

Polydiphenylenephthalide: Optical Spectroscopy and DFT Calculations

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crossref <http://dx.doi.org/10.5755/j01.ms.17.3.591>

Received 21 September 2010; accepted 12 January 2011

The results of spectral and luminescent studies of polydiphenylenephthalide (PDF) solutions and thin films as well as molecule structure and its energy levels DFT modelling within the Gaussian-03 software package are presented. It is shown that structural unit (diphenylenephthalide) can form four polymer conformations with a similar energy gap. The most probable polymer conformation is the spiral cis-form with phthalide groups turned in opposite directions. At long-wave optical transition the electronic density moves on a chain of a molecule from diphenyl part to somehow distant phthalide one. Fluorescence excitation spectra reveal a transition band on a long-wave tail of the absorption spectrum. Spectral and time measurements of the luminescence allow to assume the presence of conformation transformations of PDF molecule under its optical excitation.

Keywords: polydiphenylenephthalide, fluorescence, spectroscopy, DFT calculations, helical structure.

1. INTRODUCTION

Organic electroactive polymers have found numerous applications in electronic devices [1, 2]. The wide range of such polymers with various unique properties is developed [3, 4] by this time. However, the synthesis of new polymers is urgent. One of the polymers with unusual properties is PDF and its derivatives. PDF is a carbocyclic polymer with high chemical and thermal stability (the glass transition temperature $T_g = 420^\circ\text{C}$, destruction temperature $T_d = 440^\circ\text{C}$), a full transparency in a visible range, high mechanical and excellent film-forming properties [5, 6] which is widely applied to formation of fibers, films and coatings. Excellent operational properties, and also sensitivity of electric and optical properties to external influences (temperature, pressure, various kinds of radiation, electric and magnetic fields, etc.) make PDF a perspective material for applications in various electronic devices [7]. In particular, piezoelectric effect [8], electronic switching effect [9], electroluminescence [10], field emission [11], etc. have been found, giving an opportunity for wide range of practical applications.

Structural unit of PDF polymer can be presented as in the following way (Fig. 1). PDF molecule is formed by binding of phenyl rings.

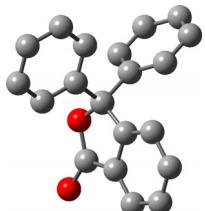


Fig. 1. Structural unit of PDF molecule

It is necessary to note that such structural unit is very similar to a phenolphthalein molecule, possessing high

sensitivity to pH of surrounding medium. However, PDF is absolutely inert for chemical influences though PDF solution in the concentrated sulfuric acid is strongly coloured [12]. PDF is capable of luminescence, while the phenolphthalein is almost not luminescing. It is possible to expect that some transformations of PDF molecule in oxidation-reduction processes can be similar to the same of phenolphthalein. PDF molecule consists of diphenyl and phthalide chromophores, transitions in which can be shown in optical spectra. Some optical properties of this molecule were already studied [13]. The aim of the present work is the further study of PDF spectral and luminescent properties as well as spatial and electronic structures of this macromolecule.

2. EXPERIMENTAL AND CALCULATION DETAILS

Thin films of 70 nm and 260 nm thickness were obtained by a spin coating with the subsequent solvent removing in drying chamber in vacuum at temperature $T = 150^\circ\text{C}$. Optical absorption, excitation and fluorescence spectra were measured with Cary 500 Scan UV-VIS-NIR (Varian) spectrophotometer and SFL-1211A (Solar TII, Belarus) spectrofluorometer accordingly. Fluorescence decay was measured with a special spectrofluorometer equipped by correlated photon counting. The fluorescence decay in the range $10^{-10} - 10^{-3}$ sec can be easily measured.

To determine optical properties and geometry of this compound and for analysis of molecular orbitals electronic structure, calculations of molecular characteristics by means of the software package of quantum-chemical calculations Gaussian 03 within the framework of the density functional theory (DFT) [14] were fulfilled. In recent years, DFT and its time-dependent extension (TD-DFT) has emerged as a reliable standard tool for the theoretical study of geometrical and electronic properties of big conjugated organic molecules, therefore it became the most widespread tool of molecular excited states studies [15, 16].

