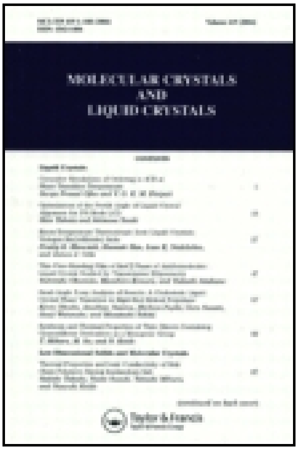

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Thermochromic Transition of Nanosize Polysilane

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Thermochromic Transition of Nanosize Polysilane

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*Photoluminescence and photoluminescence excitation spectra of nanosize poly(di-*n*-hexylsilane) embedded in the SBA-15 with 6 nm diameter pore were investigated in the temperature range of 10–290 K. We clearly demonstrate the thermochromic transition at 265 K between* trans- *and* gauche- *conformations of an isolated polymer chains embedded in the nanoporous material. Existence of the polymer chain having trans-conformation in a separate pore of 6 nm diameter was prooved. The location and packing of the polymer chains in this pore was simulated using the quantum chemistry calculations in the cluster approximation. The investigation of the polarized luminescence dynamics of the nanosize polymer with pore diameters of 6 and 10 nm has shown that the polymer chains are aligned by embedding.*

Keywords: mesoporous silica; nanosize poly(di-n-hexylsilane); optical spectra; thermochromic transition

INTRODUCTION

Polysilanes, Si-based polymers with organic substituents, are a type of silicon-organic polymer that possesses σ-electron conjugated backbones [1]. Delocalization of σ-electrons along the chain of Si atoms results in unique optoelectronic and electrophysical properties of polysilanes, which are thefore of interest as potential photodiodes, photoresists, and materials for non-linear optics [2].

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Poly(di-*n*-hexylsilane) (PDHS), which is a thermochromic polymer, is one of the most widely studied polysilanes [1]. Its electronic transitions are variable depending on the changes of temperature-dependent conformations both of the main chain and of the side chains [1,3]. Evidently, the structural organization of these polymers in the solid state predetermines the functioning of polymer-based devices, therefore, understanding the optical and electric features depending on the polymer structural arrangement is an important issue. Embedding PDHS in nanoporous materials like MCM-41 and SBA-15 is an effective way of production and control of nanostructure composites [4–6]. PDHS/SBA-15 nanocomposites were prepared by the liquid-phase self-assembly via insertion of PDHS macromolecules inside mesoporous silica with the pore diameter ranging from 2.8 to 10 nm. The first studies showed that the optical spectra of the nanosized PDHS significantly differ from the spectra of the bulk films and depend on the size of the pores [4]. It was shown that this difference is essentially due to the change of the conformation of the polymer chains resulting from the polymer-polymer and the polymer-surface interactions [4,7]. We have shown recently that the photoluminescence (PL) properties of the composite with the pore diameter of 10 nm are determined by the coexistence of weakly coupled three structural forms of the polymer with spectral properties of isolated *gauche*- and *trans*-conformations and of the aggregated states [6,8]. We discovered two thermochromic transitions between these forms on the same composite [8].

On the other hand, the PL spectrum of the composite with the pore diameter of 6 nm consists of a single band [4]. We assumed that this band is connected with the isolated polymer chain having the trans-conformation. It is known that the Si-backbone of this polymer has the trans-conformation below 300 K. Transition from the trans-conformation to the disordered gauche–conformation occurs above 315 K. So, if our assumption about the nature of this band is true, the band of the trans-conformer will be replaced by the gauche-conformer band above the temperature of the phase transition and the opposite transition will take plase by decreasing the temperature. To confirm our assumption, the studies of the PL and photoluminescence excitation spectra (PLE) of PDHS embedded in the SBA-15 with pore diameter of 6 nm in the temperature range of 5–290 K are presented. We clearly demonstrate the thermochromic transition between *trans*- and *gauche*-conformations of the isolated polymer chains embedded in the nanoporous material. Therefore, the existence of the polymer chain having trans-conformation in a pore of 6 nm diameter was prooved. Additionally, the polarized luminescence dynamics of the composites with pore diameters of 6 and 10 nm were measured. The location and packing of the polymer chains in these pores was simulated using the quantum chemistry calculations in the cluster approximation.

