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Optical Spectra of Polygermane/Mesoporous Silica Nanocomposites

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Summary: The monitoring of poly(di-n-hexylgermane) (PDHG) optical spectra in a variety of structures ranging from a bulk film to a nanosize polymer confined into a nanopore of SBA-15 was performed using the fluorescence and fluorescence excitation spectra in the temperature range from 5 to 240 K as well as the absorption and FTIR spectra at room temperature. The observed data were compared with those obtained for poly(di-n-hexylsilane). It was shown that PDHG film absorption and fluorescence spectra strongly depend on the polymer thickness and consist of a number of bands which were assigned to centers with different amount of trans- and gauche- conformers of the polymer chains. Conformations of the polymer chains found in a thin film and in a 10 nm pore are similar while differing from the conformations of a thick film. Optical spectra of the confined PDHG are blue-shifted relative to those of a thin film. The PDHG polymer chain conformation becomes disordered with the decrease of the polymer film thickness and the nanopore size from 10 to 6 nm.

Keywords: nanocomposites; optical spectra; poly(di-n-hexylgermane); SBA-15; films

Introduction

σ-conjugated polymers, polysilanes and polygermanes $[MR_2]_n$, (M stands for silicon or germanium and R is an organic molecule) have unique optoelectronic and electrophysical properties arising from delocalization of σ-electrons along the chain of M atoms. Significant interest to the investigations of these polymers is due to perspectives of their potential applications such as materials for photodiodes, photoresists, and materials for non-linear optics.[1]

The manufacture of the nanosize polymers opened an exciting new direction in the modification of the photophysical properties of the ultrathin polymer films. One of the reliable techniques of the fabrication of nanosize polymers is by filling polymers into the nanosize pores of the mesoporous silicas.

The optical spectra of nanocomposites based on poly(di-n-hexylsilane) PDHS and poly(methylphenylsilane) PMPS confined into mesoporous silicas were studied for the systems prepared by this method.[2–5] An essential influence of the space confinement on 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 nanosize polymer that are not observed in bulk films.[2–4]

In the family of polygermanes, poly(di-n-hexylgermane) PDHG has the 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 length is longer than that of the Si–Si bond, intramolecular interaction is expected to be less pronounced compared to PDHS. This suggests that PDHG has more flexibility

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near its backbone[6] and conformational changes in the polymer chain are more probable for PDHG than for PDHS. As a result the polymer-surface interaction as well as the optical spectra of PDHG film could change.

This paper presents a study of the monitoring of changes of the PDHG optical spectra varying the structure from that of a bulk film to a nanosize polymer. The nanocomposites PDHG/SBA-15 were fabricated by the incorporation of the polymer chains intro the pore of the mesoporous silicas of the SBA-15 type with pore diameter of 6 and 10 nm. PDHG films and composites were investigated using fluorescence (FL) and excitation spectra at (5–240) K as well as absorption and FTIR spectra at room temperature.

According to the analysis of the PDHG films absorption spectra published in literature,[7–9] a significant discrepancy exists between the results obtained by different authors. It was assumed that this discrepancy could be due to different conditions of the film preparation and could essentially depend on the polymer's molecular weight.[9] Our comprehensive study of the room temperature absorption and low-temperature (5–240 K) FL spectra of PDHG films and toluene solution has shown that the discrepancies observed between the reported absorption spectra are due to the different thickness of the polymer films. The nature of the absorption and fluorescence centers in PDHG films and the PDHG/SBA-15 nanocomposites is analyzed by comparing with the similar well-known data obtained on the previously studied PDHS films and PDHS/SBA-15 nanocomposites.[2–5]

Experimental Part

PDHG was synthesized as described in Ref.[8] Details of the preparation of the SBA-15 mesoporous silica was described in Ref.[10]

The parameters of the mesoporous system were calculated by the DFT method from the isotherm absorption branches. The resulting size distributions for pores are shown in Figure 1. The measurements showed quite a narrow scatter in the pore diameters.

