
SPECTROSCOPY OF POLYGERMANE FILMS**N. OSTAPENKO, N. KOZLOVA, S. SUTO¹, M. NANJO², K. MOCHIDA³**UDC 78.40.Me;78.66.On;61.25.Hq
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Absorption spectra in the temperature range 293–423 K and fluorescence spectra (5 K) of films, powders, and solutions of poly(di-*n*-hexylgermane) (PDHG) are investigated. Special attention is paid to the dependence of the spectra on the thickness of films and temperature. The obtained results are compared to data for poly(di-*n*-hexylsilane) (PDHS). It is shown that the structure of the absorption and fluorescence spectra of PDHG is caused by the presence of several structural forms of the polymer, whose polymer chains have different compositions of *trans*- and *gauche*-conformers.

1. Introduction

$\sigma - \sigma$ conjugate polymers of the $(R_2M)_n$ type, where $M=Si$ and Ge , while R are organic molecules, have unique optoelectronic and electrophysical properties due to the delocalization of σ -electrons along a polymer chain consisting of atoms of M . The investigation of the properties of these polymers attracts the attention of scientists because of their possible use as photodiodes, photoresistors, and materials for nonlinear optics. The polymer with the best investigated properties is polysilane – poly(di-*n*-hexylsilane) (PDHS), whose polymer chain contains Si atom, while side groups are presented by C_6H_{13} . It's known that PDHS is a thermochromic polymer [1]. The absorption spectrum of its film (several microns in thickness) contains two bands with maxima at 365 and 315 nm associated with the $\sigma - \sigma^*$ transitions in polymer chains having *trans*- and *gauche*-conformations, respectively, [1]. In

the fluorescence spectrum of such a film, one observes the 371-nm band ($T = 5$ K). As the thickness of the film d decreases down to 22 nm, the intensity of the *gauche*-conformation band in the absorption spectrum starts to essentially increase, and, at $d = 7$ nm, only this band is observed [2]. At the same time, in the fluorescence spectrum, there appears a new short-wave band with a maximum at 343 nm, whose intensity increases with decrease in d . When d reaches a value of 7 nm, only this band remains in the spectrum. It was assumed that this new band was caused by both the disordering of the polymer chain and the increase of the share of *gauche*-conformers in it [2]. The appearance of two fluorescence bands was also observed in the spectra of poly(di-*n*-methylphenylsilane) films in the case of a decrease of their thickness [3], as well as in the spectra of diluted solutions of this polymer [4]. This structure was associated with the presence of polymer chains with different distributions of short and long segments over their lengths.

In polygermane series, the structure similar to PDHS belongs to PDHG (see the inset in Fig. 1). However, the absorption spectra of PDHG films essentially differ in publications of different authors [5–7], whereas the fluorescence spectra are insufficiently investigated [5]. It was assumed that the differences in PDHG spectra were caused by different preparations of films and essentially depend on the molecular mass of a polymer [7].

In order to clarify the nature of these differences, the present work is devoted to the detailed investigations of

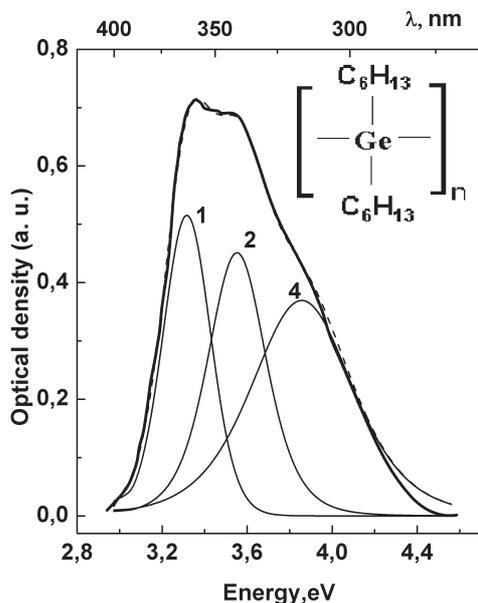


Fig. 1. Absorption spectrum of a thick PDHG film at room temperature and its decomposition into three bands 1, 2, 4 (see the Table)

absorption spectra in the temperature range 293–423 K as well as fluorescence spectra of films, powders, and solutions of PDHG with a molecular mass of 10600 at 5 K. The principal attention is paid to the dependence of optical spectra on the thickness of films and temperature. It is shown that the changes observed in these spectra are caused by different thicknesses of polymer films. The nature of the absorption and fluorescence centers of this polymer is investigated on the basis of the temperature dependences of spectra and the comparison of the obtained data with those for PDHS.