EXPERIMENT

PDHS embedded in the nanoporous material SBA-15 was obtained by following procedure. In order to incorporate the PDHS polymer (Mw = 53600) into the pores, the prepared silica matrixes were immersed in the 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 location of the polymer in the pores was determined by the X-ray diffraction method by monitoring the presence of the characteristic silica framework structure. Details of the preparation of the nanoporous silica material SBA-15 with the pore diameter of 6 nm was described elsewhere [9]. Thin PDHS films were obtained by deposition on quartz by the spin-coating.

The Perken Elmer LS 50 B spectrometer in line with an optical closed cycle helium cryostat was used for studies of the phtoluminescence and excitation spectra in the slow cooling regime in the range of 10–290 K. The samples were cooled down at less than 0.5 K/min rate, and the subsequent measurements were performed after 20 minutes equilibration at any given temperature. PL spectra were measured with the excitation at $\lambda_e = 313$ nm.

Intercalation of the composite PDHS/SBA-15 within the 6 nm diameter pores was simulated using the quantum chemistry calculations in the cluster approximation. Total amount of atoms in the system under study has been 8964 and the characteristic size of the system has been near 80 A. Big size of the components for simulation leads to molecular mechanics and semiempirical duantum chemistry method only. We used semiempirical method PM 3.

The polarization investigation of the PL spectra was performed using the following scheme Four spectra in the following combinations of the excitation and registration were measured: parallel-parallel (denoted by VV), parallel-perpendicular (VH) as well as HV and HH. It is noteworthy that only the first combination corresponds to the parallel polarization, while all others correspond to the perpendicular polarization. As the registration of the perpendicular component was less effective than that of the parallel, the second spectrum (VH) has been corrected. The correcting factor has been obtained from the ratio of the curves 3 and 4 as the excitation was performed in the same manner. Therefore, the first VV spectrum was not changed while the true spectrum of the perpendicular polarization VH was the product of the initial second spectrum (VH) by the correcting factor.

RESULTS

The PL and PLE spectra of PDHS/SBA-15 with pore diameter of 6 nm measured at $T = 10\,K$ are presented in Figure 1a. The inset depicts the structural formula of PDHS. The PL spectrum consists of a single band with the maximum at 353 nm defined as PL2. The excitation spectrum shows also a single band peaking at 346 nm (PLE2) by detecting at PL2 band.

Dependence of the PL spectra on the temperature in the 10–265 K range are shown in Figure 2. Note that no qualitative changes in