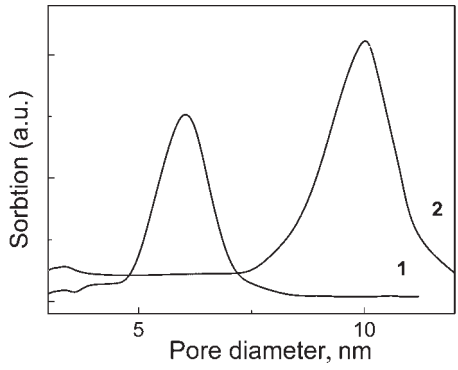

Figure 1.
Pore size distributions for the parent SBA-15 with the pore diameter of 6 nm (1) and 10 nm (2) derived from a nitrogen sorption isotherm (desorption branche, DFT method).

In order to incorporate the PDHG polymer (Mw = 10600) into nanopores of SBA-15 with the pore diameter of 6 nm and 10 nm, 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 evaporation of the solvent. Then the composite was twice washed in dark for approximately 2 h by stirring it in the fresh toluene to remove the polymer from the exterior surface. The PDHG films with different thickness 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 240 K. FL is excited by a xenon lamp with the monochromator selected wavelength of 313 nm. The absorption spectra were recorded by KSVU-23 at room temperature. FTIR spectra of a polymer film and PDHG/SBA-15 composites were recorded by FTIR-66 Bruker instrument.

Results and Discussion

Absorption Spectra of PDHG Films

Figure 2 shows the room temperature absorption spectrum of PDHG thick polymer film and the result of the computer curve-fitting analysis. Insert depicts the structural formula of PDHG. It is seen that this spectrum consists of three bands with maxima at 373, 348 and 323 nm. It is worth mentioning that the band centered at 373 nm is two times narrower than the band centered at 323 nm. The spectrum is similar to the absorption spectrum reported in[9] for the PDHG with $M_w = 259660$. In Figure 3, the absorption spectra are show as a function of the film thickness. The film thickness varied from several micrometers to about 30 nm. As could be seen from Figure 3, a significant dependence of the absorption spectra on the film thickness is observed. In particular, when the film thickness decreases, the intensity of the short-wavelength absorption bands increases.

For example, in Figure 3, the spectrum depicted with the curve 2 shows the strongest band at 350 nm. It should be noted that this absorption spectrum is similar to the spectrum reported in[9] for the polymer with $M_w = 73940$. With further decreasing the film thickness, the short-wavelength band centered at 323 nm dominates the absorption spectrum. This spectrum coincides with the spectrum reported in[8] for polymers with the M_w within the range 7600–11400. 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 (Figure 3, curve 4).

We would like to attract attention to the fact that the PDHG film absorption spectrum exhibits different patterns at room temperature, which, as known from the literature, were obtained by changing the polymer molecular weight. However, we have obtained the same spectral patterns for a polymer of a fixed molecular weight by changing the only thickness of the film. So, we have shown that the absorption spectra of the PDHG film strongly depend on the film thickness and consist of four bands with the maxima at 373, 348, 335 and

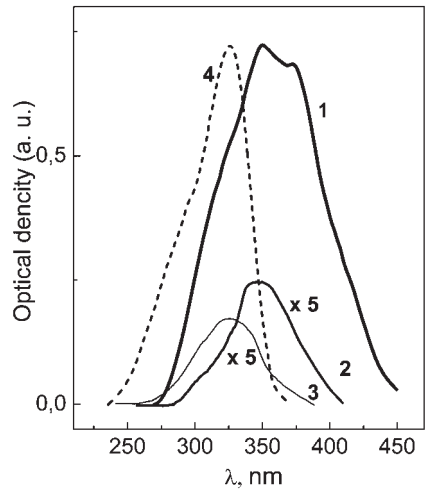

Figure 3.
Thickness dependence of the absorption spectra of PDHG films (293 K). Thickness of the films decreases from several micrometers (curve 1) down to 30 nm (curves 3). For a comparison the absorption spectrum of the PDHG toluene solution was measured (curve 4).