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The gas phase molecular geometries were optimised separately in the neutral, anion and cation states, by means of DFT with hybrid exchange correlation B3LYP functional with the average account of the exchange interactions contribution and with basis set 6-31G(d) that it is enough for good correlation of the theory and the experiment for molecules of such size. The calculations on the cationic and anionic species have been performed using the unrestricted B3LYP formalism. Boundary conditions and the algorithm were standard. Then from ground state geometry singlet excited states energies and oscillator strengths of transitions have been calculated by TD DFT method. Such calculations were carried out also with the use of B3LYP functional and basis set 6-31G(d) which gives wavelengths for the majority of important transitions of the conjugated molecules. Transition conditions reference is based on the excitation giving the basic contribution. Vertical electronic transitions spectra of the molecules were simulated using GaussSum 2.2 program [17]. Maxima in the spectra can be compared easily with the experimental data.

Vertical ionisation potential (IP_v) values were calculated as the energy difference between the energy of the cation at neutral geometry and the neutral molecule at neutral geometry; and adiabatic potentials (IP_a) as the difference between the cation at the relaxed cation geometry and the neutral molecule at neutral geometry. Similarly, vertical and adiabatic excess electron affinities values (EA_v and EA_a) are received as the difference between the energy of the anion at neutral geometry and the neutral species at neutral geometry and as the energy difference between the relaxed anion and neutral molecule, respectively.

3. RESULTS AND DISCUSSION

For the PDF molecule structure analysis we will consider possible ways of binding structural units with each other. Polymer formation can result in four types of molecular structures differing in direction of an angle between phenyl groups attached to every phthalide group forming the sawtooth trans-configuration (1) or the helical cis-configuration (2) of a molecule chain, and with position of the phthalide groups turned to opposite directions (a) or placed in one direction (b). Due to the steric factor cis-isomers are less stable usually, than trans-isomers. The optimisation of PDF molecule geometry with various quantity of structural units has shown that energy of the molecule consisting of two structural units, is slightly more preferable for sawtooth structure, than for helical. In the case of three structural units the energy difference is 0.017 eV. With the increase of quantity of structural units this difference starts to decrease and, beginning from five-six structural units the helical structure becomes more preferable (the energy difference is -0.16 eV for six structural units). This energy difference is not so essential, therefore polymeric chain structure can be both spiral or sawtooth with some probability. Transition from one configuration to another is possible at least, for example while heating.

On the other hand, the energy of molecules with phthalide groups turned to different directions is slightly

more preferable. For molecule containing two structural units in this case the energy is 0.006 eV lower, than for molecule with phthalide groups turned in the same direction, both for spiral and sawtooth configurations. The increase in quantity of structural units does not lead to essential shift of energies of the orbitals. As energy distinction is small, an order 0.1 eV, all four configurations are possible, though the most preferable is helical (see Fig. 2 for molecule containing six structural units), with the shifted axis and phthalide groups located outside of spiral.

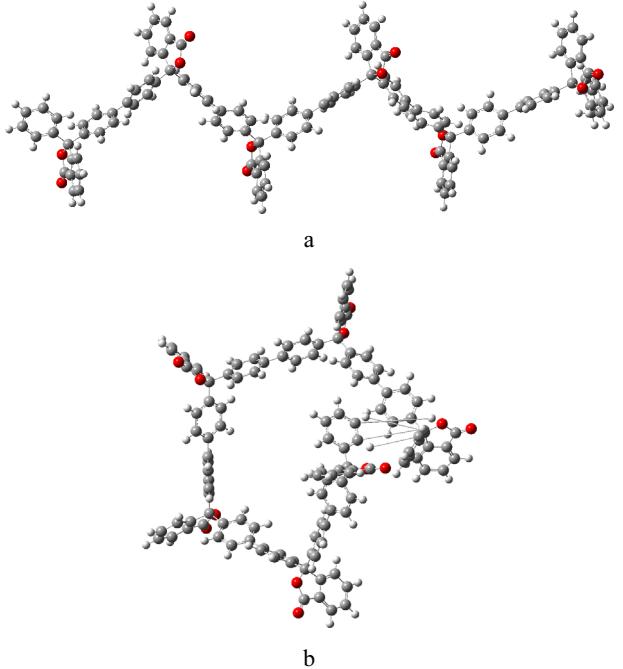


Fig. 2. Sawtooth (a) and helical (b) PDF molecule structure containing 6 structural units

For the case of 12 structural units a diameter of helical configuration ring (between diphenyl fragments axes and with the account of phthalide groups) is equal (1.6–1.8) nm and (2.5–2.7) nm, accordingly, the distance between chains is (0.57–0.99) nm. AFM-studies [18] have shown that the polymer fiber thickness is approximately 2 nm that is in good correlation with the diameter of helical molecule.