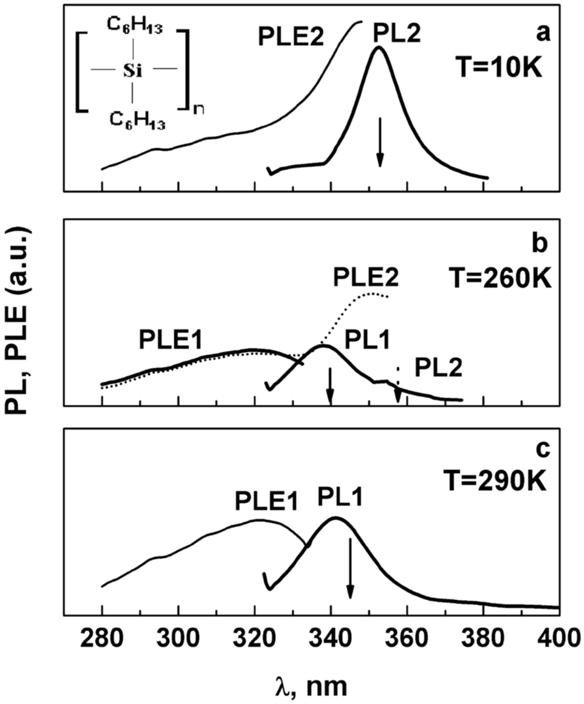

FIGURE 1 PL and PLE spectra of PDHS/SBA-15 composite measured at different temperatures. The PL spectra were measured for excitation at $\lambda_e = 313\,\text{nm}$, the PLE detection wavelengths are indicated by arrows. The inset shows the structural formula of PDHS.

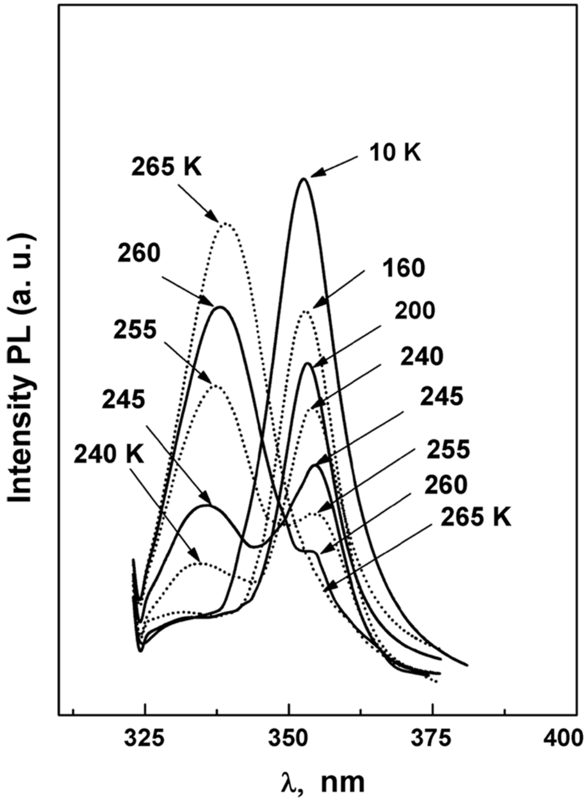

FIGURE 2 PL spectra of PDHS/SBA-15 composite in 10–265 K temperature range for excitation at $\lambda_e = 313\,\text{nm}$.

either PL or PLE spectra are observed in the temperature range from 20 to 230 K. The PL2 and PL3 bands are observable at 230 K with a slight red-shift of their maxima in comparison with those measured at 10 K.

It can be seen that the most dramatic modification of the spectra is taking place in the range from 240 to 265 K. At 240 K the new PL1 band emerges in the PL spectrum. When increasing temperature from 240 to 265 K the PL2 band is replaced by PL1 band (Fig. 1b). At 265 K the PL2 band is absent. The PLE spectrum detected at the PL1 band (at 340 nm) contains a single PLE1 band peaking at 320 nm (Fig. 1c). Thus, it can be concluded that the polymer form responsible for the PL2 and PLE2 bands are absent at 265 K. The single PL1 band of the new polymer form is present at high temperature (Fig. 1c). The temperature dependence of the maximum positions of the corresponding

PL bands (PL1 and PL2) is shown in Figure 3. Temperature-induced spectral modifications below 290 K are completely reversible, the samples may be cooled down and heated several times and the spectra remain the same at any given temperature.

Figure 4 shows the simulation of the composite PDHS/SBA-15 with pore diameter of 6 nm using quantum chemistry calculations. It is seen that the pore of the SBA-15 cluster can hold three PDHS molecules of oligomer $Si_{20}Hex_{42}$, every one of which contains 818 atoms. These three molecules, in trans-conformation only, occupy three corners in the hexahedron pore of the cluster. Total number of atoms in this system is 8664.

