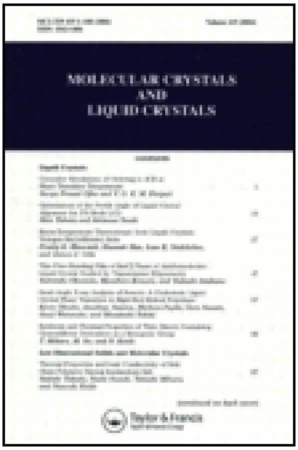

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Visible Luminescence of Nanosized Polysilane Photoconductors, Incorporated into Mesoporous Silica

N. Ostapenko [a] , N. Kotova [a] , V. Lukashenko [a] , G. Telbiz [b] , S. Suto [c] & A. Watanabe [d]

[a] Institute of Physics of NASU, Kyiv, Ukraine

[b] Institute of Physical Chemistry of NASU, Kyiv, Ukraine

[c] Department of Physics, Tohoku University, Sendai, Japan

[d] Institute of Multidisciplinary Research for Advanced Materials, Sendai, Japan

Version of record first published: 31 Aug 2006

To cite this article: N. Ostapenko, N. Kotova, V. Lukashenko, G. Telbiz, S. Suto & A. Watanabe (2005): Visible Luminescence of Nanosized Polysilane Photoconductors, Incorporated into Mesoporous Silica, Molecular Crystals and Liquid Crystals, 426:1, 149-156

To link to this article: http://dx.doi.org/10.1080/15421400590891047

Mol. Cryst. Liq. Cryst., Vol. 426, pp. 149–156, 2005
Copyright © Taylor & Francis Inc.
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400590891047

Visible Luminescence of Nanosized Polysilane Photoconductors, Incorporated into Mesoporous Silica

N. Ostapenko
N. Kotova
V. Lukashenko
Institute of Physics of NASU, Kyiv, Ukraine

G. Telbiz
Institute of Physical Chemistry of NASU, Kyiv, Ukraine

S. Suto
Department of Physics, Tohoku University, Sendai, Japan

A. Watanabe
Institute of Multidisciplinary Research for Advanced Materials,
Sendai, Japan

The dependence of the low-temperature (5–150 K) photoluminescence spectra of poly(di-n-hexylsilane) (PDHS) incorporated into mesoporous silicas on sizes and a geometry of pores was investigated. It was shown that visible luminescence in nanosized PDHS is observed only when the polymer is incorporated into the hexagonal pores of 2.8 nm in diameter, but it is absent for the bulk film, dissolved polymer, and polymer incorporated into cubic pores of 2.8 nm in diameter or into hexagonal pores of 5.8 nm in diameter. We suggest that the appearance of visible luminescence in nanosized PDHS is connected with the transition from electronic states localized on the conformational defect of the polymer chain.

Keywords: conformational defects; mesoporous silica; nanosized composites; photoluminescence; poly(di-n-hexylsilane); size and geometry of the pore; X-ray diffraction

INTRODUCTION

Nanosized polymers in a confined space are attractive candidates for various applications in microelectronics and in electroluminescent

Address correspondence to N. Ostapenko, Institute of Physics of NASU, Prospent Nayk 46, Kyiv 03028, Ukraine. Tel.: 38044,265-30-14, Fax: 380-44-2651587, E-mail: ostap@iop.kiev.ua

devices [1,2]. A considerable interest in the study of the structure and morphology of these polymers is aroused by the possibility of modifying their optical and electronic properties as their thickness decreases. Under these conditions, the processes of interaction of the polymers with the surface become compared to those of the intermolecular interaction between the polymer chains that can lead to essential changes of the polymer chain structure near the surface. The results of Monte Carlo simulations of the polymer confined between two plates confirm that the structure of the polymer chain is strongly perturbed compared to the Gaussian statistics expected in a bulk phase [3]. Composite systems based on polymers embedded in mesoporous silicas with nanosized pores are a new class of structures [4–7] that allow the investigating and monitoring of the polymer properties in the course of the transition from a bulk film to a nanostructure. Here, we report a successful attempt to produce nanocomposites by introducing a photoconducting polymer poly(di-n-hexylsilane) PDHS (Fig. 1, a) into siliceous mesoporous silicas. It is known that mesoporous silicas consist of the equal pores with the same distance between them (Fig. 1, b and c).