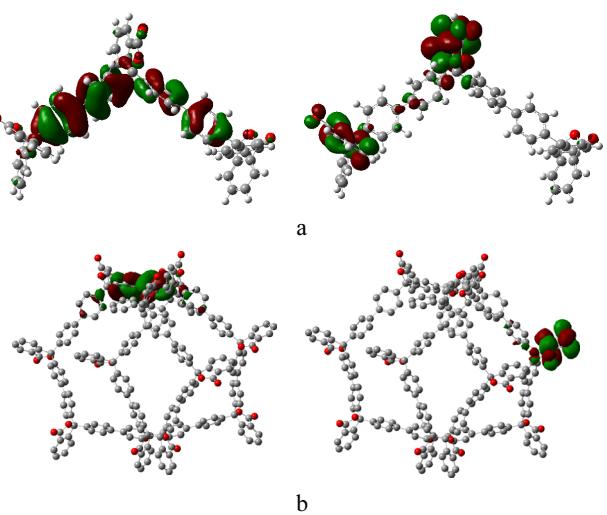


Fig. 3. HOMO (left) and LUMO (right) for PDF molecule consisting from 3 (a) and 12 (b) structural units

Table 1. The energy values (in eV) of main orbitals, optical gap, full energy difference (ΔE), ionization potentials and electron affinities, dipole moments μ (D), for molecule containing three structural units

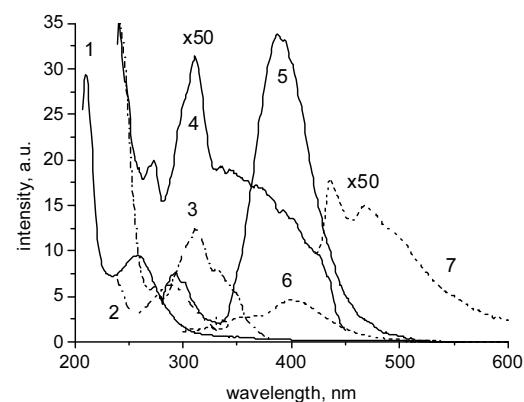
	HOMO-1	HOMO	LUMO	LUMO+1	gap	ΔE	μ	IPa	IPv	EAa	EAv
1a	-6.34	-6.26	-1.66	-1.63	4.6	0	5.6				
1b	-6.34	-6.20	-1.66	-1.61	4.54	0.0117	11.4				
2a	-6.39	-6.23	-1.66	-1.63	4.57	0.0175	10.5	7.11	7.24	0.88	0.82
2b	-6.34	-6.26	-1.66	-1.63	4.6	0.0160	11.4				

In case of the sawtooth form the distance between "saw teeths" is 1.6 nm, the greatest distance between ends of phthalide groups is 1.5 nm that is less, than results of AFM-measurements. Such molecule structure complicates molecules aggregation and provides amorphous morphology of polymer films. This structure of the polymeric chain is probably responsible also for unique properties of the polymer. Note that helical molecular structure is in accordance with the data for many other polymers [19, 20].

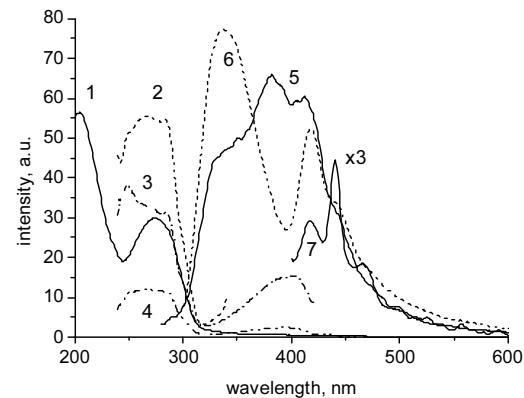
Fig. 3 illustrates the electronic density distribution in bottom occupied (HOMO) and in top unoccupied (LUMO) molecular orbitals for the most preferable structure of the molecule consisting of three and 12 structural units. At long-wave optical transition the electronic density moves from diphenyl molecule part to phthalide one in the similar way for all four configurations. For a molecule with twelve structural units the electronic density moves not to next phthalide group, but it moves to phthalide group located on some distance from the considered diphenyl. The energy difference between HOMO and LUMO orbitals and optical gap is small, an order of 0.01 eV (see Table 1). Therefore the presence of such configurations is difficult to detect by spectral methods. The optical HOMO-LUMO gap in case of the free molecule consisting of three structural units is 4.57 eV (Table 1), i. e. it is close enough to the experimental value for PDF film (4.2 eV). The increase in quantity of structural units reduces the gap value gradually. The most essential distinctions for each configuration are found in polarity calculated values. All configurations are polar enough. The least polarity (5.6 D) has a sawtooth shaped molecule with phthalide groups turned in different directions, dipole moment of a helical molecule with the same phthalide groups arrangement is almost twice higher (10.5 D). The ionisation potential of a helical free molecule from three units is 7.11 eV (adiabatic) and 7.24 eV (vertical), the external electron attachment energy is nearby 0.8 eV that is good correlated with experimental data for diphenyl phthalide [21].