2. Experimental Technique

PDHG with a molecular mass of 10600 was synthesized by a technique described in [6]. A quartz substrate was coated with polymer films by means of centrifugation from polymer solutions in toluene of various concentrations (1 and 0.01%). In order to obtain the fluorescence spectra ($T = 5$ K), a DFS-12 spectrophotometer integrated with a helium cryostat was used. For the excitation of fluorescence, we used light with a wavelength of 313 nm extracted from that emitted by a DRSh-250-3 high-pressure mercury lamp with the help of a filter transmitting a group of lines in this region. The absorption spectra ($T = 293 \div 423$ K) of films and solutions in toluene (with the concentration

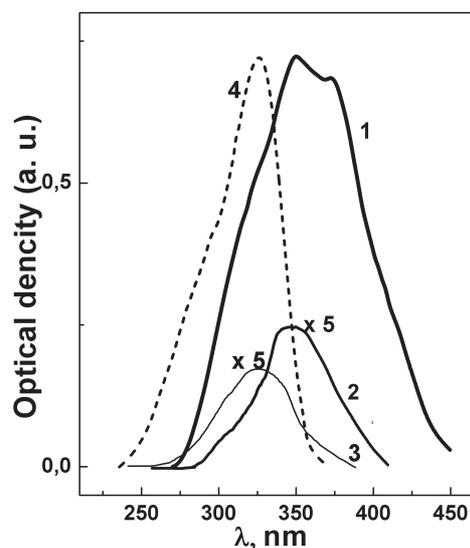


Fig. 2. Dependence of the absorption spectrum of PDHG films on the thickness (293 K). The thickness of the films decreases from several μm to approximately 30 nm (curves 1–3, respectively). The absorption spectrum of a PDHG solution in toluene is presented for comparison (4)

varying from 1% and 0.01%) were investigated using a KSVU-23 spectral-computing system.

3. Experimental Results

3.1. Absorption spectra of poly(*di-n-hexyl-germane*) films

Figure 1 presents the absorption spectrum of a thick PDHG film obtained at room temperature. The inset depicts the structural formula of this polymer. From Fig. 1, one can see that the spectrum has a complex contour, which consists, after the computer resolution, of three bands with maxima at 373, 348, and 323 nm. It's worth noting that the band with a maximum at 373 nm is narrower than that with a maximum at 323 nm by a factor of two. This spectrum coincides with the absorption spectrum obtained in [7] for PDHG with a molecular mass of 259,660. Figure 2 demonstrates the dependences of the absorption spectra on the thickness

Bands in the absorption and fluorescence spectra of PDHG and their classification

N of a bands	1	2	3	4
λ_{max}^1 absorption, nm	373	348	335	323
λ_{max}^2 fluorescence, nm	376	366	352	–
$\lambda_{\text{max}}^2 - \lambda_{\text{max}}^1$, nm	3	18	17	–
Conformation of polymer chains	T	>T+G	>G+T	G

Notations: T – *trans*-conformation, G – *gauche*-conformation

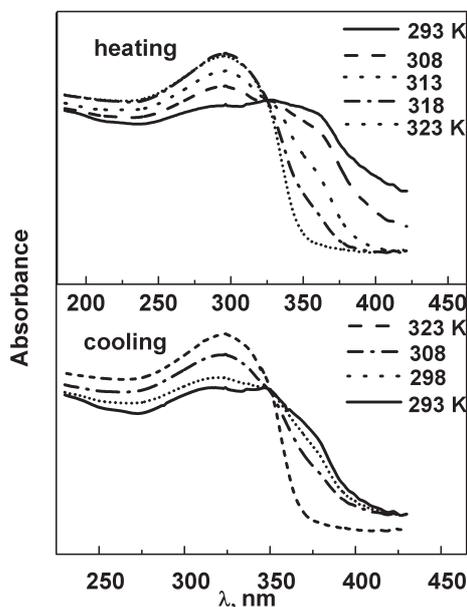


Fig. 3. Temperature dependences of the absorption spectrum of a thick PDHG film in the case of its heating in the range 293–323 K and cooling in the range 323–293 K

of films. The latter were varied from several μm to approximately 30 nm. For the sake of comparison, the absorption spectrum of a solution is also presented. From Fig. 2, one can see that the absorption spectrum depends essentially on the film thickness. Namely, with decrease of the thickness (from several μm to 30 nm), the intensities of bands with shorter wavelength increase. For example, in the spectrum presented by curve 2, the most intense band is that with a maximum at 350 nm. It's worth noting that this absorption spectrum is similar to that obtained in [7] for a polymer with a molecular mass of 73,940. After a further decrease of the thickness of the film, the absorption spectrum mainly consists of the short-wavelength band with a maximum close to 323 nm. This spectrum coincides with that obtained in [5] for polymers with a molecular mass changing in the range 7,600–11,400. It's worth noting that the band with a maximum at 323 nm is also observed in the absorption spectrum of the polymer in a toluene solution (Fig. 2, curve 4).