The use of nanosized polysilane as transport layers in multilayer electroluminescent devices [8] and active electroluminescent materials in the UV region [1,9] also stimulate these investigations. In this connection, the work gives a special attention to the study of the origin of the visible luminescence of polysilane which is widely discussed in the literature [10–17]. For an explanation of this effect, a model of charge transfer from the polymer chain to the aryl ring of a side group and a defect model have been proposed. So far, there is no experimental

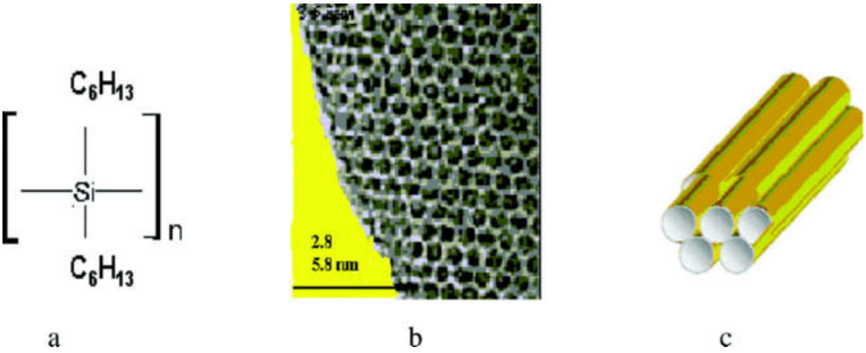

FIGURE 1 a- monomeric unit of poly(di-n-hexylsilane), b and c- TEM images and schematic illustration of the pore structure of MCM-41.

evidence for the reliability of the charge-transfer model. At the same time, the existent experimental results suggest a relation between the visible luminescence and the branching point of Si-Si chains [11–13], where a silicon atom is surrounded by three neighboring atoms (see the insert a in Fig. 2). It has been hypothesized [14,17] that the formation of such structural defects can occur only in polymers containing both the aryl side groups and alkyl side groups, the latter are shorter than pentyl.

PDHS has no aryl side groups, and its alkyl side groups are hexyl. Therefore, no visible luminescense should be observed for this polymer. This is correct for the bulk film and a polymer solution. Nevertheless, in the course of the investigation of a nanosized PDHS polymer embedded into the pores of 2.8 nm in size, we observed a rather intense visible luminescence [18].

In this work, we investigated the dependence of the above-men tioned low-temperature (5–150 K) photoluminescence (PL) of PDHS/mesoporous silica composites on the size and geometry of pores. We used mesoporous silicas MCM-41 and SBA-15 with pores of 2.8 and 5.8 nm in size and the hexagonal geometry as well as MCM-48 with pores of

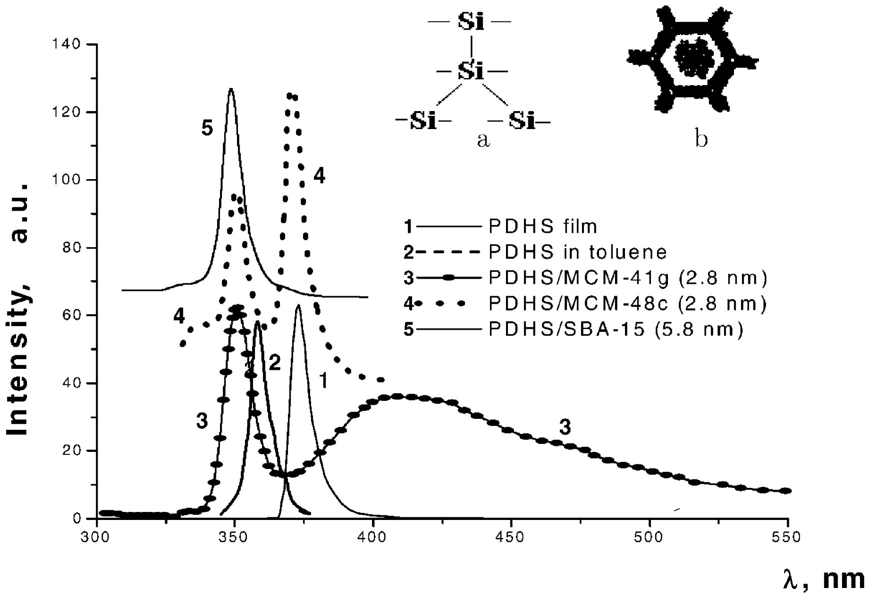

FIGURE 2 PL spectra of PDHS at 5 K (curves 2 and 3 are normalized by the intensity of curve 1, the insert shows: a-the branching point of Si-Si chains; b-composite PDHS/MCM-41).

