Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 03 Mar 2011

To cite this article: N. Ostapenko, P. Vodolazkyy, D. Peckus, V. Gulbinas, V. Moiseenko, N. Surovtseva, S. Suto & A. Watanabe (2011): Spectroscopy of Nano-Sized Polysilanes Confined by Different Structures of Silica, Molecular Crystals and Liquid Crystals, 536:1, 41/[273]-49/[281]

To link to this article: http://dx.doi.org/10.1080/15421406.2011.538333

*Mol. Cryst. Liq. Cryst.*, Vol. 536: pp. 41/[273]–49/[281], 2011

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.538333

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# Spectroscopy of Nano-Sized Polysilanes Confined by Different Structures of Silica

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*Four novel nanocomposite films based on poly(di-n-hexylsilane) (PDHS) incorporated into an inorganic matrix having different structure are fabricated. Polymer chains are localized into the nanopores of $SiO_2$ and $TiO_2$ films, between globules of photonic crystals, as well as in the matrix of nano-sized $SiO_2$ particles. Photoelectronic properties of the composites have been studied using fluorescence (FL) and FL decay measurements in a wide temperature range (5–330) K.*

*The temperature dependence of FL intensities enabled us to establish the nature of a conformational structure of polymer chains, as well as to obtain information about the thermochromic transition of confined PDHS and the excitation energy transfer pathways.*

**Keywords** Inorganic matrices; lifetime; nanocomposite films; optical spectra; polysilanes



## Introduction

The wide application of nanostructurized polymers to various technologies such as those involving the fabrication of transport and luminescent layers in electroluminescent diodes, solar cells, sensors, and photoresistors stimulates the development of new structures and the investigation of their optical and electrical properties [1]. One of the promising methods to obtain nano-sized structures of polymers is to incorporate a proper polymer into ordered nano-sized pores of mesoporous silicas [2]. Recently, a possibility of the manipulation of properties of nano-sized polysilanes by incorporating them in mesoporous silica matrices such as MCM-41 and SBA-15 has been demonstrated [3–6]. It should be mentioned that this approach also leads to an essential increase in the durability of a polymer in optoelectronic devices

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[7]. It was shown that we can control the number of polymer chains entering a nanopore, their conformation and orientation, and their optical properties by changing the diameter of nanopores [3,4]. An essential influence of the space confinement on observed spectra was found as a result of the competition between the polymer-surface and polymer-polymer interactions. These investigations revealed new polymer conformational states with different degrees of disorder which are not present in polymer solutions and solid films and also gave information about the character of the polymer localization in nanopores. The formation of these new structures may be controlled by changing the diameter of nanopores, which allows a variation of the absorption and fluorescence spectra of polymers [3], excited state lifetimes [6], and inhomogeneous line broadening. It has been shown that the fabrication of such nanocomposites is an effective way to produce highly efficient optoelectronic devices. However, the use of the composites in a form of tablets pressed from powder was a significant limitation to their investigation and application.

In this work, organic polysilane – inorganic nanocomposite films have successfully been prepared by embedding nano-sized poly(di-n-hexylsilane)-PDHS in the inorganic matrices having different structures, morphologies, and orientations. The matrices are as follows: the nanoporous $SiO_2$ and $TiO_2$ films, the photonic crystals comprised of $SiO_2$ globules, and the silica matrix having 2-nm nano-sized particles (silica gel). Photoelectronic properties of these composites have been studied using fluorescence (FL) and FL decay measurements in a wide temperature range (5–330) K. These investigations allow us to prove the polymer chains localization into the nanopores of $SiO_2$ and $TiO_2$ films, between globules of the photonic crystals, as well as between nano-sized $SiO_2$ particles in silica gel. The nature of a conformation of the polymer chains and its modifications in a confined volume of inorganic matrices are observed by the temperature dependence of FL spectra of the composites and by comparison of the obtained data with those for PDHS/mesoporous silica SBA-15 [3,4]. The essential influence of the morphology of inorganic matrices and the orientation on the manifestation of a polymer chain conformation and the emission properties of nanocomposites will be shown.

