DISTINCTIVE OPTICAL PROPERTIES OF POLYSILANE/TiO$_2$ NANOCOMPOSITE FILMS

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Optimal technological conditions for the fabrication of nanocomposite films based on the poly(di-*n*-hexylsilane) (PDHS) incorporated into a TiO$_2$ nanoporous film have been developed, and such composites are fabricated. Their optical spectra have been investigated in a wide temperature range (15–330) K. It is shown that the distinctive feature of nanocomposite films is related to the predominant fluorescence band of aggregates with respect to the fluorescence bands corresponding to the gauche- and trans-conformations of polymer chains and to the observation of the intense fluorescence band of aggregates even at room temperature.

1. Introduction

Interest in studying the structure and the morphology of ultrathin polymer films and composite systems of organic polymer/porous inorganic materials is determined by the possibility of changes of the optical and electrical properties of these polymers in confined spaces [1–11]. Composite systems based on polymers that are embedded in mesoporous materials with nanoscale pores are the new class of structures, which allow the investigation of and the control over polymer properties in the transition from films to nanostructures. These studies also encourage the use of ultrathin polysilane films as transport layers in electroluminescent devices [12] or as active electroluminescent materials in the UV region, sensors, and photoresistors [13–15]. The interaction of polymers with pore surfaces and the intermolecular interactions between polymer chains significantly influence the optical properties of composite films. The combined investigations of the optical spectra and X-ray diffraction in poly(di-*n*-hexylsilane) (PDHS) and poly(methylphenylsilane) (PMPS) incorporated into globules of mesoporous MCM-41 and SBA-15 silica with different porosities have demonstrated the formation of new polymer structures, which depend on the pore diameter and are associated with the polymer-polymer and polymer-pore interactions [7–9]. These interactions allow a controlled modification of the inhomogeneous disorder of polymers [10], their absorption and emission spectra [7–9], and lifetimes [11]. Thus, this opens a possibility to control the polymer properties and enables the design and the syntheses of new nanomaterials with significantly improved parameters, as compared with those of pure polymer films. However, the study and applications of composite materials have been significantly limited, because of non-technological samples, which have been usually prepared in the form of a powder. Thereby, we developed a new method of preparation of new class organic/inorganic nanocomposites in a form of films with good optical quality on the base of PDHS incorporated into a SiO$_2$ porous film [16]. Their optical properties differ substantially from the properties of the composites based on PDHS embedded in the globules of mesoporous silica. The investigation of PMPS-silica and PMPS-titania hybrid thin films prepared via the sol-gel method showed that the PMPS-titania hybrid is more promising for applications in photoelectronic devices, because these hybrids have a higher photo-durability of the polymer segment and gave a relatively high-refractive index [17], as well as a higher photoconductivity [18].

Here, we present a new method of preparation of PDHS/TiO$_2$ nanocomposite films, as well as investigations of the absorption, fluorescence (FL), FL excitation spectra over a wide temperature range (15–330) K. This study revealed the characteristic peculiarities of the films of the novel nanocomposites which differ essentially from those for the polymer and nanocomposite films produced before [7, 8].

2. Experimental Technique

TiO_2 films have been prepared by the sol-gel template synthesis [19] on the basis of titanium tetraisopropoxide, which was subjected to prehydrolysis in a solution: water–ethanol–1 M HCl at pH 2. The solution of the templating agent of the triblock copolymer poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) – EO20PO70EO20 (Pluronic P123, Aldrich) in ethanol was added and stirred vigorously for 3 h. Composite films on a glass or quartz substrate were prepared by the "dip-coating" method with a constant drawing rate of 9 cm/min. Air-dry films on glass substrates were heat-treated in a muffle furnace with a programmable heating rate of 1.5 deg/min up to 350 °C. The specific surface area of the films calculated from the adsorption-desorption isotherms of hexane vapors was 816 m^2/g for the TiO_2 films. The average pore diameter calculated from the small-angle X-ray scattering spectra was about 10 nm. According to electron microscopy measurements, the films had a hexagonal pore structure.

