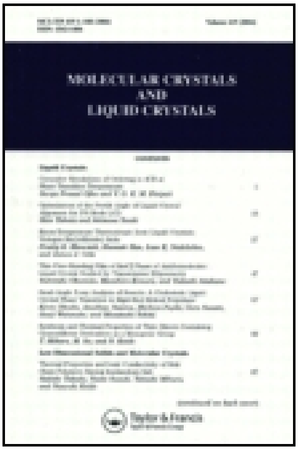

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Luminescence Kinetics of Nanosize Poly(di-n-hexyl)Silane Embedded in Nanoporous Silica

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Excited state relaxation kinetics of nanostructured poly(di-n-hexyl)silane embedded in nanoporous silica SBA-15 with the pore size of 10 nm was considered with the nanosecond and picosecond time resolution by using photomultiplier with fast response time and by means of time correlated two-pulse excitation. Measurements were carried out at room temperature. For comparative reasons the exciton relaxation kinetics of poly(di-n-hexyl)silane films are also considered. It was found that the photoluminescence of nanostructured poly(di-n-hexyl)silane decays exponentially with about 6 ns time constant, which is more than 10 times longer than that of the film. The longer decay time should be related with slower exciton diffusion and lower density of exciton quenching centers.

Keywords: nanoporous silica; nanosize polysilane; photoluminescence kinetic; polysilane film

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INTRODUCTION

Polisilanes belong to silicon-organic polymers, which consist of σ-conjugated Si backbone with organic side groups. Polisilanes are known as polymers with a remarkable photoluminescence (PL) in the UV region [1]. Apart from high PL quantum efficiency polysilanes exhibit high mobility of holes [2], thus, are promising as emitting or transport layers for electroluminescence devices [3,4]. Functioning of polymer-based devices is very sensitive to the structural organization of these polymers in the solid state; therefore, understanding of details of their optical and electrical properties is an important issue. Current trends in designing nanostructured materials for various applicative purposes can be achieved by means of different technological approaches. Embedding polysilanes in nanoporous silicas such as MCM-41 and SBA-15 is an effective way in producing and control of nanostructured composites.

Poly(di-*n*-hexyl)silane (PDHS) embedded into nanoporous silica shows significantly different properties than in films. We have recently found that several conformational forms of the polymer chain may coexist in a pore of the 10 nm diameter [5]. Two or even three PL bands corresponding to different conformations are present in the spectrum at the same time in such polymorphous material under some specific conditions indicating that the excitation energy migration in a separate nanopore is essentially slower than in the polymer film. PL relaxation kinetics provides direct information about the exciton migration and relaxation. Moreover, the exciton relaxation rate is a very important parameter of the system closely related to the luminescence yield.

Studies of PL relaxation of the PDHS film have been recently fulfilled [6]. It has been found that the PL decay kinetics strongly depends on temperature and on the observation energy, the decay time constant ranging from 350 to 500 ps. The relatively short exciton lifetime is evidently related to the exciton quenching by some impurities or structural defects reached during the exciton migration.

Here we present studies of the temporal evolution of the PL of the PDHS embedded in the nanoporous material SBA-15 with the 10 nm pore size. To measure PL kinetics on the nanosecond and picosecond time scales two different experimental methods are used.

EXPERIMENT

PDHS embedded in the nanoporous material SBA-15 was obtained by means of the 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 defined by the X-ray diffraction method by monitoring the presence of the characteristic silica framework structure. Details of preparation of the nanoporous silica material SBA-15 with the pore diameter of 10 nm was described elsewhere [7]. All measurements were carried out at room temperature.

Steady state PL and photoluminescence excitation spectra of PDHS samples were measured with the Perkin Elmer LS 50 B luminescence spectrometer. Two methods for measurement of PL kinetics were applied. The PL time evolution on a nanosecond time scale was measured with the fast photomultiplier and oscilloscope. The samples were excited with 3 ps duration laser pulses at 264 nm. The time resolution in this scheme is limited by the oscilloscope apparatus function of about 2.5 ns. In order to obtain information about the PL evolution on a picosecond time scale the two-time-separated excitation pulse technique was applied. The time-integrated PL from the sample excited by two equal intensity laser pulses (264 nm, 3 ps duration) was measured by changing delay time between excitation pulses. The method is based on the PL saturation at high excitation intensity. Because of the absorption bleaching and nonlinear exciton-exciton annihilation the integrated PL intensity drops down when separation time between excitation pulses is shorter than the exciton lifetime. Growth of the integrated PL intensity by increasing the pulse separation time gives information about the excited state relaxation kinetics.