The absorption, fluorescence and excitation spectra are presented in Fig. 4. The measurements are made for solutions and thin films, the calculations of absorption spectra are fulfilled for free molecules. The previous studies [13] have been made for PDF solutions in DMF and cyclohexanone as the best solvents for this molecule. The energy levels of these solvents are commensurable with the PDF ones. Therefore, the energy transfer from solvent on a polymer molecule can take place, and strong reabsorption of a luminescence radiation in the range up to 340 nm deforming many data for molecule, excitation and luminescence spectra in particular. For this reason ethanol was used as solvent in which PDF has sufficient solubility for optical measurements. The absorption spectra of PDF films and solutions are similar (see Fig. 4). They have a

short-wave band (with maximum at 205 nm–210 nm), a long-wave band (with maximum at 273 nm in film and 258 nm in solution) and a long tail. The maximum of a long-wave absorption band of PDF film and its dioxane solution is practically the same. The long tail belongs to weak n–π transition as a rule. Excitation spectra of PDF films measured at three registration wavelengths, coincide by position in the field of a long-wave absorption band, though they are not bell-shaped owing to radiation reabsorption; in the field of the absorption long-wave tail there is an expressed band with a maximum about 400 nm in an excitation spectrum the intensity of which grows with excitation wavelength decrease. This fact indicates the presence of the real absorption band in this spectral region.



a



b

Fig. 4. Absorption (1), excitation (2–4) and fluorescence spectra (5–7) for PDF ethanol solutions (a) and thin films (b); registration wavelength 350 (2), 395 (3, a), 440 (3, b) and 500 nm (4); excitation wavelength 240 (5), 280 (6) and 385 nm (7)

The excitation spectrum coincides with an absorption one, as a rule. The form of excitation spectra for PDF ethanol solution differs from absorption spectrum form, however the behaviour for all three registration wavelengths is identical. It means that the fluorescence quantum yield changes with wavelength that can be caused by complexes formation in excited states, reabsorption, change of molecule configuration etc. The most long-wave band maximum in the excitation spectrum is located near 300 nm. It is possible that the polymer molecule can change the form or form complexes with solvent in a solution that influences excitation spectra. It has been shown earlier [13] that for PDF in cyclohexanone the excitation spectra strongly depend on the solution concentration, that is connected, apparently, with reabsorption by solvent. To check it in PDF ethanol solution is impossible because of weak PDF solubility in this solvent. Note that measurement of excitation spectra at wavelengths shorter than 235 nm, i. e. in the short-wave band range completely, is practically impossible owing to quartz substrate luminescence or considerable reabsorption of ethanol.

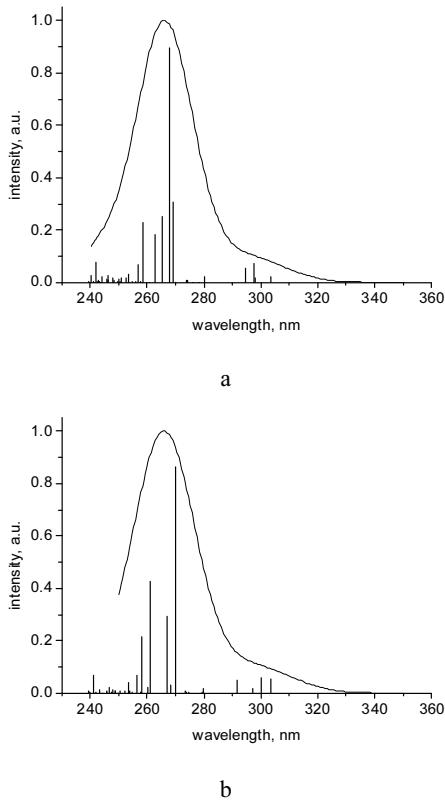


Fig. 5. Calculated oscillator strengths (bars) and absorption spectra for PDF free molecule (a) and solution (b)