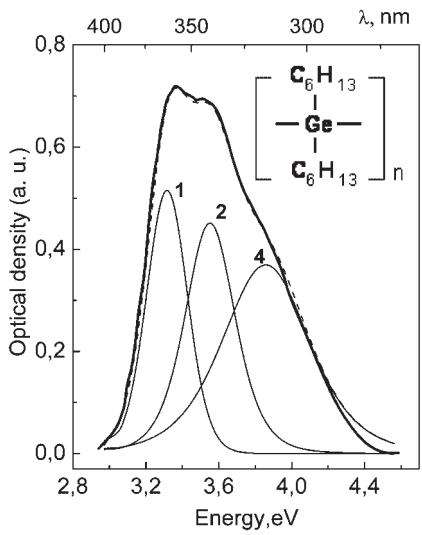

Figure 2.
A room temperature absorption spectrum of a thick PDHG film and the results of the computer curve-fitting analysis after base line substraction.

323 nm. Therefore, there are four types of absorption centers in PDHG film.

Like PDHS, PDHG is a thermochromic polymer. Its electron transition strongly depends on the conformation of the polymer chain. We have observed the thermochromic transition on heating the PDHG film from the room temperature to 323 K: the band at 373 nm is replaced by a broad band at 323 nm at this temperature. This temperature evolution of the absorption spectrum, reflecting the thermochromic transition, shows similarity to that, reported by Bukalov et al.[9] Since the Ge-Ge bond length is longer than that of the Si-Si bond, intramolecular interaction is expected to be less than 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 for PDHS. This fact may be responsible for the existence of four bands in the absorption spectra of the PDHG film instead of two bands observed in the spectra of PDHS. The presence of several bands in PDHG film absorption spectra at room temperature correlates well with the X-ray data[6] showing that PDHG is less ordered than PDHS. We suppose that these bands originate from the absorption centers with different amount of trans- and gauche-conformers of the polymer chain. For example, absorption centers of the type 1 (corresponding to the absorption band centered at 373 nm) may be associated with trans-conformation of the polymer chains, whereas the absorption centers of the type 4 (corresponding to the absoption band centered at 323 nm) may involve polymer chains with disordered gauche-conformation. The fact that the difference in the peak position between the absorption bands related to trans- and gauche conformers is the same for both polymers (about 50 nm) also confirms our interpretation of the PDHG film absorption spectra. It is known that the polymer chain in a polymer solution has a disordered conformation[11] In agreement with this is the fact that the maximum of the absorption band at 323 nm is close to a similar maximum in the polymer solution spectrum. The absorption centers of the type 2 and 3 (the corresponding absorption bands centered at 348 and 335 nm, respectively) may be associated with polymer chains with different ratio of trans- and gauche-conformers. In addition, since the polymer chain length is of the same order of magnitude as the polymer film thickness, this increases the probability to observe different conformations of the polymer chain.

Fluorescence Spectra of the PDHG Films

As seen from Figure 4, the FL spectra of a PDHG powder and of a thick film consist of two bands of different intensity ratio centered at 366 and 376 nm, the band at 376 nm being higher in the FL spectrum of a thick film, whereas the band at 366 nm is higher in the powder spectrum. In the FL spectrum of the polymer dissolved in 10^{-4} mol/l toluene a single band at 363 nm is observed. FL spectra of PDHG films are also strongly dependent on the film thickness. If the thickness of PDHG film obtained from a 1% polymer toluene solution decreases the FL spectrum reduces to a single band at 366 nm. If the film is obtained from a diluted solution in toluene,