The exciton density relaxation kinetics at high excitation intensity may be expressed as follows:

$$\frac{dn}{dt} = -\gamma n^2 - kn, \tag{1}$$

where n is the exciton concentration, γ describes the exciton-exciton annihilation rate and $k = 1/\tau$ is the exciton intrinsic decay rate. When both γ and k are time independent, eq. (1) gives the following expression for the exciton density decay kinetics:

$$n = \frac{n_0 \exp[-kt]}{1 + (n_0\gamma/k)(1 - \exp[-kt])}, \tag{2}$$

where n_0 *is* the initial exciton density.

PL intensity created by two high intensity excitation pulses under such experimental conditions may be expressed as:

$$F(\tau) = \int_0^{\tau} n(t)dt + \int_0^{\infty} \frac{(n(\tau) + n_0)\exp(-kt)dt}{1 + (n(\tau) + n_0)\frac{\gamma}{k}(1 - \exp(-kt))}, \qquad (3)$$

where τ is the delay time between two excitation pulses.

This method gives a possibility of determing the PL lifetime and also provides information about exciton-exciton annihilation in this material.

RESULTS

Figure 1 demonstrates the PL and photoluminescence excitation (PLE) spectra of PDHS/SBA-15 composite and PDHS film samples at room temperature (293 K). Two PL bands PL1 and PL2, and two PLE bands PLE1 and PLE2 of the PDHS/SBA-15 composite are related to two different polymer conformations. The short-wavelength bands PL1 and PLE1 originate from single polymer chains being in the gauche- backbone conformation, while the long-wavelength bands PL2 and PLE2 belong to the aggregated polymer chains in trans- conformation [5]. A single PL band at 380 nm is observed in the spectrum of the film, whereas the PLE spectra of the film show two bands assigned to the gauche- and to the trans-conformers [1]. It implies that PL from gauche-conformers in the film sample is completely quenched by trans-conformers.

Both composite and film samples were excited with light pulses at 264 nm. Figure 2a shows normalized PL intensity decay curves

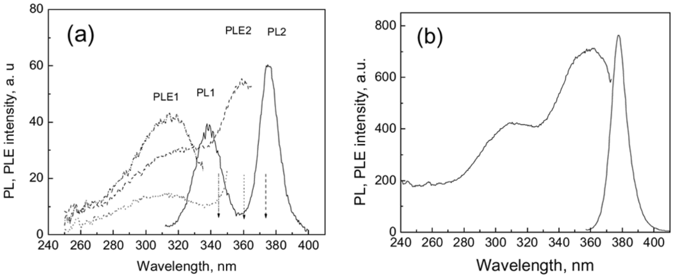

FIGURE 1 Photoluminescence and luminescence excitation spectra of PDHS/SBA-15 composite (a), and PDHS film (b). Arrows in (a) indicate the wavelengths used to measure the corresponding luminescence excitation spectra (as marked by the same lines). The excitation spectrum in (b) was measured at 380 nm.

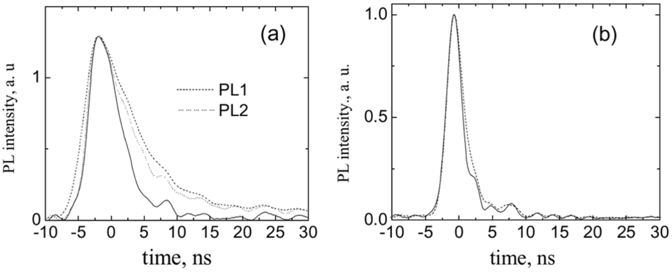

FIGURE 2 Photoluminescence kinetics measured by photomultiplier and osciloscope at 380 nm (corresponding to PL2) and at 340 nm (corresponding to PL1) in the PDHS/SBA-15 composite (a), and at the luminescence band of the PDHS film (b). The solid line shows the apparatus function.

measured in the PDHS/SBA-15 composite at two spectral positions (340 and 380 nm) where the composite has distinctive PL bands. The PL decay times are of comparable duration to the apparatus resolution time function, therefore, PL relaxation times were obtained by using the deconvolution procedure. The exponential decay with time constants of (6.0 ± 1.0) ns and (4.5 ± 1.0) ns were obtained for the PL1 and PL2 bands, respectively. Thus, we cannot clearly distinguish the difference between the two band decays. PL kinetics for the PDHS film was very close to the apparatus function (Fig. 2b). The value of (0.5 ± 0.3) ns for the film PL relaxation follows from the deconvolution procedure.

