Luminescence features of nanocomposites of silicon-organic polymer/porous SiO2 and TiO2 films

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1. Introduction

α-Conjugated luminescent polymers are promising materials for various photonic applications, such as active layers of light-emitting diodes [1–3], luminescent sensors and bioprobos [4–6]. Photoluminescence (PL) quantum yield, which desirably should be close to 100%, is one of the major parameters determining their application perspectives. Polymers usually have to be used in a solid state as thin films where macromolecules tend to form aggregates. It is known that aggregation of the organic polymers often leads to a partial or even complete quenching of their PL, simultaneously a decrease in the PL lifetimes is observed. This effect has limited the scope of technological applications of the polymers. Therefore substantial challenge is to discover and explore the mechanisms and new functional properties of polymers when aggregation plays a constructive, rather than destructive role. Several conceptions have been proposed to produce polymers with aggregation-enhanced emission (AEE): conformational planarization, J-aggregate formation, twisted intramolecular charge transfer and restriction of the intramolecular rotation of individual parts of macromolecules [7–10]. Theoretical and experimental research of a number of authors [10,11] showed that the restriction of the intramolecular motion of macromolecules blocking the nonradiative relaxation paths and activating the radiative decay is the most important mechanism of the AEE effect. As a result, polymers with AEE were synthesized by attaching propeller-like molecular structures of active hexaphenylsilanes or tetraphenylenethenes to the polymer backbones [12,13].

We have recently investigated poly(di-n-hexylsilane) (PDHS) embedded into the SBA-15 nanoporous silica, obtained in a form of tablets pressed from porous powder [14]. It was shown that the PL quenching of the PDHS embedded in limited volumes of SBA-15 nanopores is less effective. In the present work we analyze a different way to obtain active polymers with AEE properties by incorporating macromolecules into nanopores of porous films. For this purpose we have developed a method of preparation of organic/inorganic nanocomposite films, and investigated their PL spectra and PL lifetimes in a wide temperature range 15–300 K. As inorganic matrixes, we used nanoporous SiO2 and TiO2 films with given pore sizes and high surface area, as well as films of dispersive SiO2 nanoparticles (nanosized SiO2). We have chosen α-conjugated silicon organic polymer PDHS as an organic component. This photoconductive and electroluminescent polymer has high PL quantum yield and high mobility of holes, which enables its application for emitting and transporting layers in electroluminescent devices [15]. Our research results suggest that exciton diffusion and related PL quenching are less efficient in PDHS in nanoporous SiO2 and TiO2 films than in neat PDHS film or in PDHS dispersed between SiO2 nanoparticles. Weak exciton diffusion also causes weak temperature dependence of the PL intensity.
strength of the polymer chains with the matrix was strong enough to prevent desorption, and allows as to suggest that polymer chains were dominantly located in the pores. A simple dispersion interaction may be sufficient to keep the polymer adsorption on the surface of the pores. This is also evidenced by the fact that the polymer film, which was deposited by spin coating on the outer surface of the porous film, was easily washed with toluene within 15 min. However, we cannot exclude a possibility that fractions of long polymer chains remained outside the pores.

To get another kind of the samples, we will call them as PDHS/nanosized SiO₂ composites, nanosized SiO₂ particles of about 2 nm in diameter were dispersed in the 10⁻³ mol/l polymer solution in toluene and slowly stirred in dark for several hours. Then this solution was deposited on a glass substrate by spin coating.

Neat polymer films were also prepared for comparison by applying PDHS solution in toluene with concentration of 4.3 × 10⁻² mol/l on surfaces of porous films or on glass substrates and drying without further washing.

PL spectra and decay kinetics of the samples were measured using Edinburgh Instruments time-correlated single photon counting (TCSPC) fluorescence spectrometer F900. The sample excitation was performed by light emitted diode with 283 nm peak wavelength and about 15 nm bandwidth. The pulse duration was of about 750 ps and the repetition rate was 20 kHz. A liquid helium cold finger cryostat (Janis CCS-100/204) was used for temperature dependent measurements in 15–300 K range in a slow cooling regime. PL relaxation lifetimes measured by TCSPC were determined by approximation of emission kinetics with multieponential functions together with deconvolution of the apparatus function. Deconvolution procedure allowed us to determine shorter relaxation times than the excitation pulse duration.

3. Result and discussion

3.1. Photoluminescence spectra of PDHS/inorganic nanocomposite films

Fig. 2a shows absorption and PL spectra of PDHS/SiO₂ and PDHS/TiO₂ nanocomposite films at room temperature. Absorption spectra show two clearly separated bands with slightly different peak positions for SiO₂ and TiO₂ matrices. Based on the analysis of the PDHS polymorphism [18,19] the absorption band at about 310 nm should be attributed to the gauche polymer chain conformation, while the long wavelength band at about 360 nm, to the aggregate states. The strong aggregate band indicates that several polymer chains are situated inside single pore and a large fraction of them form aggregates. Despite the sample excitation to the gauche conformer absorption band, the PL spectra are dominated by the aggregate band at about 380 nm, while gauche conformer band at about 340 nm has only low intensity. It indicates that excitation energy is efficiently transferred from gauche conformers to aggregate states.