The obtained annealed TiO_2porous films were immersed in a PDHS solution in toluene with concentrations of 10^{-4}, 10^{-3}, 10^{-2}, and 4.3×10^{-2} mol/l to incorporate polymer chains into the film pores. To establish the adsorption equilibrium, after which the absorption spectrum did not change, the optimal time was found for each solution concentration. Then the samples were washed in toluene to remove the polymer from the surface and dried to remove the solvent. Neat PDHS films on the surface of porous films were also prepared for comparison reasons, by depositing the excess PDHS solution in toluene with a concentration of 4.3×10^{-2} mol/l and drying without a subsequent washing with the solvent.

The absorption spectra of initial porous films, neat PDHS films, as well as PDHS/TiO_2 nanocomposite films, were recorded with a KSVU-23 spectrometer at room temperature. The fluorescence (FL) spectra at different temperatures were measured with an Edinburgh Instruments Fluorescence spectrometer F900 and a closed cycle liquid helium cold finger cryostat (Janis CCS-100/204) in a slow cooling regime in the temperature range 15–330 K. The samples were excited at 280 nm with a pulsed subnanosecond (750 ps) light-emitted diode (LED) at the 20-kHz pulse rate.

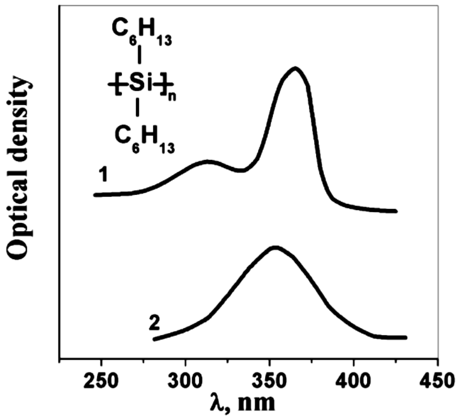

Fig. 1. Room temperature absorption spectra of neat PDHS polymer films (*1*), PDHS/TiO_2 nanocomposite film (*2*). The inset shows the structural formula of the PDHS polymer

3. Results

3.1. Optical spectra of nanocomposite films PDHS/TiO_2

Optical spectra of the PDHS/TiO_2 nanocomposite films were studied in a wide range of polymer concentrations in the toluene solution, and the temperature varied within 15–330 K. The inset to Fig. 1 shows the structural formula of the PDHS polymer.

The absorption spectrum of the neat PDHS film on quartz, obtained from a toluene solution with a concentration of 4.3×10^{-2} mol/l at room temperature, consists of two bands with maxima at 313 and 365 nm (Fig. 1, curve *1*). A PDHS film formed on the surface of porous films has an absorption spectrum, which almost coincides with its spectrum on quartz. This film was removed away from the surfaces of other samples by their washing in toluene for 15 min. The initial porous TiO_2 films have absorption band edges at 320 nm and do not contribute to the absorption of composite films at longer wavelengths [20]. The absorption spectra of nanocomposites differ substantially from the spectrum of a neat polymer film. The absorption spectrum of the PDHS/TiO_2 nanocomposite ($C = 4.3\times10^{-2}$ mol/l) consists of one very broad band with a maximum at 354 nm (Fig. 1, curve *2*), which is apparently composed of two broadened bands with maxima at 325 and 358 nm. This fact was confirmed in the study of FL excitation spectra of the composite (see below). This band shifted toward longer wavelengths by about 6 nm with increasing the adsorption time. The treatment of such a composite with toluene for 150 min resulted only in a proportional

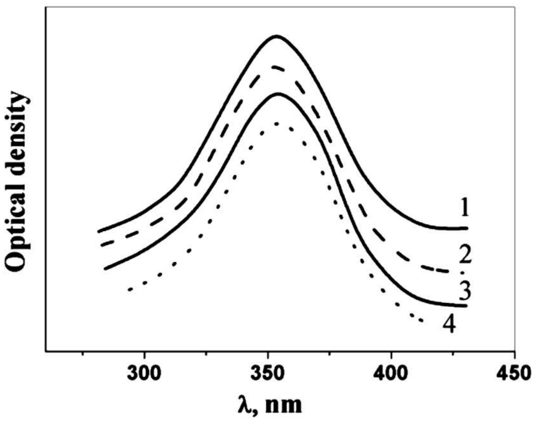

Fig. 2. Dependence of the absorption spectrum of the PDHS/TiO_2 nanocomposite on the duration of the processing in toluene: 10 (*1*), 20 (*2*), 30 (*3*), and 150 (*4*) min