2.8 nm in size and the cubic geometry. A comparison was made with the spectra of bulk films and a polymer solution. The location of the polymer in the pore was determined by X-ray diffraction analysis.

EXPERIMENTAL

The synthesis of silicas MCM-41 and SBA-15 has been described in [20,21]. The materials obtained were washed and dried in air at 323 K. For the removal of the template, MCM-41 was baked in dry air at 813 K for 23 h. The removal of the template was monitored by IR spectroscopy methods (a Specord IR 75). The preservation of the matrix structure after processing was confirmed by X-ray diffraction (a DRON-3M). The nitrogen adsorption and desorption isotherms were measured on an ASAP-2000. For the removal of the residual moisture, the samples were dried at room temperature for 12 h and then stored in an exsiccator.

Composites (polymer/mesoporous material) with different pore diameters and geometries were created by the identical method. This was done by pouring a 1 wt.% solution of the polymer, PDHS ($M = 53600$), in toluene over the correspondent mesoporous material. The sample was placed into a dark vessel and slowly agitated for several hours at 293 K and then held until the solvent evaporated. The resulting composite was washed twice in fresh toluene to remove the polymer from the outer surface. For the removal of moisture, the sample was dried at room temperature for 12 h. The polymer films were deposited on a quartz substrate by centrifuging. The PL spectrum of a polymer solution in toluene was investigated for a concentration of 10^{-7} mol/l. The PL and phosphorescence spectra in the temperature interval 5–150 K were obtained with the use of a Hitachi MPF-4. For the excitation of PL, the wavelengths of 260 and 313 nm were selected by using a xenon lamp and a monochromator.

RESULTS AND DISCUSSION

The PL spectrum of a PDHS film (5 K) is shown by curve 1 in Figure 2. It is known that this spectrum consist of a single narrow band at 371 nm assigned to the transition in the Si backbone. Curve 3 in Figure 2 demonstrates the PL (5 K, $\lambda_{ex} = 313$ nm) of PDHS incorporated into the mesoporous silica with a pore size of 2.8 nm and the hexagonal geometry. This PL spectrum shows two bands: the narrow band with the maximum at 350 nm and the broad intense band in the visible region with the maximum at 410 nm. The PL spectra of the incorporated and bulk polymers differ significantly. Firstly, in the case of the composite, the narrow PL band is shifted by 20 nm to the blue side. In the second place, a new PL band is observed in the visible region named visible luminescence. This significant blue shift confirms that the polymer chains are indeed incorporated into pores. The size of the monomeric unit of a PDHS macromolecule is about 1.6 nm. Therefore, only one polymer chain can be incorporated into a mesopore with a diameter of 2.8 nm (the insert b to Fig. 2). So, the blue shift of the narrow PL band at 350 nm is due to a reduction of the intermolecular interactions between polymer chains. In this case, the maximum of the narrow PL band in the composite system should be close to a similar maximum in the correspondent spectrum of a polymer solution. Indeed, the maximum of the narrow PL band in the composite system is shifted even to the blue side from the position of the PL band in a polymer solution at 358 nm (curve 2 in Fig. 2).

The location of the polymer in a pore is confirmed also by the analysis of the intensity of X-ray diffraction lines. Curves 1 and 2 in Figure 3 show the X-ray diffraction patterns of the mesoporous silica and the composite PDHS/mesoporous silica (2.8 nm), respectively. The reduction of the line intensity in the case of composite confirms that the polymer is incorporated into the mesoporous silica.