As for luminescence spectra, in both cases three bands with a mirror symmetry to absorption spectra are observed. PDF solution excitation at wavelength between long-wave and short-wave absorption bands gives an intensive unstructured luminescence band with a maximum at 385 nm and weaker band at 295 nm. The excitation at the long-wave shoulder of long-wave band with the optical density ca. 40 % from optical density of the previous measurements, gives the luminescence with intensity of 10 % from the intensity of previous measurements and maxima at 350 nm and 400 nm. The excitation at the edge

of a long-wave tail gives a weak broadband luminescence with the maximum at 450 nm. For the film the same excitation wavelengths give the wide intensive structural luminescence spectra forming, apparently, three independent bands. The intensity of the most long-wave band is about 10 %–15 % of the intensity of the short-waves bands. Such difference is possibly caused by luminescence quantum yield changing due to the molecule rearrangements, complex formation, etc. Comparing experimental absorption spectra with the calculated (see Fig. 5), it is possible to notice that their maxima are close to each other. The shoulder in the range of 305 nm in the calculated spectrum takes place in the experimental one also. The long-wave absorption band practically coincides with a phenolphthalein spectrum. The bottom triplet transition takes place at 3.19 eV, singlet-triplet splitting (0.89 eV) is great, so the singlet-triplet conversion is inefficient.

Usually, the increase in the quantity of molecule structural units leads to spectral shift in the long-wave region. However, PDF spectrum is located in short-wave region, providing full transparency, and the increase in quantity of cycles practically does not influence the absorption spectrum.

Table 2. PDF fluorescence decay and abundance

	Excitation wavelength, nm	Decay, nsec	Abundance, %
Thin film	440	0.19	93.79
		1.38	6.21
Solution	440	0.69	93.63
		1.91	6.37
	500	0.72	88.77
		2.41	11.23

PDF luminescence decays quickly and exponentially (Table 2). For ethanol solution at excitation at 380 nm and registration at two wavelengths of 440 nm and 500 nm two exponents are observed; one component has $\tau \sim 0.7$ ns (about 90 % from total intensity) and the other component has $\tau \sim 2$ ns (about 10 %).

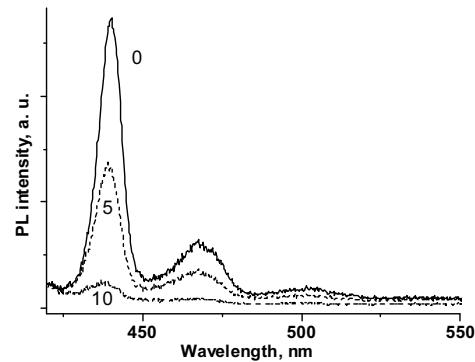


Fig. 6. Fluorescence spectra under irradiation of PDF film by laser at 380 nm during different time (in minutes near curves)

Luminescence decay of the film consists of two exponents also with approximately the same contributions of each exponent, however short-wave component is 3.5

times shorter, and long-wave is 2 times shorter. The luminescence duration decrease can be connected with configuration changes, or with intermolecular interactions. The comparison of the data for luminescence decay with the excitation and luminescence spectra allows to conclude the presence of conformation changes in the molecule at transition from solution to film. Longtime decay in microsecond area is not revealed within three orders of intensity magnitude at excitation by laser with wavelength 266 nm and registration in all range of the luminescence spectrum up to 700 nm.

Fig. 6 illustrates photodegradation of PDF film under intense laser irradiation in the long-wave spectral region. It can be seen that powerful radiation essentially decreases the photoluminescence intensity without any spectral changes. This data confirm essential photostability of this compound.

4. CONCLUSIONS

Thus, spectral and luminescent studies of PDF solutions and films and simulation of the molecule structure and its energy levels within the framework of the software package Gaussian-03 have allowed to receive a new information on the molecule structure and on transformation of optical excitation energy. The studies allow to assume the presence of conformation transformations of PDF molecule under its optical excitation. It is shown that structural unit (diphenylenephthalide) can form four polymer conformations with a similar energy gap. The most probable polymer conformation is the spiral cis-form with phthalide groups turned in opposite directions. At long-wave optical transition the electronic density moves on a chain of a molecule from diphenyl part to somehow distant phthalide one. Fluorescence excitation spectra reveal a transition band on a long-wave tail of the absorption spectrum. The internal space of the helical molecule can be used for introduction of various organic and inorganic structures.

Acknowledgments

The authors are thankful to E. E. Kolesnik (Institute of Physics, Minsk) for help during spectroscopic measurements, and A. N. Lachinov (Institute of Physics of Molecules and Crystals, Ufa) for PDF supply.

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*Presented at the International Conference
"Baltic Polymer Symposium 2010"
(Palanga, Lithuania, September 8–11, 2010)*