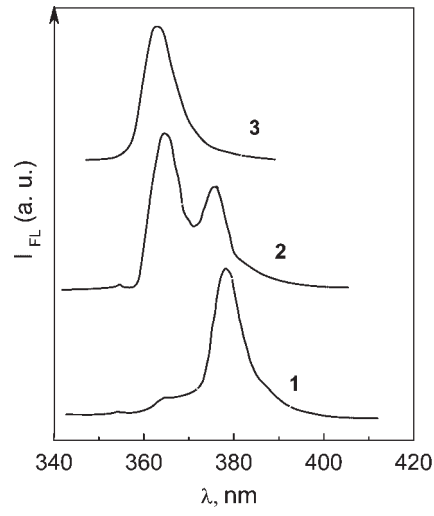

Figure 4.
Fluorescence spectra of the PDHG film, powder and solution at 5 K (curves 1–3, respectively).

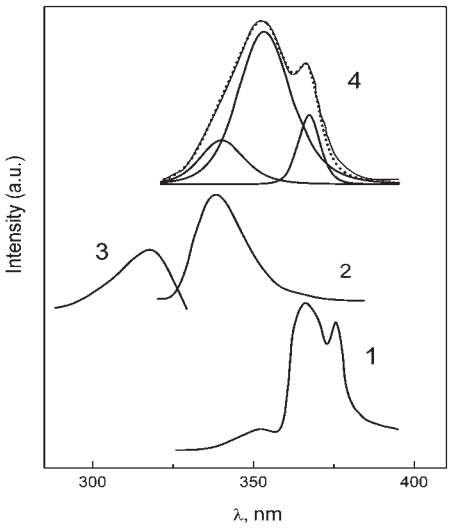

Figure 5.
Fluorescence spectra (T = 5 K, λ_{exc} = 313 nm): of PDHG thin film obtained from the diluted toluene solution (1), PDHG/SBA-15 composite with pore diameter of 6 nm (2) (the curve 3 corresponds the excitation spectrum of the composite); PDHS/SBA-15 composite with pore diameter of 10 nm and the result of the computer curve-fitting analysis (4).

an intensive blue band with a maximum at 352 nm appears in addition to the bands at 376 and 366 nm (Figure 5, curve 1). Since, in the PDHG film FL spectra recorded at 5 K, one can simultaneously observe several emission bands depending on the film thickness, this suggests that the emitting centers are spatially independent and located at different distances from the substrate, which results in a slow excitation energy transfer between them.

Analysis of the obtained data has shown that, in a whole, three bands centered at 352, 366 and 376 nm are observed in the FL spectrum of PDHG film. We suppose that these bands originate from the emission centers with different amount of trans-and gauche-conformers of the polymer chain. For example, we connected the band at 376 nm with the polymer chain having trans-conformation. The band at 366 nm was assigned to the polymer chains with different distribution of trans and gauche conformers over its length. Appearance of the shorter wavelength band in FL spectrum of PDHG film can indicate the shortening of the polymer segments having gauche conformation. So, when the PDHG film thickness decreases some polymer chains located close to the substrate become more disordered. Similar data was received for PDHS films. It is known that the FL spectrum (T = 5 K) of the thick PDHS film consists of a single band at 371 nm assigned to the trans-conformation of the polymer chain. A new blue band was observed in the room temperature optical spectra of PDHS film only when decreasing the film thickness to 7 nm.[12] The short-wavelength FL band at 343 nm and the corresponding absorption band at 316 nm were assigned to the gauche conformation of the Si backbone. Similar doublets were observed in the FL spectrum of the PMPS thin film[13] and in the diluted PMPS solution.[4] They were assigned to the polymer chains with different distributions of short and long segments over the backbone. Considering that the absorption and FL spectrum of PDHG films are more structured than the similar spectra of PDHS film, we can conclude that the PDHG films are less ordered than those of PDHS.

Low-Temperature Optical Spectra of Nanocomposite PDHG/SBA-15

The FL (λ_{ex} = 313 nm) and excitation spectra of PDHG incorporated in SBA-15 with pore diameter of 6 nm observed at 5 K are presented in Figure 5 (curve 2, 3). FL spectrum shows a single intensive broad band with a maximum at 338 nm. The excitation spectrum monitored for this FL band shows a single band with the maximum at 317 nm.