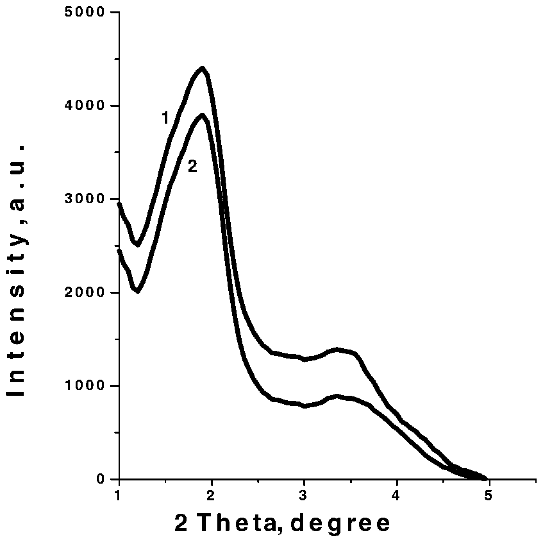

FIGURE 3 X-ray powder diffraction patterns for calcined MCM-41 mesoporous silicas with a pore size of 2.8 nm (1) and its composite with PDHS polymer (2).

The results obtained demonstrate that the visible luminescence of nanostructured PDHS emerges only in the case where the polymer chain is incorporated into a hexagonal 2.8-nm pore (curve 3 in Fig. 2). It is not observed for the films spincoated either on the quartz or mesoporous silica substrate [18] and for a dissolved polymer, as well as for PDHS incorporated into a cubic 2.8-nm pore or into a hexagonal 5.8-nm one (curves 1, 2, 4, and 5 in Fig. 2, respectively). We suggest that the visible fluorescence of confined PDHS should be attributed to electronic states localized at the defects of polymer chains. These defects are caused by the surface-induced orientation of polymer chains being at contact with the pore walls. We assume that a part of the PDHS macromolecule incorporated into the 2.8-nm pore is aligned along the pore walls. Such an orientation of the polymer chain near the surface has been argued experimentally [4,7,21].

The interaction of the polymer with the surface of a pore may change the conformation of polymer chains. The large Stokes shift of the maximum of visible luminescence by 60 nm confirms a change of the Si-Si chain geometry in the excited state. It is known that the electronic properties of the polymer strongly depend on the conformation of the Si backbone [22] and the conformation changes may induce localized excited states resulting in the emergence of a new band in the PL spectrum.

The reduction of the intensity of visible luminescence band with increase in the temperature from 5 to 150 K is an additional evidence for its defect nature (Fig. 4). The absence of visible luminescence for

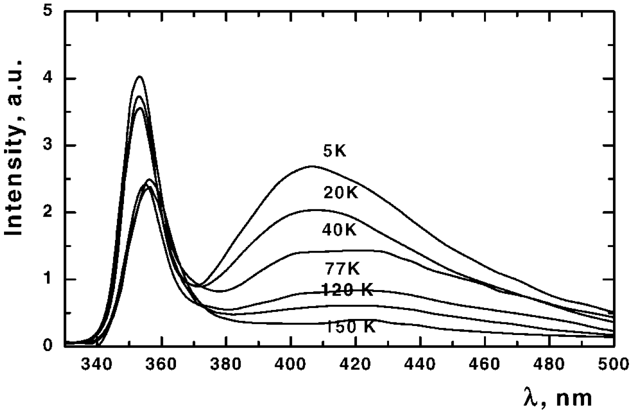

FIGURE 4 Temperature dependence of the PL spectra of PDHS/MCM-41 composite.

the PDHS imbedded into the silica with a pore size of 2.8 nm and the cubic geometry or into large 5.8-nm pores and the hexagonal geometry confirms also our assumption about its defect origin (curves 4 and 5 in Fig. 2). To embed the polymer into PDHS with a 2.8-nm pore and the cubic geometry is problematic because of significant changes of the pore profile along its length. In such a case, a substantial part of macromolecules appears to be outside the pore. In this case, there are two narrow bands in the PL spectrum: one with maximum at 350 nm and another with maximum at 371 nm which coincides with the correspondent band in the PL spectrum of a film. In the case where PDHS is embedded into the silica with large 5.8-nm pores, more that one molecule can fit into the pore, and the chains of macromolecules can be oriented not only along the pore surface but also one along another. The intermolecular interaction between the polymer chains is much stronger than the interaction of the polymer with the pore walls. In this case, the conformation of the macromolecules would not be changed as compared to the case of the bulk polymer, and no visible luminescence at 410 nm would appear. Indeed, this band is not observed in the respective spectrum of the polymer imbedded into silica with larger pores.