## Experimental

$SiO_2$ and $TiO_2$ porous films have been synthesised by the template sol-gel method [8]. Porous films were drawn down on glass or quartz substrates from a precursor using the ''dip-coating'' procedure with a constant velocity of 9 cm/min. The obtained films were gradually heated in an oven from room temperature to 350°C with a heating rate of 1.5°/min and afterwards were annealed for 3 h at a constant temperature of 350°c. The surface area of films estimated from of adsorption-desorption isotherms of hexane vapour was of the order of 660 and 820 $m^2/g$, respectively. The effective diameter of pores in the films determined from low-angle X-ray scattering data was of about 10 nm. The pores in the films had a hexagonal shape.

Nanodisperse silica globules were synthesized according to modified Stober's method [9] through the hydrolysis of tetraethoxysilane $Si(OC_2H_5)_4$ in a water-ethanol solution in the presence of ammonium hydroxide as a catalyst. The molar ratio of components in the reaction mixture was as follows: $NH_4OH:H_2O:C_2H_5OH:Si(OC_2H_5)_4 = (0.1–1):(2–20):(11–14):0.14$. The synthesis of globules of silicon dioxide was performed at a high concentration of water. The diameter of a globule

was 255 nm, and the interstitive distance was about 70 nm. The structure of the samples and their optical properties have been characterized by SEM analysis, FTIR reflectance, and absorbance spectroscopy [10].

The nanocomposites were prepared in the following way: $SiO_2$ and $TiO_2$ films and photonic crystals were calcined in an oven at 350°C for 3 h. In order to incorporate the PDHS polymer (Mw = 53600) into these inorganic matrices ($SiO_2$ and $TiO_2$ films, photonic crystals, and the $SiO_2$ matrix consisting of 2-nm particles), they were placed in a $10^{-3}$ mol/l solution of the polymer in toluene and slowly stirred in dark for two days at 293 K. Then the nanocomposites were washed in dark by stirring in toluene for approximately 15 min to remove the polymer from the exterior surface. Finally, the samples were dried in dark overnight to remove the residual moisture.

The PDHS/silica gel films were obtained by the deposition of a solution of silica particles and PDHS on substrates by the spin-coating.

FL spectra and the kinetics were measured by using an Edinburgh Instruments TCSPC spectrometer F900. A LED with the 280-nm emission wavelength generating 750-ps pulses at a repetition rate of 20 kHz was used for the excitation of samples. A liquid helium cold finger cryostat (Janis CCS-100/204) has been used in measurements in the range 15–330 K.

## Results and Discussion

*Temperature dependence of fluorescence spectra of nanocomposites.* FL spectra ($T = 15$ K, $\lambda_{ex} = 280$ nm) of the investigated nanocomposites on the base of PDHS incorporated in inorganic matrices with different nanoscale morphologies are presented in Figure 1. The inset shows the PDHS structural formula and the FL

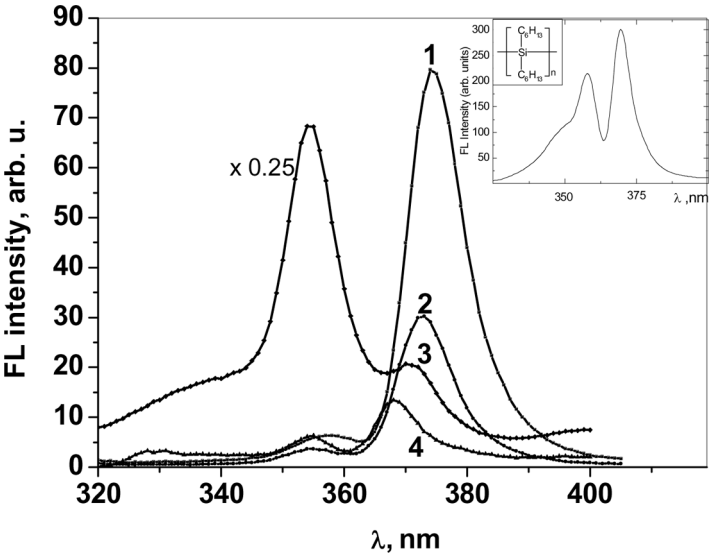


**Figure 1.** Fluorescence spectra at 15 K of PDHS incorporated in: $SiO_2$ porous film (1), $TiO_2$ porous film (2), photonic crystal (3), and silica gel (4). The inset shows the structural formula of PDHS and the FL spectrum of PDHS/CBA-15 composite at 10 K [4].