Figure 5 shows the polarization investigations of PL of the PDHS/SBA-15 composite with the pore diameter of 6 nm with excitation light polarized along the pore direction at 10 and 290 K. The solid VV curve shows the collected emission polarized along the pore direction while the dotted VH curve is for the collected emission polarized perpendicular to the pore direction. Figure 6 shows the PL of the PDHS/SBA-15 composite with the pore diameter of 10 nm with the excitation light polarized along the pore direction at 120 and 290 K.

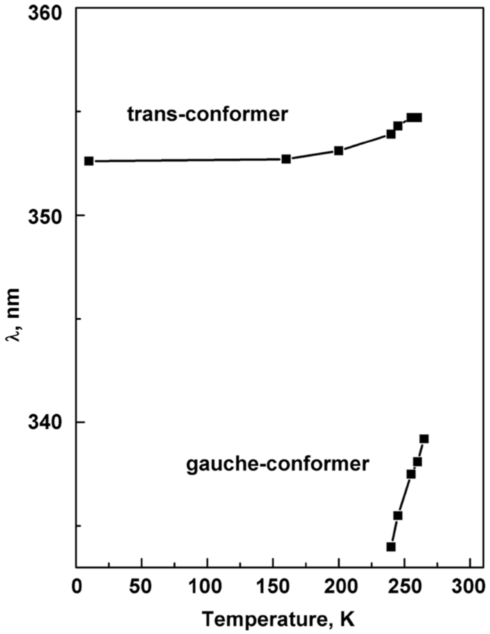

FIGURE 3 The simulation of the oligomer $Si_{20}Hex_{42}$ inside the SBA-15 cluster (6 nm, 8964 atoms) using quantum chemistry calculations.

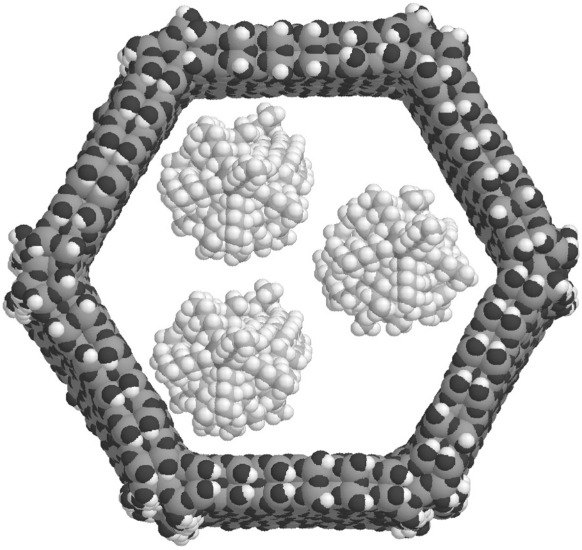

FIGURE 4 The temperature dependence of the positions of the maxima of the PL band of trans and gauche conformational forms of PDHS in SBA-15.

DISCUSSION

The simulation of the nanocomposite PDHS/SBA-15 with pore diameter of 6 nm shows that three PDHS macromolecules in the trans-conformation can exist in a pore (Fig. 4). Optical spectra of this composite at 10 K show a single band in the PL spectrum (PL2) with a maximum at 353 as well as a single band peaking at 346 nm (PLE2) in the excitation spectrum (Fig. 1a). The maxima of these bands are close to the maxima of the narrow bands in the spectra of PDHS/MCM-41 composite when a single isolated polymer chain fits in a pore [4]. This allows to attribute these bands to the transition from the isolated polymer chain. So, we assume that PL2 and PLE2 bands are connected with the transition in an isolated polymer chain having trans-conformation. PDHS is a termochromic polymer, its electronic transitions strongly depend on conformations of the polymer chains. It is known that a Si-backbone of this polymer has a trans-conformation below 300 K and the gauche–conformation above 315 K. If our assumption about the nature of these bands is true, the band of the trans form will be replaced by the gauche-form band by increasing the temperature and consequently the relative intensity of these bands should experience essential changes. Such changes related to the *trans-gauche* rearrangement were observed experimentally in