The obtained data testify to the fact that, as a whole, one observes four bands with maxima at 373, 348, 335, and 323 nm in the absorption spectrum of a PDHG film. As the thickness of the film decreases, the spectrum shifts to the short-wavelength side.

Figure 3 demonstrates the temperature dependence of the absorption spectrum of a thick film in the case of heating the sample in the temperature range 293–323 K,

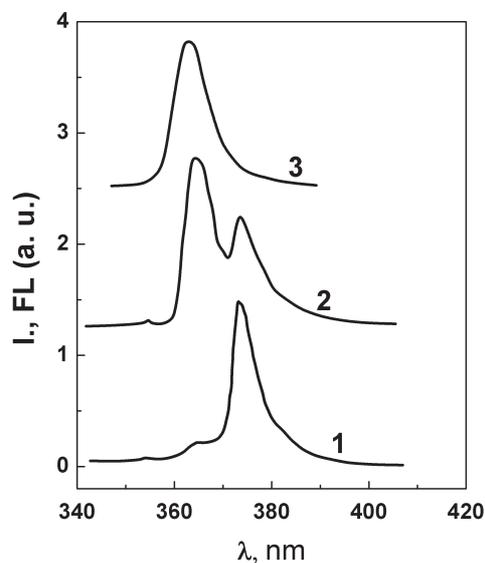


Fig. 4. Fluorescence spectra of a PDHG film (1), powder (2), and solution in toluene (3) at 5 K

as well as in the case of its cooling from 323 down to 293 K. Essential changes observed in the spectrum with temperature variation correspond to the thermochromic transition observed at 323 K and are concerned with a change of the conformation of the polymer chain from *trans*- to *gauche*-form [7]. As one can see from Fig. 3, the heating first results in the disappearance of the 373-nm band and then of the 348-nm one. At 323 K, one mainly observes a very wide band with a maximum at 323 nm. If the film after heating is cooled down to room temperature (Fig. 3), the bands with maxima at 323 and 348 nm become clearer, whereas the intensity of the 373-nm band is partially reproduced only in several days. Thus, the initial spectrum recorded before annealing isn't reproduced immediately. However, after the further heating and cooling, the band with a maximum at 373 nm practically cannot be reproduced.

3.2. Fluorescence spectra of poly(*di-n*-hexylgermane) films

Figure 4 demonstrates the fluorescence spectra of the film, powder, and toluene solution of PDHG polymer recorded at 5 K. From the figure, one can see that the fluorescence spectra of the thick PDHG film and powder mainly consist of two bands with maxima close to 366 and 376 nm characterized with different ratios of intensities. In the fluorescence spectrum of the film, the most intense band is the 366-nm one, while in that of the powder – the 376-nm band. The fluorescence spectrum

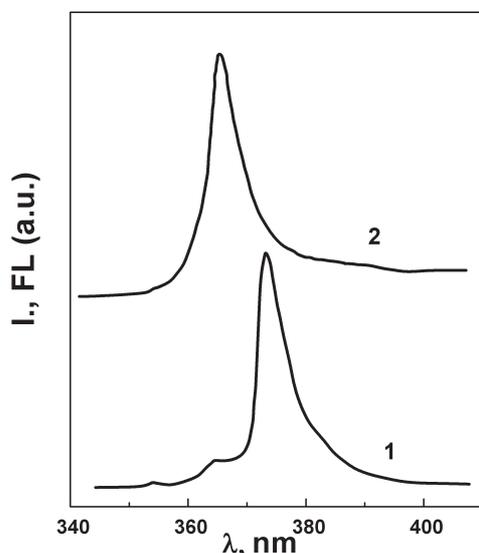


Fig. 5. Fluorescence spectra ($T = 5$ K) of a PDHG film for two thicknesses. Curve 1 corresponds to a film of larger thickness

of the polymer solution with a concentration of 10^{-4} mole/l contains only one band with a maximum at 364 nm. The fluorescence spectrum of PDHG films also essentially depends on their thickness (Fig. 5). One can see that, in the case of a thick film (the same sample as in Fig. 2, curve 1), the spectrum consists of three bands with maxima at 376, 366, and 352 nm. Moreover, the most intense band is the 376-nm one, while the band at 352 nm is very weak. In the sample of lower thickness (the same sample as in Fig. 2, curve 3), the 376-nm band disappears and the spectrum includes only an intense band with a maximum at 366 nm and a weak 352-nm band. In the fluorescence spectrum of the thick film after its heating to 323 K and cooling down to 5 K, one observes an increase of the relative intensity of the 366-nm band which essentially broadens after repeated heating.

