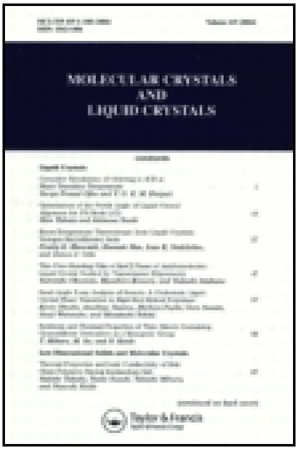

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Effect of Disorder on the Optical Spectra of Polygermane Films and Nanocomposites

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Effect of Disorder on the Optical Spectra of Polygermane Films and Nanocomposites

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The fluorescence and fluorescence excitation spectra, as well as the absorption spectra of a poly(di-n-hexylgermane) film and a nano-sized polymer confined into nanopores of SBA-15 with pore diameters of 6 and 10 nm, were measured in the temperature range from 5 to 250 K. The observed data were compared with those obtained for poly(di-n-hexylsilane).

The optical spectra of nano-sized poly(di-n-hexylgermane) differ significantly from those of a bulk film and depend on the pore diameters. These spectra correspond to the polymer chains with even less ordered segments and interchain aggregates. This is confirmed by the absence of the thermochromic transition in the composites contrary to the film. The poly(di-n-hexylgermane) polymer chain conformation in the restricted pore volume becomes disordered with a decrease of the nanopore size from 10 to 6 nm.

Keywords: films; mesoporous silica; nanocomposites; optical spectra; poly(di-n-hexylgermane); poly(di-n-hexylsilane)

INTRODUCTION

The manufacture of the nano-sized polymers opened an exciting new direction in the modification of the photophysical properties of ultra-thin polymer films. One of the reliable techniques of the fabrication of nano-sized polymers is the introduction of polymers into the nano-sized pores of mesoporous silica.

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The optical spectra of nanocomposites based on poly(di-n-hexylsilane) PDHS and poly(methylphenylsilane) PMPS confined into mesoporous silica were studied for the systems prepared by this method [1–4]. An essential influence of the space confinement on the observed spectra was found to be a result of the competition between the polymer-surface and polymer-polymer interactions. It was shown that these interactions lead to new structures of nano-sized polymer that are not observed in bulk films [1–3].

Poly(di-n-hexylgermane) (PDHG) has structure similar to that of PDHS, where the monomer unit Si $(C_6H_{13})_2$ is replaced by Ge $(C_6H_{13})_2$. Since the Ge-Ge bond is longer than the Si-Si bond, the intramolecular interaction is expected to be less pronounced as compared with PDHS. This suggests that PDHG has more flexibility near its backbone [5], and conformational changes in the polymer chain are more probable for PDHG than those for PDHS. As a result, the optical spectra of a PDHG film and PDHG/CBA-15 nanocomposites can be different.

This work presents the results of a study of the monitoring of the PDHG optical spectra varying the structure from a bulk polymer film to a nano-sized polymer incorporated into mesoporous silica. The nanocomposites PDHG/SBA-15 were fabricated by the incorporation of the polymer chains intro pores of the SBA-15 mesoporous silica with a pore diameter of 6 and 10 nm. PDHG films and composites were investigated using fluorescence (FL) and excitation spectra at (5-250) K, as well as the absorption spectra at room temperature.

The nature of the absorption and fluorescence centers in PDHG films and the PDHG/SBA-15 nanocomposites is analyzed by comparing the data with the similar well-known results studies of PDHS films and PDHS/SBA-15 nanocomposites [1–4].

EXPERIMENTAL

PDHG was synthesized as described in [6]. Details of the preparation of the mesoporous silica material SBA-15 was described in [7].

The parameters of the porous system were calculated by the Barrett—Joiner—Halenda method from the isotherm absorption branches. The measurements showed quite a narrow scatter in the pore diameters.