At 15 K temperature (Fig. 2b) the aggregate band shifts to the short wavelength side, while the gauche PL band is replaced by the new band at about 355 nm, which shall be attributed to the trans polymer chain conformation formed at low temperature [18,19]. It should be also noted, that the relative intensities of the two bands depend on the polymer concentration in the solution used for the film preparation; intensity of the short wavelength band grows up with decreasing the polymer concentration down to C = 10⁻⁴ mol/l. It indicates that occupation of the film pores decreases at low solution concentration, and less aggregate states are being formed. The long wavelength band in the PL spectrum of PDHS/SiO₂ is about 2.5 times as intense as that in the spectrum of PDHS/TiO₂. Fig. 2c shows PL spectra at 15 K of the PDHS/nanosized SiO₂ and of near
PDHS polymer films, as well as that of PDHS/SBA-15 (curve 4) nanocomposite powders with pore diameter of 10 nm discussed in Ref. [18].

Comparison of the PL spectra of composite films with the earlier reported spectra of the PDHS/SBA-15 powders gives us more information about the conformation of PDHS polymer chains in limited volumes of silicon and titanium dioxide pores in films. It is well known that conformation of the PDHS polymer chains localized in the SBA-15 nanoporous silica, and consequently their spectra are significantly different from the conformation and spectra of the neat polymer films. As Fig. 2c shows the PL spectrum of the neat polymer film consists of a single band with a maximum at 373 nm, while PDHS/SBA-15 composite has three spatially independent centers of the polymer, which correspond to isolated polymer chains in the gauche- and trans-conformations and to their aggregates [14,20]. The gauche-, trans- and aggregate centers have PL bands at 337, 355 and 369 nm (T = 15 K) respectively. Fig. 2c shows that the PL spectrum of the PDHS/nanosized SiO2 composite has almost identical PL bands to those of PDHS/SBA-15 composite. This fact allows us to attribute the long wavelength PL band of PDHS/nanosized SiO2 composite to the PDHS aggregates [21]. The PL spectra of PDHS/SiO2 and PDHS/TiO2 nanocomposite films show the same bands and hence the same conformations of the polymer chains, however, intensities of the bands are different (Fig. 2).

Thus, PDHS polymer chains in limited volumes of SiO2 and TiO2 nanopores, basically, form aggregates and the bands corresponding to the transitions in the isolated polymer chains in gauche- and trans-conformations are very weak. Less efficient aggregate formation in SBA-15 silica matrix is most probably related to lower relative occupation of the matrix pores by polymer chains. Different morphologies of the porous materials apparently are also important for the aggregate formation. SBA-15 synthesized using the same template – Pluronic P123, but without applying to the substrate has higher degree of order than porous films, because influence of the substrate leads to the structure destruction during drying and heat treatment of the films [16,22]. The fact that the pores of the film are closed on the one side by the substrate can create additional steric hindrance for penetration of long polymer chains into the pores, with depths of about 50 nm, comparable with the polymer chain lengths. In this case, the ends of the polymer chains leaving from the neighboring pores can form aggregates due to van der Waals interactions between them.

Relative PL intensities of the PDHS/SiO2 and PDHS/TiO2 composites deserve additional consideration. PDHS/TiO2 film had approximately twice as large optical density at excitation wavelength as PDHS/SiO2 film, but its PL intensity was about 2.5 times lower, indicating about 5 times lower PL yield. TiO2 is a strong electron acceptor, and is expected to strongly quench polymer PL by electron transfer from photo-excited polymer macromolecules to the electron-acceptor centers, namely coordinative unsaturated titanium ions and oxygen vacancies [23,24]. Therefore relatively weak PL quenching remains not completely clear. One of the possible explanations is that the polymer chains touch walls of the pores only by their long hexyl substitutions, keeping relatively large distances between polymer backbone and TiO2, and thus preventing fast electron transfer. Another possibility is that only the ends of the polymer chains sticking out of the pores are responsible for the PDHS/TiO2 PL. The later explanation is less likely, because PL spectra of PDHS/TiO2 and PDHS/SiO2 composites are very similar, while polymer chains inside and outside pores are expected to have different spectra. Therefore PL spectra of the two composites are also expected to be different if only polymers chain segments located outside pores are responsible for the PDHS/TiO2 film PL, while PL of PDHS/SiO2 film originates both from segments inside and outside pores.