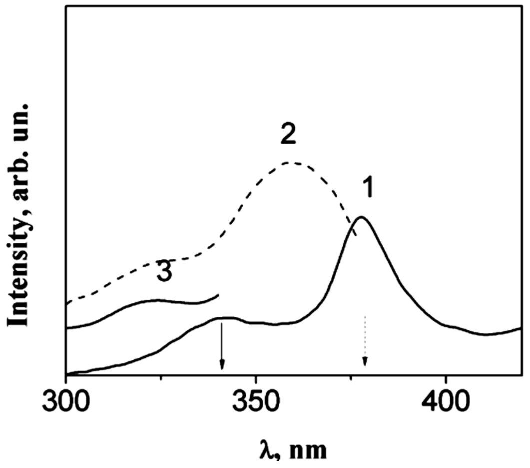

Fig. 3. Fluorescence spectra of the PDHS/TiO_2 nanocomposites at room temperature (10^{-4} mol/l, curve *1*) and FL excitation spectra under FL detection at 343 nm (curve *2*) and at 378 nm (curve *3*)

weakening of the entire absorption spectrum, by indicating a partial dissolution (Fig. 2).

Figure 3 shows the FL and FL excitation spectra of nanocomposites at room temperature. PDHS/TiO_2 composites show two FL bands at about 343 and 378 (Fig. 3, curve *1*). The FL excitation spectrum of nanocomposites reveals two absorption bands (Fig. 3 curves *2* and *3*). The absorption band at about 325 nm appears in the spectrum measured by detecting the fluorescence at λ = 343 nm. The excitation spectrum detected at λ = 378 nm exhibits an additional band at λ = 358 nm. The FL excitation bands, as well as the absorption bands of the PDHS/TiO_2 composite, are significantly broadened, however still more clearly than the absorption spectrum reveal the two absorption components.

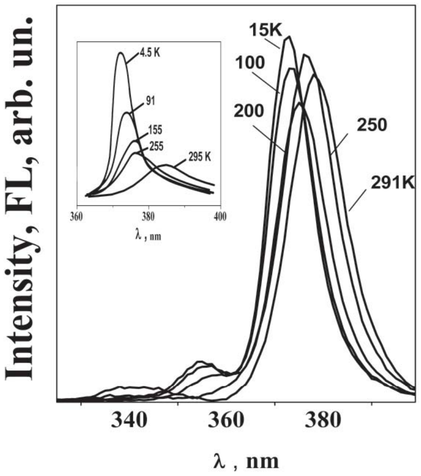

Fig. 4. Temperature dependence of the fluorescence spectra of a PDHS/TiO_2 nanocomposite film and a neat PDHS film the inset [21]

3.2. Temperature dependences of FL of PDHS/TiO_2 nanocomposites

Figure 4 shows the temperature dependences of the FL spectra of the composites under excitation at λ = 280 nm. The temperature dependence of the FL spectrum of the neat polymer film is also presented for comparison (Fig. 4) [21]. The FL spectrum of PDHS/TiO_2 nanocomposites at T = 15 K is composed of two bands: a strong band at 372 nm and a weak band at 354 nm, which appears at decreasing the concentration of the polymer in the solution to $C \sim 10^{-4}$ mol/l. With increasing the temperature, the weak band intensity decreases and disappears at 260 K. A new band at 343 nm simultaneously emerges. The temperature dependence of the amplitude of the band at 372 nm is shown in Fig. 5. It is seen from Fig. 5 that the intensity of the strong band at 372 nm shows a complex temperature dependence: its intensity slightly decreases in the temperature range 15–200 K, but its intensity significantly increases in the temperature range 200–310 K. It should be noted that the intensity of this FL band starts to decrease again at temperatures above 310 K, when a FL maximum at 343 nm increases (Fig. 6).