In order to incorporate the PDHG polymer ($M_w = 10600$) into nanopores of SBA-15, the prepared silica matrixes were immersed in a 1% wt. solution of the polymer in toluene and slowly stirred in dark at 293 K for several hours and then kept in dark till the evaporation of the solvent. Then the composite was twice washed in dark for approximately 2 h by stirring it in fresh toluene to remove the polymer from the exterior surface. The location of the polymer in pores was determined by the X-ray diffraction method by monitoring the presence of the characteristic silica framework structure. The PDHG films were obtained by deposition on a quartz substrate by spin-coating.

The FL and excitation spectra were recorded by a DFS-12 and a Hitachi MPF-4 integrated with a helium cryostat in the temperature range from 5 to 250 K. FL is excited by a xenon lamp at a monochromator-selected wavelength of 313 nm. The absorption spectra were recorded by KSVU-23 at room temperature.

RESULTS AND DISCUSSION

1. Absorption and Fluorescence Spectra of PDHG Films

Figure 1 shows the absorption spectra measured at room temperature and the fluorescence spectra ($T = 5\,K$) of: (a) the PDHS film, (b) the PDHG film. Insets depict the structural formula of both polymers. It is seen that the spectra of the PDHS film show two absorption bands

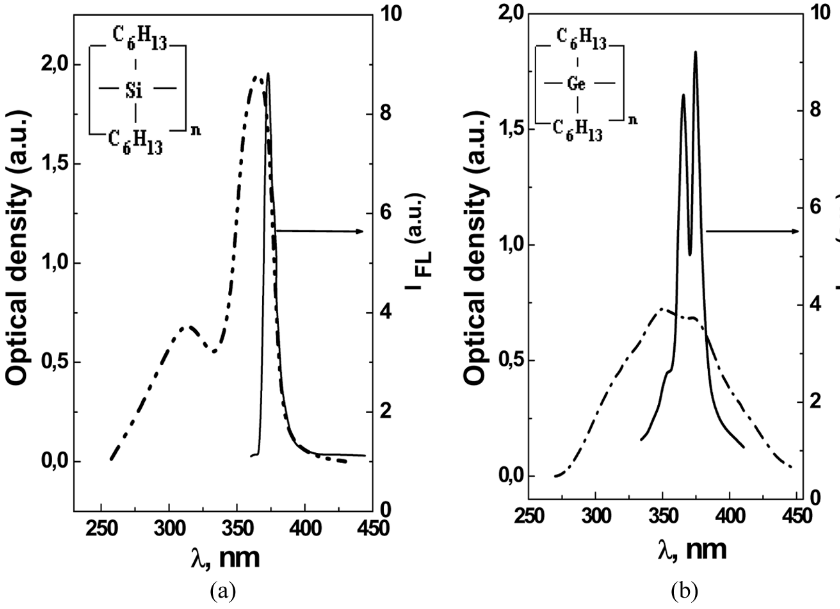


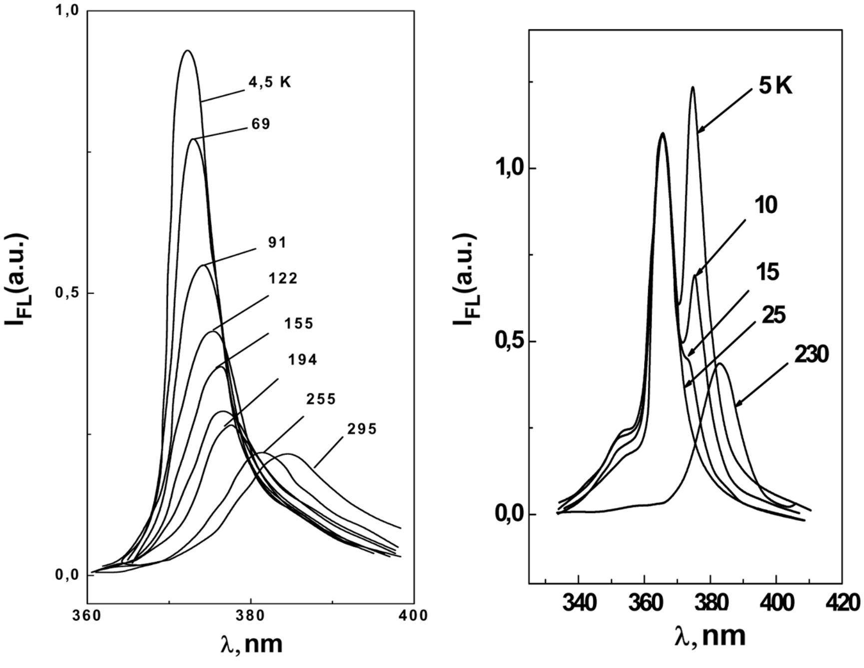
FIGURE 1 Absorption spectra at room temperature and fluorescence spectra ($T = 5\,K$) of: (a) a PDHS film, (b) a PDHG film. Insets depict the structural formula of both polymers.