spectrum of PDHS/SBA-15 composite (pore diameter of 10 nm). The FL spectrum of PDHS/SBA-15 composite at 10 K achieved by the slow cooling consists of two bands at 355 and 369 nm attributed to the polymer chains in the *trans*-conformation and their aggregates, respectively [4]. A shoulder below 350 nm is related to the *gauche*-conformation. We also observe three bands in the FL spectra of novel composites which can be also attributed, by comparison with PDHS/SBA-15 spectra, to the *trans*- or *gauche*-conformation and aggregate states. The relative intensities of the FL bands of new composites and their maxima positions are significantly redistributed. The four new samples have approximately the same polymer concentration, but their FL intensities are clearly different due to different influences of different inorganic matrices on PDHS conformations. The *trans*-conformation band has the highest relative intensity in the PDHS/Phot.Cryst spectrum. Despite the fact that the pore dimensions in the photonic crystal are relatively large (of about 70 nm), the polymer chains localized in these pores have basically the *trans*-conformation. This is evidently related to the strong orientation of the polymer chains along the pore walls formed by the photonic crystal. PDHS/$SiO_2$ and PDHS/$TiO_2$ films reveal the highest relative intensity of the aggregate band. It is also worth noting that the FL spectrum of a PDHS/$SiO_2$ film is much more intense than that of a PDHS/$TiO_2$ film. According to our estimation, the length of the pores in $SiO_2$ and $TiO_2$ films are of about 100 nm. It can be assumed that, in this case, the polymer chain tags, which remain out of the pores, could form aggregates. The FL spectrum of the PDHS/Phot.Cryst is more intense than that of other nanocomposites. The different structures of photonic crystal and other porous films evidently have a strong influence on the formation of different polymer chain conformations. The fact that the FL spectrum of PDHS incorporated in $SiO_2$ gel is similar to that of a PDHS/$SiO_2$ porous film allows us to conclude that polymer chains are located between long chains formed by the association of nano-sized $SiO_2$ particles [11].

The PDHS polymer chains in a neat film have, in general, the *trans*-conformation at low temperatures and the *gauche*-conformation at room temperature [12]. It is known that the FL spectrum of PDHS/SBA-15 composite at 290 K contains two bands at 343 nm and 380 nm attributed to polymer chains in the *gauche*-conformation and aggregates, respectively [4].

Figure 2 shows the temperature dependence of the fluorescence spectra of the PDHS nanocomposites in the temperature range (15–330) K. The most dramatic modifications of spectra are observed in the interval 200–290 K. As the temperature increases, the *trans*-conformation bands are replaced by the *gauche*-conformation ones, while the temperature dependences of the intensities of aggregate bands are very different for different samples. The *trans*-conformation and aggregate FL bands shift clearly to the long-wave side, as the temperature increases. The temperature-induced spectral modifications below 290 K are completely reversible. The samples can be cooled down and heated up several times, and the spectra remain almost the same at any given temperature.

The thermochromic *trans-gauche* transition for a confined isolated polymer chain takes place at 265 K. It is essentially higher (by 42 K) than the transition temperature of the PDHS polymer in solutions [13].

The FL spectra of composites were analyzed by approximating them by several Gaussian bands. Three parameters were obtained for each band: the wave number, width, and amplitude. Figure 3 shows the temperature dependence of the integral intensities of different FL bands. As it was already mentioned, the intensity of the