Figure 6 shows the temperature dependence of the FL spectra of the PDHG/SBA-15 composite. With increasing temperature, the intensive peak at 338 nm shows a red shift and a strong broadening. The intensity of this band decreases with increasing temperature.

As seen in Figure 5 (curve 2, 1), the FL spectra of the confined PDHG and the

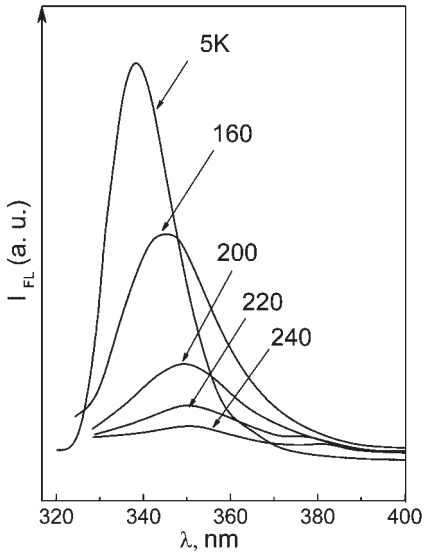

Figure 6.
Temperature dependence of the fluorescence spectra of PDHG/SBA-15 composite with the pore diameter of 6 nm.

PDHG thin film significantly differ. The FL spectrum of the PDHG confined in 6 nm pores displays a single band at 338 nm shifted by 14 nm to the short-wavelength side relative to the FL band in the spectrum of a thin film at 352 nm which has been assigned to the polymer chain having gauche-conformation. The PDHG monomer unit is 1.7 nm long. The simulation of the PDHS/ SBA-15 nanocomposite with the hexagonal pore with the diameter of 6 nm shows that this pore can hold three macromolecules in three alternate corners.[14] 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 the pores of the SBA-15. Only a single band was observed also in the FL spectra of the PDHS/SBA-15 composite with the pore diameter of 6 nm.[2,3] Yet, 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[14] whereas the confined PDHG polymer chain has a gauche-conformation.

The temperature dependence of the band centered at 338 nm in FL spectrum of PDHG/SBA-15 is evidence in favour of our assumption. In the case of PDHS/ SBA-15 composite the band of the trans-form was replaced by the gauche- form band in the process of the thermochromic transition when the temperature was raised from 10 to 290 K,[5,14] whereas the temperature dependence of FL band at 338 nm in 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 spectrum of this composite can indicate also the shortening of the polymer chains and their transformation into a disordered conformation.

As seen in Figure 5 (curve 4), the FL spectrum of PDHG/SBA-15 nanocomposite with a diameter pore of 10 nm becomes more structured exhibiting three bands instead of one. Note, that three bands in the composite spectrum (10 nm) are shifted to blue side with respect to those in a thin film (curve 1). The bands peaking at 339 and 354 nm, assigned to the polymer chains with more disordered conformations, are blue-shifted by 13 nm. The band at 368 nm, assigned to trans-conformers, has a smaller shift. So, we can conclude that the bands at 339 and 354 nm are connected with the transitions from the individual polymer chains, but the band at 368 nm is connected with the aggregates. Three bands were observed also in the spectrum of the PDHS/ SBA-15 composite with a pore diameter of 10 nm. The nature of these bands is well-known.[5] However, the data for PDHG composite differ from those for PDHS composite. In the case of PDHS composite, the band at 354 is assigned to the polymer chain with the trans-conformation,[5] whereas the similar band in the spectrum of PDHG composite is assigned to the polymer chain with both the trans- and gauche–conformers.

So, it can be assumed that these three bands could be attributed to different

structural forms of the PDHG polymer chains coexisting in a restricted pore volume of SBA-15: the polymer chains of the gauche- conformers, the polymer chains with different number of trans- and gauche-conformers, and their aggregates, correspondingly.