at 362 and 313 nm assigned to the σ–σ^* transitions of the Si backbone and a sharp fluorescence band at 371 nm (Fig. 1a). The absorption band at 362 nm was assigned to the polymer chain having *trans*-conformation, and the other band was assigned to the polymer chain having *gauche*-conformation. The spectra of the PDHG film become more structured and consist of three absorption bands with maxima at 373, 348, and 323 nm, respectively, and three fluorescence bands ($\lambda_e = 313$ nm, $T = 5$ K) at 352, 366, and 376 nm (Fig. 1b).

Like PDHS, PDHG is a thermochromic polymer. Its electron transition strongly depends on the conformation of the polymer chain which should transform from the *trans*-conformation to the *gauche*-conformation with increase in the temperature. It is known that PDHG has the thermochromic transition at 323 K [8,9]. As the temperature increases, the band at 373 nm is replaced by a broad band at 323 nm. Note that the band centered at 323 nm is similar to the absorption band observed in the spectrum of the polymer in a toluene solution. It is known that the polymer chain in a polymer solution has a disordered conformation [10].

Since the Ge-Ge bond is longer than that of the Si-Si bond, the intramolecular interaction is expected to be less than that in PDHS. This suggests that PDHG has more flexibility near the backbone, and conformational changes in the polymer chain are more probable for PDHG than those for PDHS. This fact may be responsible for the existence of several bands in the absorption spectra of a PDHG film instead of two bands observed in the spectra of PDHS (Fig. 1). The presence of several absorption bands in the spectrum of the PDHG film correlates well with the X-ray data [5] showing that the PDHG film is less ordered than the PDHS film. We suppose that these bands originate from the absorption centers with different amounts of *gauche*- and *trans*-conformers along polymer chains. The presence of several FL bands in the spectrum of the PDHG film allows us to suggest that these centers are spatially independent, which results in the slow excitation energy transfer between them.

The temperature dependence of the FL spectra of the both polymer films is presented in Figure 2 ($\lambda_e = 313$ nm, $T = 5$ K). It is seen that the FL band in the PDHS spectrum shifts to the red side and broadens, and its intensity decreases with increase in the temperature (Fig. 2a) [11]. The PDHG FL bands show a different temperature dependence. As the temperature grows from 5 to 250 K, both bands at 366 and 352 nm reveal the temperature dependence similar to that observed for the band in the PDHS spectrum. The intensity of the band at 376 nm drastically decreases with increase in the temperature and disappears at 25 K (see Fig. 2b). These data confirm our assumption that



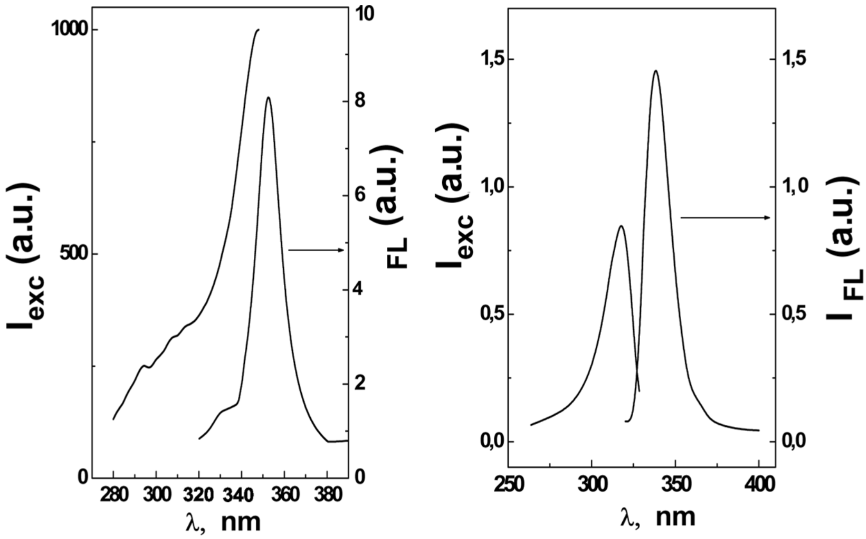
(a) (b)