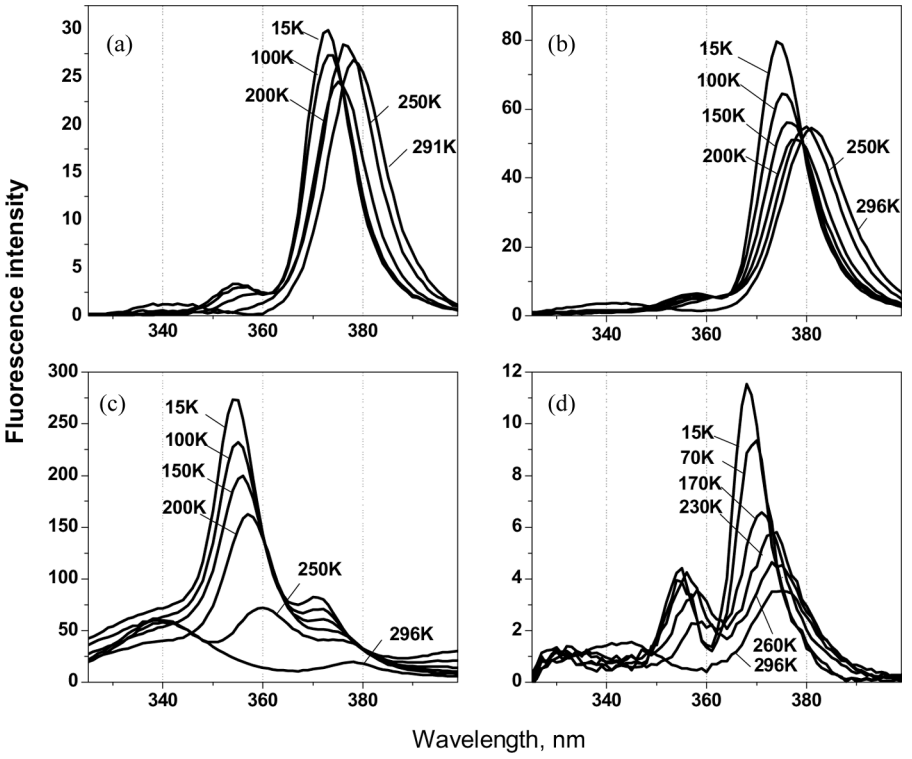


**Figure 2.** Temperature dependence of fluorescence spectra of PDHS incorporated in: porous $TiO_2$ (a) and $SiO_2$(b) films, photonic crystal (c), and $SiO_2$ gel (d).

*trans*-conformation FL band in all samples monotonically decreases with increase in the temperature. The *gauche*-conformation band intensities in a photonic crystal and $SiO_2$ gel slightly decrease, as the temperature increases from 15 to 250 K, and then strongly increases, when the *trans-gauche* transformation takes place. The *gauche*-conformation bands in porous $SiO_2$ and $TiO_2$ films appear only above the *trans-gauche* transformation temperature. The presence of the *gauche* fluorescence band in the photonic crystal and $SiO_2$ gel at low temperatures is the indication that polymer chains in these matrices have a less freedom of conformational motions and cannot form the more ordered *trans*-conformation. This is in contrast to polymers in porous films, where the *gauche* FL band is completely absent at low temperatures. The aggregate FL intensities in the photonic crystal and silica gel gradually decrease with increase in the temperature, whereas the temperature dependences are more complex in porous films: the FL intensity gradually decreases with increase in the temperature below the *trans-gauche* transition, while, at higher temperatures, it increases up to 310 K, when the aggregates are thermally destroyed. The increase in FL is evidently caused by the formation of *trans*-conformation chains which are more ordered and tend to form aggregate states. This is not the case in the photonic crystal and $SiO_2$ gel, where the formation of *trans*-conformation chains does not lead to an increase in the aggregate FL. This observation is in line with the conclusion that polymer chains in these matrices have a less freedom of conformational