4. Discussion

As far as PDHS is a thermochromic polymer, the conformation of its polymer chains strongly depends on

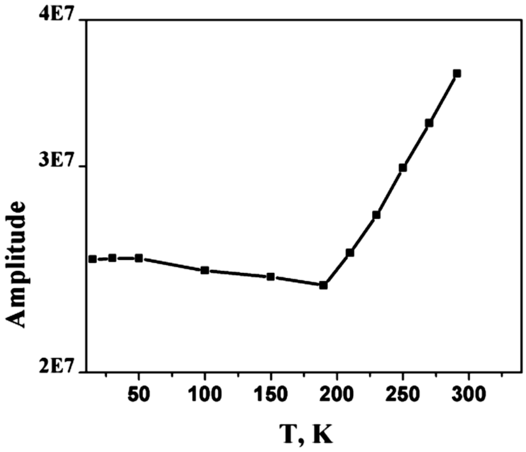

Fig. 5. Temperature dependence of the band amplitude of aggregates

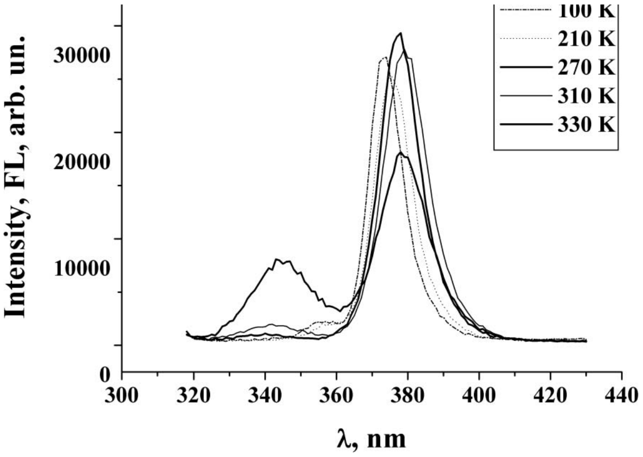

Fig. 6. Temperature dependence of the fluorescence spectrum of the PDHS/TiO_2 nanocomposite film in the region 100–310 K

the temperature. At room temperature, the polymer chains are mainly in the trans- conformation characterized by the intense absorption band peaking at 365 nm. A small fraction of segments has also a gauche conformation (more disordered) characterized by a weak broad band at 313 nm (Fig. 1, curve *1*). TiO_2 porous films are transparent in the polymer absorption region.

The absorption spectrum of PDHS/TiO_2 differs drastically from that of the PDHS film (Fig. 1, curve *2*), as well as from the absorption spectrum of the PDHS/SiO_2 nanocomposite [16]. Polymer chains are stably incorporated into substrate TiO_2 pores, so that the absorption band intensity remains even after the long-term processing by toluene (Fig. 2). This indicates that the polymer chains are indeed localized inside pores. This is supported by the fact that the polymer film, which was located on the outer surface of the TiO_2 porous films, was washed with toluene during 15 min. The temperature dependence of FL nanocomposites also confirms the localization of polymer chains inside pores. As Fig. 4 shows, it differs significantly from the analogous dependence obtained for the neat polymer film. In the case of a neat PDHS film, a significant broadening and a shift of the FL band toward longer wavelengths have been observed, together with a sharp decrease in its intensity. In the case of PDHS/TiO_2 nanocomposites, only a weak shift of the FL bands of composites toward longer wavelengths with increasing temperature was observed, and the intensity of the strongest band even increased, when sample was heated above 200 K (Fig. 4).

The most specific difference is an increase of the strong band intensity with the temperature even while heating over 200 K (Fig. 4). The intensity of this band is greater at 290 K than that at 15 K (Fig. 5). This peculiarity is more distinct in the spectra of the PDHS/TiO_2 nanocomposite as compared with the respective dependence for the PDHS/SiO_2 nanocomposite [16].

Information about the conformations of PDHS polymer chains has been obtained by the comparison of the FL spectra of nanocomposite films, neat polymer films, PDHS/SBA-15 powders as well as PDHS/SiO_2 nanocomposites. PDHS/TiO_2 nanocomposite films have similar FL bands and, hence, the same conformations of polymer chains, as in the case of PDHS/SBA-15 and PDHS/SiO_2 composites. It was demonstrated that three spatially independent polymer centers, which correspond to isolated polymer chains in the gauche- and trans-conformations, and their aggregates also are present in PDHS/TiO_2 composites. At $T = 15$ K, these centers are represented by FL at 340, 354, and 372 nm respectively. However, their relative intensities are different (Fig. 4). PDHS/TiO_2 nanocomposites have strong long wavelength FL bands assigned to aggregates. Thus, the high density of aggregate states is formed by introducing PDHS into porous TiO_2 films. This is the main difference from PDHS/SBA-15 composites. The difference observed in the absorption spectra of the PDHS/TiO_2 and PDHS/SiO_2 nanocomposites demonstrates also that the PDHS/TiO_2 polymer chains forming aggregates contribute more essentially than its chains with gauche-conformation.