FIGURE 2 Temperature dependence of FL spectra of a PDHS film (a) and a PDHG film (b) ($\lambda_e = 313$ nm).

the polymer chains of a PDHG film generally consist of *gauche*-conformers [9], while the randomly ordered segments behave as defects. The comparison of the observed data with those obtained for PDHS allowed us to conclude that the polymer chains of the PDHG film are more disordered than those of the PDHS film.

2. Fluorescence and Excitation Spectra of Nanocomposite PDHG/SBA-15

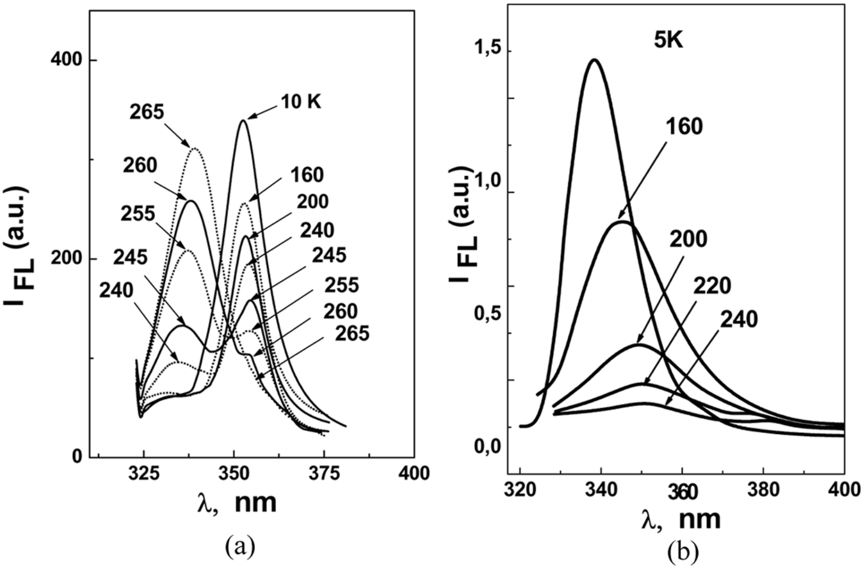
The FL spectrum of PDHS/SBA-15 composite with a pore diameter of 6 nm ($T = 5$ K) consists of the single band with a peak at 350 nm (Fig. 3a). This band was assigned to the polymer chain having the *trans*-conformation [12]. The excitation spectrum of this composite shows the single band with a maximum at 346 nm. The FL ($\lambda_e = 313$ nm) and excitation spectra of PDHG incorporated in SBA-15 with a pore diameter of 6 nm observed at 5 K are presented in



(a) (b)

FIGURE 3 FL and excitation spectra of the PDHS/SBA-15 composite (a) and the PDHG/SBA-15 composite (b) ($T = 5\,\text{K}$, a pore diameter of 6 nm).