Fig. 3 shows temperature dependences of the integral intensities of the aggregate PL bands of the investigated samples in the temperature range of 15–296 K. The temperature dependences obtained for the PDHS/SiO2 and PDHS/TiO2 films are significantly different from those obtained for the PDHS/nanosized SiO2 composite and for the neat polymer film: intensity of the aggregate band of the PDHS/SiO2 and PDHS/TiO2 films weakly depend on temperature, even slightly increases above 200 K, while PL intensity drops down twice at room temperature in the case of PDHS/nanosized SiO2 composite and of neat PDHS film. Similar temperature independent PL relaxation has been determined for PDHS/SBA-15 composite.
powder [25] and attributed to the weak exciton diffusion. The same conclusion is evidently also valid for the composite films. Polymer chains located in different film pores are separated from each other, preventing exciton transfer between them. Even if PL of the composite film partly originates from the polymer chains sticking out of the pores, the density of such chains is apparently too low to create sufficiently dense network for efficient exciton migration. In contrast, polymer chains in neat PDHS film and in PDHS/nanosized SiO$_2$ composite are closely packed, enabling efficient and temperature dependent exciton migration and consequently quenching by some impurities, defects, or other kind of quenching centers present in the polymer. Fig. 4 presents the temperature dependences of the aggregate PL band peak positions and of the band widths. Both these dependences are significantly weaker for the nanocomposite films than for the neat PDHS film. It supports the conclusion that the exciton diffusion is much less efficient in the nanocomposite films; excitons localize on the low energy sites in the neat film causing the relatively strong bathochromic PL band shift and the band broadening with temperature.

3.2. Photoluminescence relaxation dynamics of PDHS/inorganic nanocomposite films

Fig. 5 shows the PL relaxation traces measured at 30K and at room temperature. The PL kinetics were approximated by bi-exponential relaxation function with deconvolution of the apparatus function. Deconvolution procedure allowed us to determine shorter relaxation times than the excitation pulse duration. In addition to the main relaxation component with subnanosecond lifetime, all kinetics have a weak component with several ns lifetime. The weak component is probably caused by some impurities present in nanocomposites. Its contribution is less than 1% therefore we did not analyze it in detail. The PL decay kinetics of the investigated PDHS samples are in good agreement with the above described temperature dependences of the PL intensity. The dominating PL lifetimes of both nanocomposite films are slightly longer at 296K than at 30K in agreement with the temperature dependence of the PL intensity. A similar temperature independent PL decay has been observed for PDHS in SBA-15 matrix [25]. In contrast, PL lifetimes of the PDHS/nanosized SiO$_2$ composite decrease about 1.3 times by their heating from 30K to room temperature, similarly as was reported for the neat PDHS films [26]. Attributes the PL decay to the exciton quenching via temperature activated diffusion, we conclude that exciton diffusion in PDHS embedded in porous films is relatively slow, like in SBA-15 matrix, while in PDHS/nanosized SiO$_2$ film the diffusion is much more effective, like in neat PDHS films. It should be also noted, that the PL lifetimes of nanocomposite films are still about 1.5–2 times shorter than in SBA-15 silica [25]. It suggests that the polymer chains in nanoporous films are less ordered and/or isolated from quenching centers than in SBA-15 matrix.

Comparing PL decay kinetics in porous SiO$_2$ and TiO$_2$ films we observe even less significant difference between PL lifetimes than between their intensities. This disagreement may be attributed to the very fast quenching component of PDHS/TiO$_2$ film PL, unresolved by our measurements, however it may be also caused to some experimental problems like film inhomogeneity, sample positioning, degradation etc., causing inaccuracy of the PL intensity measurements.

4. Conclusions

Photoluminescence properties of nanocomposite PDHS/SiO$_2$ and PDHS/TiO$_2$ films, as well as of the PDHS/nanosized SiO$_2$ composite and of the neat PDHS film have been investigated in a
temperature range of 15–300 K. PDHS PL yield is about 5 times lower and its lifetime about 1.4 times shorter in porous TiO2 film than in porous SiO2 film. We suggest that the relatively weak PL quenching TiO2 film is caused by the long hexyl side groups, which prevent close contacts between polymer backbone and pore surface preventing electron transfer, or, less probably, by PL of the polymer segments sticking out of the porous film. PL of the all investigated composites is dominated by the aggregate band. Weak temperature dependences of the PDHS PL intensities, lifetimes, band positions, and bandwidths of nanocomposite films in comparison with those of the neat PDHS film indicate that the exciton diffusion is much less efficient in composite films than in the neat film, and consequently PL quenching by some quenching centers present in polymer is less efficient. Thus, nanocomposite films is a promising technologically convenient approach of preparation of polymer films with improved PL properties.

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References