The visible luminescence of the nanostructured polymer was observed only in PDHS incorporated into a hexagonal pore of 2.8 nm in size. This fact testifies to that the determining factor for the appearance of this PL is the orientation of polymer chains along the pore walls. Only in such a case, the polymer interacts with the pore surface and the change of a polymer chain conformation occurs.

The results of experiments open the possibility for a very promising technique of a controlled modification of the optical properties of nanostructured polymers aligned along the surfaces of pores by a proper choice of the pore sizes.

REFERENCES

[1] Ebihara, K., Matsushita, S., Koshihara, S., Minami, F., Miyazawa, T., Obata, H., & Kira, M. (1997). *J. Lumin.*, *43*, 72–74.

[2] Hoshino, S., Furukawa, K., Ebata, K., Brey, J., & Suzuki, H. (2000). *J. Appl. Phys.*, *88*, 3408.

[3] Kumar, S. K., Vacatello, V., & Yoon, D. V. (1988). *J. Chem. Phys.*, *89*, 5206.

[4] Wu, C.-G. & Bein, T. (1994). *Stud. Surf. Sci. Catal.*, *84*, 2269.

[5] Marlow, F., Hoffmann, K., Hill, W., Kornatovski, J., & Caro, J. (1994). *Stud. Surf. Sci. Catal.*, *84*, 2277.

[6] Telbiz, G., Shvets, O., Korzhak, G., Brodyn, M., Shevel, S., & Vozny, V. (1998). *Functional Materials*, *5*, 367.

[7] Wu, J., Gross, A. F., & Tolbert, S. H. (1999). *J. Phys. Chem.*, *103*, 2374.

[8] Suzuki, A. H., Meyer, H., Hohino, S., & Haarer, D. (1995). *J. Appl. Phys.*, *78*, 2684.
[9] Fuyii, A., Yoshimoto, K., Yoshida, M., Ohwori, Y., & Yochino, H. (1995). *Jpn. J. Appl. Phys.*, *34*, 1365.
[10] Ito, O., Terajima, M., Azumi, T., Matsumoto, N., Takeda, K., & Fujino, M. (1989). *Macromolecules*, *22*, 1718.
[11] Fujiki, M. (1992). *Chem. Phys. Lett.*, *198*, 177.
[12] Wilson, W. I. & Weidman, T. W. (1991). *J. Phys. Chem.*, *95*, 4568.
[13] Kanemitsu, Y. & Suzuki, K. (1995). *Phys. Rev.*, *51*, 13103.
[14] Toyoda, S. & Fujiki, M. (1998). *Chem. Phys. Lett.*, *293*, 38.
[15] Watanabe, A., Nanyo, M., Sunaga, T., & Sekiguchi, A. (2001). *J. Phys. Chem. A*, *105*, 6436.
[16] Watanabe, A., Sato, T., & Matsuda, M. (2001). *Jpn. J. Appl. Phys.*, *40*, 6457.
[17] Toyoda, S. & Fujiki, M. (2001). *Macromolecules*, *34*, 2630.
[18] Ostapenko, N., Telbiz, G., Ilyin, V., Suto, S., & Watanabe, H. (2004). *Chem. Phys. Lett.*, *383*, 456.
[19] Kresge, C. T., Leonowicz, M. E., Roth, W. J., Vartuli, J. C., & Beck, J. S. (1992). *Nature, 359*, 710.
[20] Zhao, D. Y., Feng, J. L., Huo, Q. S., Melosh, N., Fredrickson, G. H., Chmelka, B. F., & Stucky, G. D. (1998). *Science*, *279*, 548.
[21] Israelashvili, J. N. & Kott, S. J. (1988). *J. Chem. Phys.*, *88*, 7162.
[22] Miller, R. D. & Michl, J. (1989). *Chem. Rev.*, *89*, 1359.