(Fig. 3b). The FL spectrum shows the single intensive broad band with a maximum at 338 nm. The excitation spectrum monitored for this FL band shows the single band with a maximum at 317 nm. As seen in Figures 3b and 1b, the FL spectra of the confined PDHG and the PDHG film significantly differ. The FL spectrum of PDHG confined in 6-nm pores displays the single band at 338 nm shifted by 14 nm to the short-wavelength side relative to the FL band in the spectrum of a film at 352 nm which has been assigned to the polymer chain having a *gauche*-conformation [9]. A PDHG monomer unit is 1.7 nm long. The simulation of the PDHS/SBA-15 nanocomposite with the hexagonal pore with a diameter of 6 nm shows that this pore can hold three macromolecules in three alternate corners [12]. So, this significant blue shift is due to the reduction of the intermolecular interaction between the polymer chains. This confirms that the polymer chains are indeed incorporated into pores of SBA-15. Only the single band was observed also in the FL spectra of the PDHS/SBA-15 composite with a pore diameter of 6 nm [1,2]. Moreover, the result obtained for the PDHS/SBA-15 composite differs from those for the PDHG/SBA-15 composite in that significant aspect that the confined PDHS polymer chain has a *trans*-conformation [12], whereas the confined PDHG polymer chain has a *gauche*-conformation.



(a) (b)

FIGURE 4 Temperature dependence of FL spectra of the PDHS/SBA-15 composite (a) and the PDHG/SBA-15 composite (b) (a pore diameter of 6 nm).

Figures 4a and 4b show the temperature dependence of the FL spectra of the PDHS/SBA-15 and PDHG/SBA-15 composites, respectively. In the case of PDHS/SBA-15 composite, the band of *trans*-conformers was replaced by that of *gauche*-conformers in the process of thermochromic transition, when the temperature was raised from 10 to 290 K [12], whereas the temperature dependence of the FL band at 338 nm in the spectra of PDHG/SBA-15 is similar to those observed for the bulk film, i.e., the band broadens, and its intensity decreases. We can conclude that a blue shift observed in the FL spectra of the PDHG/SBA-15 composite can indicate also the shortening of polymer chains and their transformation into a disordered conformation.

The FL and excitation spectra ($\lambda_e = 313$ nm, $T = 5$ K) of PDHG incorporated in SBA-15 with a pore diameter of 10 nm are presented in Figure 5b. Note that three bands in the spectrum of the composite with 10 nm pores are shifted to the blue side with respect to those in a thin film (Fig. 1b). The bands peaking at 339 and 354 nm are blue-shifted by 13 nm. The band at 368 nm has a smaller shift. The excitation spectra obtained by choosing these FL bands for detection demonstrate distinct differences. Namely, the excitation bands at 317, 330, and 340 nm correspond to the FL bands at 339, 354, and 368 nm, respectively.

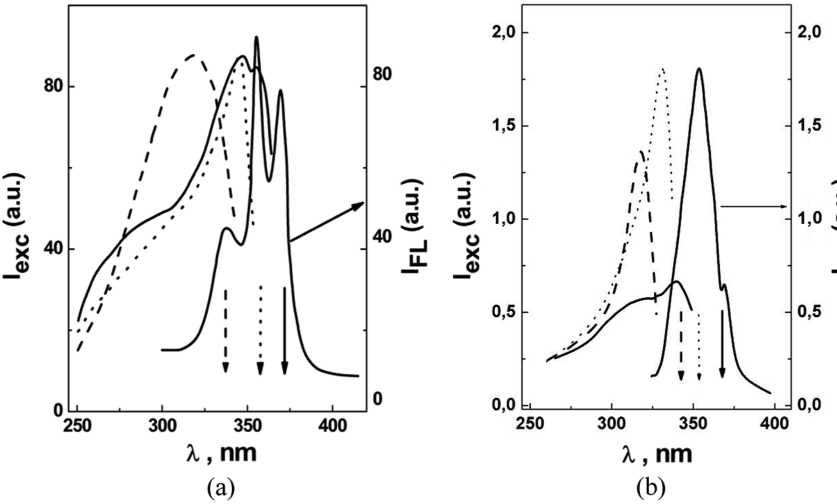
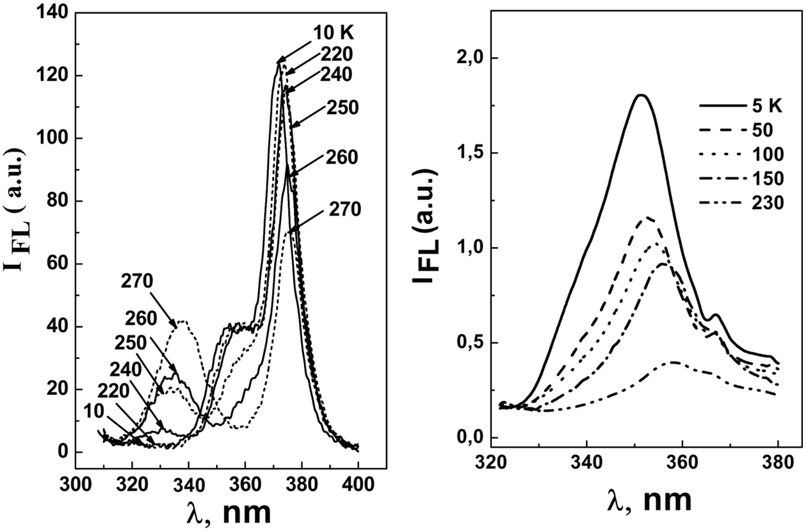