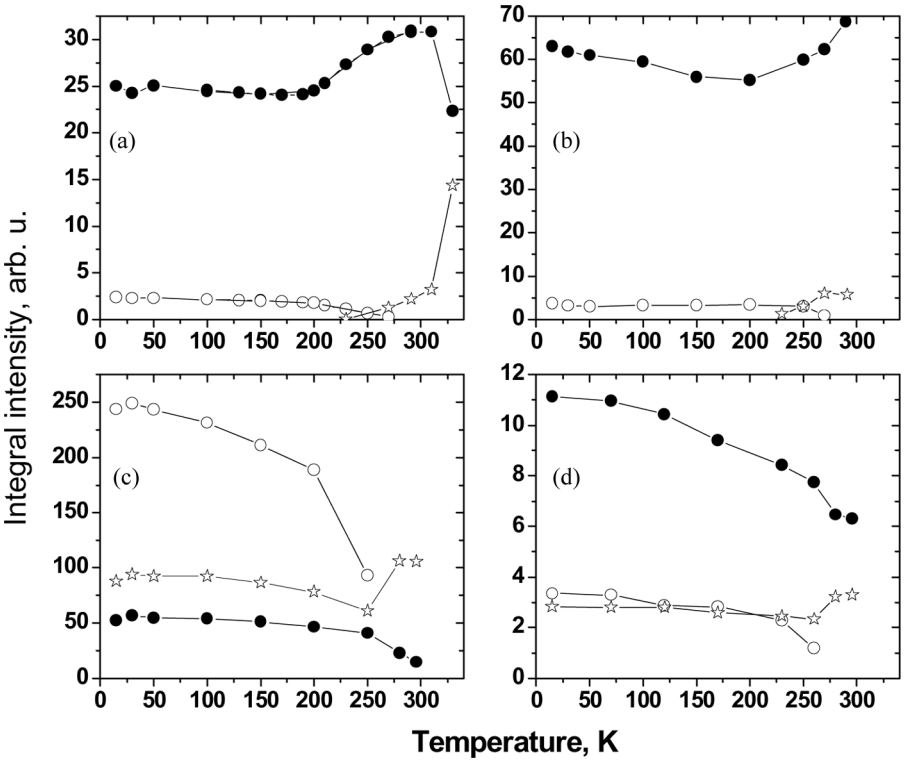


**Figure 3.** Integrated intensities of the *trans*-conformation (open circles), *gauche*-conformation (open stars), and aggregates (solid circles) fluorescence bands of PDHS in $TiO_2$ porous film (a), $SiO_2$ porous film (b), photonic crystal (c), and $SiO_2$ gel (d).

motions: *trans*-conformation polymer chains cannot rearrange and form aggregate states.

The analysis of the FL spectra of composites shows that the intensity and the width of the FL bands of these composites have a weak temperature dependence in the range 15–200 K, which is opposite to a strong broadening, shift, and drastic decrease of the intensity of the FL band observed for the PDHS film [15].

*Fluorescence relaxation.* The FL relaxation kinetics of all composites was measured in the temperature range 30–296 K. The FL kinetics was approximated by a bi-exponential relaxation function with the deconvolution of an apparatus function. The deconvolution procedure allowed us to determine shorter relaxation times than the excitation pulse duration. In addition to the main relaxation component with a subnanosecond lifetime, the kinetics contains a weak component with the lifetime of several nanoseconds. This component is probably caused by some impurities present in nanocomposites. Therefore, we did not analyze it in detail. Table 1 presents the lifetimes and amplitudes of the subnanosecond relaxation component. The FL lifetimes only weakly depend on the sample. Thus, we conclude that different FL intensities of different FL bands are caused by different concentrations of different species present in different samples rather than by their excited state relaxation. The aggregate fluorescence has the longest lifetime. Moreover, the lifetime depends more significantly on the sample and the temperature.

**Table 1.** Fluorescence lifetimes ($\tau$) and amplitudes (A) of the subnanosecond decay component

| | | Conformation | | | | | |
|---|---|---|---|---|---|---|---|
| | | Gauche | | Trans | | Aggregate | |
| PDHS composites | *T*, K | $\tau$ | A | $\tau$ | A | $\tau$ | A |
| PDHS in $SiO_2$ gel | 30 | – | – | 170 | 94 | 380 | 98 |
| | 296 | 200 | 80 | – | – | 280 | 98 |
| PDHS in Ph. Cryst. | 30 | – | – | 160 | 98 | 300 | 93 |
| | 296 | 120 | 97 | – | – | 420 | 95 |
| PDHS in $SiO_2$ nanopores | 30 | – | – | 150 | 98 | 470 | 100 |
| | 291 | 120 | 94 | – | – | 550 | 100 |
| PDHS in $TiO_2$ nanopores | 30 | – | – | 120 | 98 | 330 | 100 |
| | 291 | 120 | 97 | – | – | 390 | 100 |



The FL lifetimes were analyzed in more details for PDHS in the photonic crystal. Figure 4 shows the temperature dependence of the FL lifetimes of all FL bands. The *trans*-conformation lifetime is independent of the temperature, the *gauche*-conformation lifetime decreases above the *trans-gauche* transition, while the aggregate lifetime increases surprisingly above the transition temperature. This is in contrast with about a twofold decrease of the aggregate FL lifetime, as observed in the neat polymer film and the solution [15].