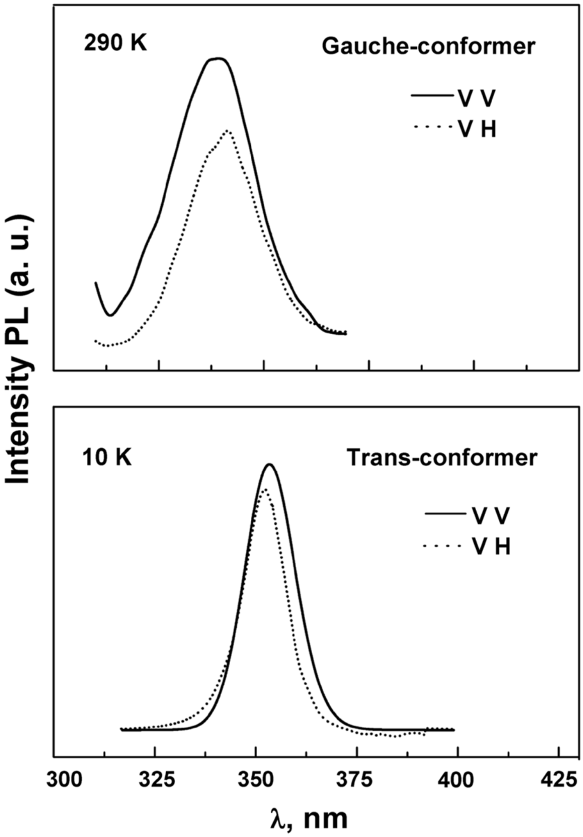

FIGURE 5 The polarization study of PL of the PDHS/SBA-15 composite with the pore diameter of 6 nm with excitation light polarized along the pore direction at 10 and 290 K. The solid VV curve shows the collected emission polarized along the pore direction while the dotted VH curve is for the collected emission polarized perpendicular to the pore direction.

the 10–265 K temperature range (Fig. 2). It can seen from Figure 2 that PL2 band is replaced by the PL1 band by increasing temperature from 10 to 265 K and the opposite transition takes place by the sample cooling. Note that the PL2 band disappears completely with increasing the temperature above 265 K (Fig. 1b). Only the polymer species with the PL1 and PLE1 bands are presented in the spectra at this temperature (Fig. 1c). The spectra corresponding to two conformations of the polymer chains are presented in Figures 1a, c and the temperature dependence of the maxima of the attributed bands (PL1 and PL2) is shown in Figure 3. These species with the PL1 and PLE1 bands are

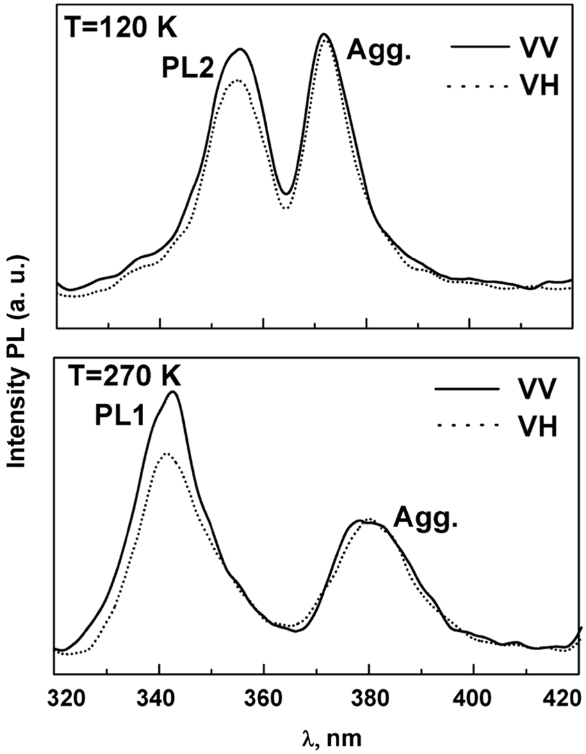

FIGURE 6 The polarization investigations the PL of the PDHS/SBA-15 composite with the pore diameter of 10 nm with the excitation light polarized along the pore direction at 120 and 290 K.