FIGURE 5 FL and excitation spectra of PDHS (a) and PDHG (b) incorporated into SBA-15 with a pore diameter of 10 nm ($T = 5$ K). The FL spectrum was measured, when exciting at $\lambda_e = 313$ nm. The excitation spectra are observed at the FL peak of 339 (dashed line), 354 (dotted line), and 368 nm (solid line), respectively.

The obtained results are compared to data for the nanocomposite PDHS/SBA-15 (Fig. 5a). It is seen that three bands are observed also in the spectrum of the PDHS/SBA-15 composite with a pore diameter of 10 nm. The temperature dependence of FL bands in the PDHS/SBA-14 composite spectra (Fig. 6a) allowed us to conclude that these three bands correspond to different structural forms of the polymer coexisting in a restricted pore volume: the separate polymer chains in the *trans*- and *gauche*-conformations, and their aggregates [4].

The temperature dependence of FL bands in the PDHG/SBA-15 composite spectra is shown in Figure 6b. It is seen that, in contrast to the confined PDHS (Fig. 6a) [4], we did not observe a clear thermochromic transition for the PDHG/SBA-15 composite. This means that the PDHG polymer chains in a SBA-15 pore consist generally from *gauche*-conformers and a small amount of *trans*-conformers.

The data for the PDHG/SBA-15 composite differ from those for the PDHS/SBA-15 composite. In the case of PDHS/SBA-15 composite, the band at 354 nm is assigned to the polymer chain with a *trans*-conformation [4], whereas the similar band in the spectrum of the PDHG/SBA-15 composite is assigned to the polymer chain with both *trans*- and *gauche*-conformers. So, it can be assumed that these three



(a) (b)

FIGURE 6 Temperature dependence of the FL spectra of the PDHS/SBA-15 composite (a) and the PDHG/SBA-15 composite (b) (a pore diameter of 10 nm).

bands can be attributed to different structural forms of PDHG polymer chains coexisting in a restricted pore volume of SBA-15: the polymer chains of *gauche*-conformers, the polymer chains with different numbers of *trans*- and *gauche*-conformers, and their aggregates, respectively.

CONCLUSIONS

We have investigated the PDHG low temperature optical spectra under the transformation of the conformation ranging from a bulk film to a nano-sized polymer confined into the SBA-15 nanopores with various diameters.

It is shown that the optical spectra of the PDHG nanocomposites depend on the pore diameters and differ significantly from those of the bulk film. In the restricted volume of a 6-nm pore, there is a one polymer state having a *gauche*-conformation, whereas, in 10-nm pores, there are three spatially separated polymer states having *gauche*-conformers, different amounts of *gauche*- and *trans*-conformers, and their aggregates. The PDHG polymer chain conformation in a restricted pore volume becomes disordered with decrease in the nanopore size from 10 to 6 nm as distinct from that of PDHS.

The temperature dependence of the PDHG/SBA-15 nanocomposite shows the absence of a thermochromic transition in these composites contrary to the PDHS/SBA-15 nanocomposite. The observed data indicate that the polymer chains of a PDHG film and the PDHG/SBA-15 nanocomposite are more disordered than the PDHS chains.

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