We stress that the FL lifetimes of the aggregate states of PDHS confined in nanopores were found basically to be independent on the temperature within the experimental accuracy in the range 30–300 K (Table 1). This implies the constant FL quantum yield and consequently, the temperature-independent nonradiative

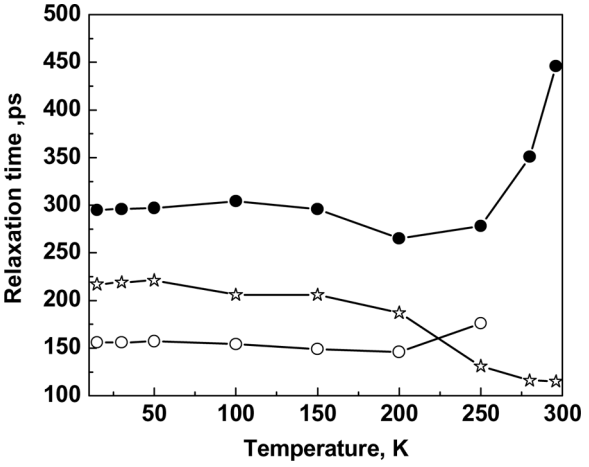


**Figure 4.** Fluorescence lifetimes of PDHS/Phot.cryst measured for the *trans*-conformation and aggregates; *trans*-conformation (open circles), *gauche*-conformation (open stars), and aggregates (solid circles).

decay. This finding indicates the strong suppression of nonradiative decay channels and the absence of the thermally activated FL quenching of polysilanes embedded in nanopores, which contradicts the results obtained for polysilane films and solutions [15]. The effect is evidently caused by the reduced exciton migration and, thus, by the suppressed nonradiative relaxation due to the strong exciton localization in low-dimensional structures. The same conclusion is evidently valid for other PDHS nanostructures. The weak temperature-enhanced nonradiative relaxation is favorable for nano-sized polysilane-based optoelectronic devices such as OLEDs.

## Conclusions

Four novel nanocomposite films of the silicon-organic polymer poly(di-n-hexylsilane) incorporated into inorganic matrices with different structures and morphologies have been fabricated. The inorganic matrices are: the porous $SiO_2$ and $TiO_2$ films, the photonic crystal, and the silica matrix consisting of nano-sized $SiO_2$ particles. A particular attention has been paid to the investigation of the temperature dependence of the FL spectra and the lifetimes of composite films in the temperature range 15–330 K. It is shown that the morphology and the orientation of the inorganic matrix influences the conformational structure of incorporated polymer chains and the emission properties of nanocomposites. The relative intensity of FL bands attributed do different conformations of polymer chains depends on the structure of an inorganic matrix. The *trans*-conformation band is more intense in the spectrum of PDHS in the photonic crystal, while the aggregate band is more intense in the spectrum of PDHS in porous films. Two thermochromic transitions of nano-sized PDHS were observed for a single polymer chain and for an aggregate.

The excited state lifetimes for these composites weakly depend on the inorganic matrix and the temperature. This fact indicates the strong suppression of nonradiative decay channels and the absence of the thermally activated FL quenching in nano-sized PDHS. This effect is most probably caused by the reduced exciton migration and, thus, by the suppressed nonradiative relaxation due to the strong exciton localization in a low-dimensional structure. This is in contrast to the results obtained for polymer films and solutions.



## Acknowledgment

This work was partially supported by the Ukrainian Ministry of Education and Science, grant No. M 139/2009 and by the Research Council of Lithuania, project V-09055.

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