characterized by the shortest wavelength and by the broadest absorption (Fig. 1c). They also experience the strongest spectral shifts with temperature (Fig. 3). The presence of such transition confirms our assignment of the PL1 and PLE1 bands as well as of the PL2 and PLE2 bands to the polymer chains having the gauche- and *trans*-conformations respectively. So, we naturally relate two PL and PLE bands measured at different temperatures or PL detection wavelengths with two different polymer chain conformations located in the 6 nm diameter pores. It was recently suggested to assign the similar spectral forms observed in the spectra of the PDHS/SBA-15 composites with the pore diameter of 10 nm to *trans*- and *gauche*-conformations of the polymer chains [8].

The *trans-gauche* thermochromic transition was observed in solutions and in films of the PDHS polymer. The thermochromic transition for PDHS in solutions occurs at 223 K [1,10] and is basically independent of the solvent [11]. In the polymer film this transition appears at 315 K [12]. The temperature of the thermochromic transition for a confined isolated polymer chain in trans-coformation is 265 K. It is essentially higher (by 42 K) than the transition temperature in solution. A slow relaxation process probably occurs due to the motions of the oriented macromolecules confined in the pores.

The orientation of the polymer chain along the pore was confirmed by the polarization investigations of the PL spectra of the PDHS/SBA-15 composite with 6 nm diameter pore (Fig. 5). It was shown that the polymer chains are more aligned in the pore compared to the bulk film. For a comparison the polarized luminescence dynamics of the composites with pore diameters of 10 nm was measured (Fig. 6). We observed a decrease of the polymer polarization with increasing wavelength. The same dependence was observed by the investigation of the PL of MEH PPV in the nanostructured composite [13]. This reduction in the polarization ratio (I_{vv}/I_{vh}) with increasing wavelength may be due to the energy migration to the polymer chain with the longest segment. Evidently a polarization memory is partly or completely lost during the migration. This is also an indication that the energy transfer can occur between the polymer chain in the same pore. However, the presence of several PL bands in the spectra of the PDHS/SBA-15 composite with 10 nm diameter pore [8] suggest a conclusion that the migration of excitation to the least energy locations is not very effective.

SUMMARY

The photoluminescence and photoluminescence excitation spectra of poly(di-*n*-hexylsilane) embedded in the mesoporous silica material SBA-15 with the pore diameter of 6 nm are sensitive to the temperature changes in a wide temperature range from 10 to 290 K. Depending on the temperature of the sample two bands in the photoluminescence spectrum are distinguished. Their presence is a result of the coexistence of two polymer forms inside a single pore and their relative intensity modulation is the result of the energy transfer between them. Single the PL band observed at 10 K is attributed to the ordered *trans* conformations while the single band related to the disordered *gauche* conformation is distinguished at 270 K.

The thermochromic transition at about 265 K is observed for the nanosize polymer. It is related to the *trans-gauche* conformational changes of the single polymer chain located in the pore. This transition is completely reversible and appears at temperature, which is significantly different from temperature of analogous transition observed in the poly(di-*n*-hexylsilane) films and solutions. A slow relaxation process probably occurs due to the motions of the oriented macromolecules confined in the pores. The orientation of the polymer chain along the pore was confirmed by the polarization investigations of the PL spectra of the PDHS/SBA-15 composite with 6 and 10 nm diameter pore. It was shown that the polymer chain is more aligned in the pore than in the bulk film.

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