FTIR Spectra of the Nanosize PDHG Incorporated into the Mesoporous Silica of SBA-15

Correlations between the changes in the electronic spectra and the structure of the side chains of the PDHG were studied with FTIR spectroscopy.

It is known that there are four major bands in the C–H stretching region (2850–3000 cm^{-1}).[15] The bands at 2851 cm^{-1} (a) and 2921 cm^{-1} (b) can be assigned to the symmetric CH_2^s and asymmetric CH_2^a stretching vibrations, respectively, while the 2871 cm^{-1} band and the 2956 cm^{-1} band (c) are assigned to the symmetric CH_3^s and the asymmetric CH_3^a stretching vibrations in the film, respectively. The two strongest bands around 2851 cm^{-1} and 2921 cm^{-1}, corresponding to the symmetric and anti-symmetric stretching modes of CH_2 groups, are conformation sensitive and their change is indicative of the modification of the trans/gauche ratio. They are shifted towards higher wavenumbers if either the content of gauche conformer or the disorder of the chain increases.[16]

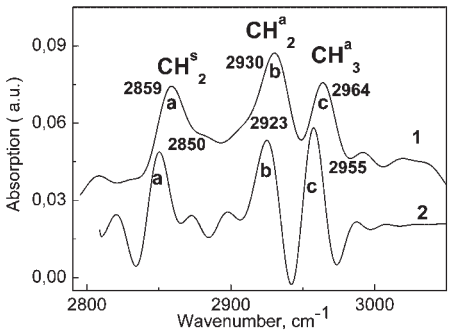

Figure 7.
FTIR spectra of PDHG in the CH stretching region for: the PDHG incorporated into SBA-15 with the diameter pore of 6 nm (1) and the bulk film on the quartz substrate (2).

Figure 7 shows the FTIR spectra of PDHG in the CH stretching region for: the PDHG incorporated into SBA-15 with diameter pore of 6 nm (1), and the bulk film on the quartz substrate (2). When PDHG is incorporated into SBA-15 with pore diameter of 6 nm, FTIR spectrum undergoes a remarkable change compared to the spectrum of the polymer film. Curve 1 in Figure 7 demonstrates these changes: both 2850 cm^{-1} (a) and 2955 cm^{-1} (c) bands experience high frequently shifts by 9 cm^{-1} from their bulk film positions, while the 2923 cm^{-1} band (b) moves by 7 cm^{-1}. An essential shift of the CH_2 and CH_3 symmetric and asymmetric stretching modes to the higher wave numbers in FTIR spectrum of PDHG/SBA-15 composite is evidence in favour of the availability of disordered conformers. These data coincide with the data for the FL spectrum of PDHG/SBA-15 composite with the pore diameter of 6 nm.

Conclusion

The optical spectra of PDHG film and PDHG/SBA-15 nanocomposites have been investigated. We have observed the same modifications of the absorption spectra of the PDHG film with changing the film thickness for the fixed molecular weight of the polymer as those which were previously reported for the case of increasing molecular weight. So, it has been shown that the absorption and fluorescence spectra of PDHG films depend strongly on the film thickness. The presence of certain bands in these spectra allowed us to conclude that there are some centers with different ratio of trans- and gauche-conformers in the polymer chain. The comparison of the observed data with those obtained for PDHS allowed a conclusion, that the polymer chains of the PDHG film are more disordered than the chains of PDHS.

The new nanosize PDHG/SBA-15 composites have been fabricated by introducing the semiconducting polymer poly(di-n-hexylgermane) into nanoporous silica with the pore diameters of 6 or 10 nm. It has

been shown that their optical spectra depend on the size of pores and differ from those of the film. The PDHG polymer chain confined in nanopores of the mesoporous silica becomes more disordered with the decrease of the pore size from 10 to 6 nm. In the restricted pore volume of 10 nm there are three spatially separated polymer states having gauche- conformers, different amount of trans- and gauche-conformers, and their aggregates.

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