Figure 3 shows the results obtained by using the two-time-separated excitation pulses. The PL of composite was measured at 380 nm, which corresponds to the PL2 band. The PL intensity was normalized to the sum of the PL intensities when one of the excitation pulses was blocked, i.e., to the values of the PL created by noninteracting pulses. A distinct PL minimum was observed when the two pulses were overlapping in time. In case of the PDHS film the PL intensity increases to the value corresponding to the condition of noninteracting pulses with a time constant of about 1.5 ns, while for the PDHS/SBA-15 composite this value is not reached even at the longest experimentally possible delay time of 2.5 ns. For the PDHS film the kinetics of the signal is faster than the kinetics obtained for the PDHS/SBA-15 composite. The experimental curves were fitted by the theoretical function determined by Eq. (3). The fitting results are presented in Figure 3. The $n_0\gamma$ product was used as a fitting parameter determining the depth of the integral PL dip at zero delay time. Both curves could be successfully fitted by assuming exponential PL decay with the mean values of (6.0 ± 1.0)

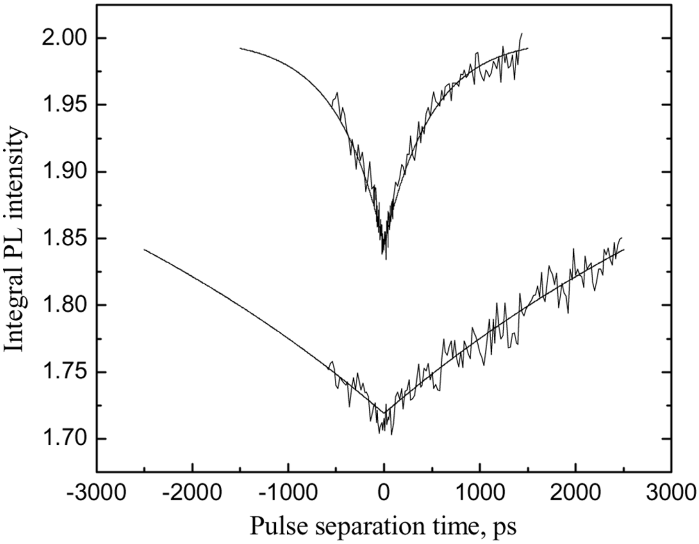

FIGURE 3 Time-integrated luminescence measured by using the the two-time-separeted excitation pulses. The upper curve corresponds the results obtained from the PDHS film and the lower curve to the PDHS/SBA-15 composite. Solid lines show fitting results: $\tau = 0.5\,\text{ns}$ was chosen for the upper curve and $\tau = 6\,\text{ns}$ for the lower curve, while the product $n_0\gamma$ was used as a fitting parameter by to reach the minimal values of the integral luminescence.

ns for nanostructured PDHS composite and of (0.5 ± 0.05) ns for the PDHS film. These values are in good agreement with the oscilloscope measurement results and do not reveal any fast relaxation processes.

DISCUSSION

PL in conjugated polymers originates from the exciton relaxation, and the PL relaxation time is strongly affected by the exciton quenching. In order to reproduce the PL time response from PDHS film the one-dimentional Frenkel exciton models with disorder limited exciton migration without and with account of the interchain exciton migration has been proposed in [6,8] respectively. Our results imply that namely the interchain migration plays a crucial role. As it is evident from the PLE spectra both samples at room temperature contain both gauche- and trans-conformeric forms of the polymer chain (Fig. 1). Moreover, the ratio of such conformers in the composite and in the film is similar (Fig. 1a,b). In spite of this fact the PL of nanosize-PDHS and of the PDHS film strongly differs. PL originating from the gauche-conformer is completely quenched by trans-conformers in the PDHS film, while both bands are evident in the composite PL spectrum indicating that the exciton migration in nanosize-PDHS is less efficient. On the other hand, the exciton migration from single chains to the aggregates still takes place in composite since both the single chain and aggregate bands are observed in the PLE spectrum measured by detecting inside the aggregate PL band. Intrachain exciton migration should not be very different in the polymer film and in the nanosize polymer, whereas the interchain migration may be essentially different. The polymer chain inside the pore has a limited number of neighboring chains. According to the size of the polymer chains, about 6 chains may fit into the pore of the 10 nm diameter. Some chains situated close to the pore boundaries have a reduced number of available neighbors for the exciton transfer. On the other hand, polymer chains in pores are more ordered and therefore have less defect states responsible for the exciton quenching. Therefore, different interchain exciton migration and lower density of quenching centers responsible for different PL relaxation times correspond to the film and to the composite (Figs. 2,3).

Slightly faster decay of the aggregate (PL2) band in comparison with the single chain (PL1) band observed in composite (Fig. 2a) may be interpreted only by assuming that the energy transfer from the singles states to aggregates is inefficient and excitations created in different states decay independently or almost independently. In the opposite case the exciton transfer from single chains to aggregates would lead to the faster decay of the single chain PL.

SUMMARY

In summary, we have performed the time-resolved luminescence measurements for the poly(di-*n*-hexylsilane) (PDHS) film and for PDHS/SBA-15 composites where polymer is embedded in nanoporous silica with pore size of 10 nm. Luminescence of PDHS/SBA-15 composites decays exponentially with the time constant of about 10 times longer than that of the PDHS film. The difference in the decay times is related to the ordered polymer chain orientation in nanopores responsible for both, different interchain exciton transfer rate and different density of exciton quenching states.

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