The observed difference of the absorption spectra of PDHS/TiO_2 and PDHS/SiO_2 nanocomposites also shows that, for PDHS/TiO_2, the percentage contribution of the polymer chains, forming aggregates, is much higher than that of the polymer chains with the gauche-conformation.

The nature of the FL bands is also confirmed by their FL temperature dependence. The intensity of the FL band at 354 nm decreases with temperature, and it disappears completely at 260 K, while the intensity of the 343-nm band increases (Fig. 4). These temperature-induced spectral changes are typical of the trans-gauche thermochromic transition. Similar changes have been observed for PDHS/SBA-15 composites [8]. Therefore, we can unambiguously assign the FL bands at 343 and 354 nm to the gauche- and trans-conformations, respectively.

The difference between PDHS/TiO_2 and PDHS/SBA-15 composites is apparently related to the strong influence of the substrate on the structure of TiO_2 porous films [19]. The fact that one end of pores of the film is closed by a substrate can create an additional steric hindrance for the penetration of long PDHS polymer chains (the length of the polymer chain is about 50 nm and is comparable with the depth of pores). In this case, the tails of polymer chains emanating from pores can form aggregates. The interaction of the individual segments of polymer chains can lead to their organization and orientation. We can assume that these targeted segments, forming aggregates, have the *trans*-conformation, and only a small fraction of segments has the gauche-conformation at room temperature. If our assumption is correct, then an additional aggregates–*gauche* thermochromic transition should be observed for the long wavelength FL band of aggregates with increasing temperature. This was confirmed experimentally. Indeed, as the temperature increases from 293 K to 330 K, the intensity of the FL band with a maximum at 378 nm decreases, and the intensity of the FL band of the *gauche*-conformation with a maximum at 343 nm increases (Fig. 6).

A rather nontrivial temperature dependence of the FL intensity of aggregates is another interesting feature of the investigated nanocomposites (Fig. 4). Its intensity slightly decreases with temperature down to 200 K, while it increases at higher temperatures up to 310 K, when the aggregates start to disintegrate. Such unusual increase in the FL intensity of aggregates is perhaps related to the formation of an additional number of aggregates from isolated polymer chains of the trans-conformation during the *trans-gauche* thermochromic transition.

Thus, the nanocomposites are expected to be promising for their application in optoelectronic units as organic LEDs.

5. Conclusions

We focus herein on the temperature dependence of the FL of nanocomposites films based on poly(di-*n*-hexylsilane), introduced in the porous films of titanium oxides in the temperature range 15–330 K. We have proved the localization of the polymer chains in the confined size of a pore; the existence of three spatially independent centers of polymer chains in a pore and the presence of two thermochromic transitions for the *trans-gauche* and aggregates-*gauche* conformations of the polymer chains. It is shown that the characteristics of nanocomposite films PDHS/TiO_2 manifest themselves in the preferential formation of aggregates relative to other conformations of polymer chains and in an unusual increase of the intensity from aggregates in the temperature range (200–310) K, which is observed for the first time for the polymer/inorganic material nanocomposites.

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ХАРАКТЕРНІ ОПТИЧНІ ВЛАСТИВОСТІ ПЛІВОК НАНОКОМПОЗИТІВ ПОЛІСИЛАНИ/TiO$_2$

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Резюме

Розроблено технологію приготування плівок нанокомпозитів на основі кремнійорганічного полімеру полі(ді-*n*-гексілсілану), введеного в нанопори плівок діоксиду титану. Знайдено оптимальні характеристики, на основі яких виготовлено плівки нанокомпозитів та досліджено їх оптичні властивості у широкому інтервалі температур 15–330 К. Доведено, що нові плівки мають характерні особливості у порівнянні з композитами, одержаними раніше, що пов'язано з переважним утворенням агрегатів і, відповідно, з суттєвим зменшенням у полімері гош- і трансконформацій полімерних ланцюгів, а також з існуванням інтенсивної смуги ФЛ агрегатів навіть при кімнатній температурі.