL^2}. \tag{3}$$

The carrier mobility was calculated by the formula

$$\mu = \frac{jL^3}{\epsilon\epsilon_0U_n^2}. \tag{4}$$

It should be noted that the estimation of μ by formula (4) gives in this case the minimum mobility of injected carriers. Figure 4 shows the equilibrium mobility and concentration of charge carriers as a function of the content of impurity molecules obtained from the analysis of CVCs in terms of the injection model. It is seen from the plotted dependences that the change in the conductivity with an increase in the percentage of PP molecules in the bulk of poly(diphenylenephthalide) film is due to an increase in the mobility of charge carriers. The assessment of the equilibrium concentration of charge carriers showed that, in the considered temperature range, the concentration remained almost unchanged (Fig. 4).

To analyze how a change in the contact parameters at the In/polymer interface influences the transport of charge carriers, we estimated the potential barrier height for electrons as a function of the dopant concentration. It has been shown earlier [25–27] that the Schottky thermionic emission is a predominant mechanism of charge transfer in the metal–PDP–

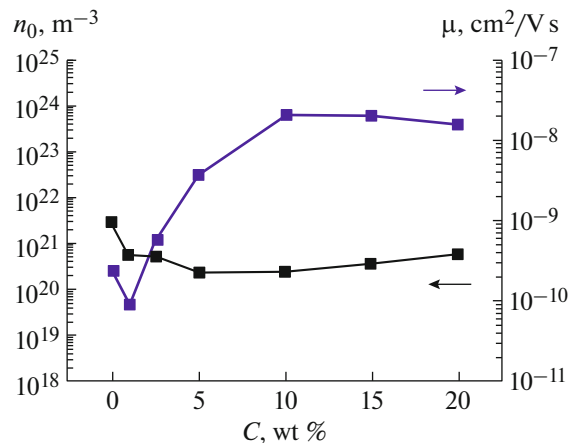


Fig. 4. Mobility and concentration of charge carriers as a function of the impurity content.

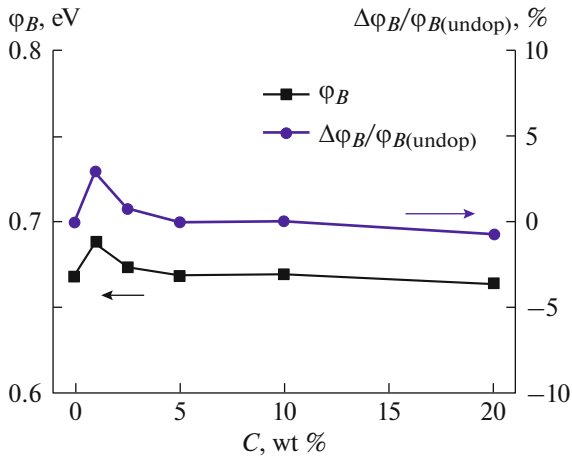


Fig. 5. Barrier height at the metal/polymer contact without taking into account the Schottky effect and relative potential barrier change $\Delta\phi_B/\phi_{B(\text{undop})}$ as a function of dopant concentration ($\phi_{B(\text{undop})}$ is the barrier height at zero concentration of the dopant).

metal structure at room temperatures and similar fields. In this case, the thermionic emission current density taking into account the barrier decreases due to the applied external field is governed by the equation

$$j = A^{**} T^2 \exp\left(-\frac{e\phi_{B0}}{kT}\right) \exp\left(-\frac{e(\Delta\phi + V)}{kT}\right), \quad (5)$$

where j is the current density, ϕ_{B0} is the asymptotic height of potential barrier at zero field, A^{**} is the effective Richardson constant, $\Delta\phi$ is the barrier decrease due to the Schottky effect, and V is the applied voltage.

Taking into account that the main aim of the present work was to estimate the relative change in the potential barrier height at the metal/polymer interface as a function of the dopant concentration, one can apply the total current method to determine the barrier height according to the formula [27]

$$\phi_B = \frac{kT}{e} \ln\left(\frac{SA^{**}T^2}{I_s}\right), \quad (6)$$

where T is the temperature, k is the Boltzmann constant, e is the electron charge, S is the contact area, A^{**} is the Richardson constant, and I_s is the saturation current. The saturation current is determined from the intersection of the linear approximation of CVC in semi-logarithmic coordinates ($\ln(I) - U$) with axis $U = 0$.

The calculated barrier height of the indium/PDP contact (Fig. 5) is overestimated compared to the value of $\phi_B \approx 0.39$ eV obtained in [25]. However, the relative change in the barrier height depending on the dopant concentration is not more than 5% and, within the error of the applied model, remains almost unchanged.

The theoretical interpretation of charge carrier transport by molecularly doped polymer is based on the analytical models of Gaussian disorder [28–31].

In particular, the model of charge transfer in weakly and strongly doped organic semiconductors [30, 31], relying on the Coulomb interaction of charge carriers with ionized impurities, quite well describes the charge carrier transport in the doped P3HT. However, the choice of the model in our case is not unambiguous. Nevertheless, the displacement of the energy level between the HOMO of the host, a polymer matrix, and the LUMO of the guest, a dopant, is a key parameter governing this transport [1–7, 30, 31].

The effect of the guest material on the mobility of the host material systematically changes depending on the LUMO energy of guests relative to the HOMO of hosts. For guests with a LUMO energy within ± 0.5 eV of the HOMO energy, competition between the formation of a deep tail in DOS and filling of electronic states is a dominant process controlling the transport [2]. In other cases, any polar pendent groups of the guest [2, 29] and changes in the morphology of the host predominate in the interactions with the host. For relatively amorphous materials of hosts, the last interaction can result in suppression of deep traps to result in an unexpected increase in the mobility by one or two orders of magnitude.

CONCLUSIONS

Doping of PDP with phenolphthalein has an impact on the conductivity of thin films, which increases with an increase in the concentration of PP in the bulk of the polymer. The presence of PP has no effect on the concentration of intrinsic charge carriers and the potential barrier height at the metal/polymer contact. The latter is likely due to the close electronic structures of the monomeric unit of PDP and the PP molecule at which the energies of lowest unoccupied and highest occupied molecular orbitals almost coincide. The increase in the conductivity is due to a significant increase in the charge carrier mobility, which can suggest the formation of additional charge transfer centers. A low voltage of the transition from linear to superlinear section of the CVC, associated with the fact that injected charges reached the concentration of intrinsic carriers, indirectly suggests that these transfer centers have a near-Fermi energy. The obtained data suggest that phenolphthalein can be used as a bistable molecular dopant to change the conductivity of thin films of nonconjugated PDP.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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