PDHG films were commonly obtained from a 1% solution of the polymer in toluene. If a film is obtained from a more diluted solution, its fluorescence spectrum at 5 K, in addition to the narrow band with a maximum at 378 nm and the wide intense band with a maximum at 366 nm, contains an intense short-wavelength wide band with a maximum at 352 nm (Fig. 6).

4. Discussion of the Results

Our investigations of the absorption and fluorescence spectra of PDHG polymer films have demonstrated that the spectra depend essentially on their thickness. Moreover, the absorption spectrum contains four bands

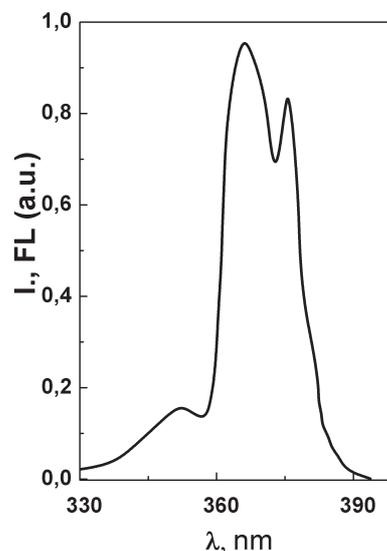


Fig. 6. Fluorescence spectrum ($T = 5$ K) of a thin PDHG film obtained from a diluted solution in toluene

with maxima at 373, 348, 335, and 323 nm (Fig. 2), while the fluorescence spectrum includes three of them with maxima at 376, 366, and 352 nm (Fig. 5). As a result, it is discovered that there exist four absorption centers in the polymer. In the same way as PDHS, PDHG is a thermochromic polymer. Electron transitions in it strongly depend on the type of conformation of the polymer chain and side groups. As the length of Ge-Ge bond is larger than that of Si-Si bond, the intermolecular interaction between segments of the polymer chain in PDHG must be weaker than that in PDHS [8]. That's why one can assume that, for PDHG, changes of the conformation of the polymer chain are more probable than those for PDHS. In addition, as the length of the polymer chain in PDHG is comparable with the thickness of films, the probability of the observation of different conformations of the polymer increases. Probably, this fact explains the presence of four bands in the absorption spectrum of PDHG rather than two as in the case of PDHS. Let's suppose that these bands correspond to centers that have different compositions of *trans*- and *gauche*-conformers along polymer chains. For example (see the Table), center 1 (the band with a maximum at 373 nm) includes polymer chains with the ordered *trans*-conformation, whereas center 4 (the absorption band with a maximum at 323 nm) corresponds to polymer chains with the disordered *gauche*-conformation. The fact that the halfwidth of band 4 is larger than that of band 1 by a factor of two verifies our assumption. Centers 2 and 3 correspond to polymer chains with different compositions of *trans*-

and *gauche*-conformers. It's known that, in a solution, polymer chains have a disordered conformation [9]. That's why the fact that the 323-nm absorption band of a thin film is close to that of the solution testifies to the correctness of our hypothesis.

It's known that the thermochromic transition in PDHG is observed at 323 K [7]. If our assumption about the nature of the absorption centers is correct, we must observe that, with increase in the temperature of a film to 323 K, the *trans*-conformation band (373 nm) is replaced by bands with different compositions of *trans*- and *gauche*-conformers, whereas, at the phase transition temperature, one must mainly observe the *gauche*-conformation band (323 nm), which is confirmed experimentally (Fig. 3).

The maxima of the bands of *trans*- and *gauche*-conformations in the absorption spectrum of PDHS as well as that of the *trans*-conformation band in its fluorescence spectrum are only slightly shifted from the positions of the corresponding bands in PDHG spectra. The fact that the difference between the positions of the maxima of the bands of *trans*- and *gauche*-conformers in the absorption spectra of these polymers is the same (~ 50 nm) also indicates that the identification of the bands in the PDHG absorption spectrum is correct.

As in the fluorescence spectra of PDHG films at 5 K, one simultaneously observes three or two bands depending on their thickness, we can assume that these centers are spatially independent, located at different distances from the substrate, and hence the energy transfer between them is weak.

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СПЕКТРОСКОПІЯ ПЛІВОК ПОЛІГЕРМАНІВ

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Резюме

Досліджено спектри поглинання в інтервалі температур 293–423 К та спектри флуоресценції (5 К) плівок, порошоків та розчинів полі(ді-*n*-гексилгерману) (PDHG). Основну увагу приділено залежності спектрів від товщини плівок та їх температури. Одержані результати порівнюються з даними для полі(ді-*n*-гексилсилану) (PDHS). Показано, що структура спектрів поглинання та флуоресценції PDHG пов'язана з наявністю декількох структурних форм полімеру, полімерні ланцюги яких мають різний склад *транс*- та *гош*-конформерів.