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MOLECULAR SPECTROSCOPY

Photoluminescence of Liquid-Crystal Azo Derivatives in Nanopores

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Abstract—The fluorescence of the nematic liquid crystal *n*-butyl-*n'*-methoxyazoxybenzene (BMAOB) in the form of a layer and in porous glasses with pores of different diameter is investigated. The fluorescence spectra of BMAOB in a layer and in small-diameter pores differ significantly from each other. A band peaked at 475 nm is observed in the stationary spectrum of a BMAOB layer, whereas the spectrum of BMAOB in pores smaller than 4 nm in diameter contains a band peaked at 550 nm. When the pore diameter decreases to 1 nm, the band at 475 nm is almost completely suppressed and only the band at 550 nm manifests itself. It is believed that the band at 550 nm is due to the excimer luminescence of azo molecules. The fluorescence of a BMAOB layer indicates the occurrence of efficient *trans-cis* isomerization upon UV excitation. At the same time, another mechanism of phototransformation is dominant for BMAOB in porous matrices. Most likely, it is photodestruction caused by interaction of BMAOB molecules with oxygen and water bound in pores. Fluorescence of porous glasses is also revealed. Their fluorescence band shifts to shorter wavelengths with a decrease in the pore diameter. The fluorescence of porous glasses with filled pores is not detected, apparently, due to nonradiative energy transfer to BMAOB molecules. © 2004 MAIK "Nauka/Interperiodica".

The properties of organic nanocomposites are of much interest from the point of view of both basic research and practical application. This interest has increased significantly in recent years, when nanotechologies allowing production of nanoobjects with unique physical properties have been developing very rapidly. The class of organic nanocomposites under study is very wide. It includes organic media filled with nanoparticles [1], porous media containing fine-grained particles of organic materials [2], layered nanostructures [3], and many other such composites.

In this paper, we report the results of studying the photoluminescence (PL) of a system formed by a liquid crystal (LC) and a porous glass. The object and the method of study were chosen for several reasons. First, it is well known that LCs form a unique class of materials. They are characterized by intermediate phases (mesophases) in the temperature range between the solid and liquid states and combine anisotropy (typical of solid crystals) with fluidity (typical of liquids). Such materials show LC properties in both macroscopic volumes and microvolumes. At the same time, according to [4, 5], there is a certain size range in which the phase transition to the LC state becomes diffuse and some LC phases are suppressed. In our opinion, this size effect is of much interest. The second reason is related to the photochemical activity of LCs. The LC under investigation is an azoxybenzene derivative, the molecules of which undergo trans-cis isomerization upon photoexcitation. The purpose of this study is to compare the character of photoisomerization of LC molecules in a macroscopic volume and in a nanodispersed state. Since the rate of such transformations for azo derivatives is determined by the free volume of the matrix [6– 8], one might expect a change in the behavior of the reaction with a decrease in the size of dispersed LC particles. Photoluminescence spectroscopy was chosen as the main method of investigation. It is shown that, despite the weak quantum yield of the PL of azobenzene derivatives, this method can be successfully used to solve the problems stated. In addition, the PL method made it possible to reveal the luminescence of a porous glass and to investigate the behavior of the luminescence spectrum with changing pore size. The effect of the phase interaction on the PL characteristics of the LC–porous glass system is discussed.

EXPERIMENTAL

Objects of Study

Porous glasses with different pore sizes, prepared at the Institute of Technical and Macromolecular Chemistry of Martin Luther University (Halle, Germany), were used as porous matrices. Porous glasses were obtained from initial sodium borosilicate glasses by the technique described in [9]. After leaching, the sodium borosilicate phase was removed. The main component of the matrix framework with through pores is SiO₂. The average pore diameter was set by varying the leaching conditions. In our case, this parameter was 1, 4, 14, and 44 nm (samples 1, 2, 3, and 4, respectively). Plates 0.5 mm thick were cut from each treated glass sample

Parameter	Sample no.			
	1	2	3	4
Specific surface, m ² /g	349	184	83	24
Specific volume of pores, cm ³ /g	0.124	0.189	0.288	0.253
Porosity, %	21	27	39	36
Average pore diameter, nm	1	4	14	44

Some characteristics of the porous glasses under study

and ground. Characterization of matrices was performed by nitrogen absorption [9]. The thus-obtained parameters of porous glasses are listed in the table. Figure 1 shows the pore diameter distribution in sample 1. This distribution is rather narrow, which indicates a high monodispersity of pores. Before filling with the LC, porous plates were treated in toluene and annealed at 400°C for 2 h.

n-Butyl-*n*'-methoxyazoxybenzene (BMAOB) was used as an LC. It is an azoxybenzene derivative with a nematic LC phase in the temperature range 21–73°C. This material (also known as ZhK434) was produced by NIOPIK (Russia). The optical, dielectric, and viscoelastic properties of BMAOB LCs were investigated in [10]. Pores in plates were filled with the LC by immersing the plates in an LC melt (T = 80°C) and keeping them there for 3 h. After plates were extracted from the melt, their surface was carefully wiped to remove melt remnants.

Experimental Methods

The main method of study was PL spectroscopy. The stationary and time-resolved PL spectra were measured using an MDR-12 monochromator equipped with



Fig. 1. Pore diameter distribution in sample 1.

a photoadapter and a computer interface. In measuring PL spectra, the spectrometer slit width was 0.2–0.4 nm. The PL excitation was performed at a wavelength of 337.1 nm by a pulsed nitrogen laser with the following parameters: pulse width 9 ns, pulse repetition frequency 100 Hz, and pulse power 5 kW. To record the kinetics and the time-resolved PL spectra, we used a sampling system with a time window of 0.1 ns [11, 12]. This system made it possible to record PL spectra with different time delays with respect to the laser pulse. During recording of the PL spectra, the time resolution of the system did not exceed 0.7 ns. In this case, it was determined by the slope of the leading edge of the laser pulse. During recording of the PL kinetics, the time resolution was determined by the oscilloscope gate (0.1 ns).

The PL spectra were investigated at 300 and 77 K. In order to avoid a photochemical effect of the laser pulse on the LC during the measurements, the laser beam was defocused in the sample plane to a diameter of 8 mm. In addition, the samples were exposed only for short times.

The UV absorption spectra of unirradiated and irradiated LC layers were measured using an Ocean Optics spectrometer (United States). The samples were exposed to UV radiation (365 nm) of a DRSh-500 mercury lamp.

RESULTS AND DISCUSSION

PL Spectra of Porous Glasses

Before considering the PL of the LC-porous glass system, we will report the luminescence characteristics of the components of this system-porous glasses and an LC (in the form of a layer). It was found that porous glasses fluoresce and the intensity of their PL is sufficient to perform measurements. The corresponding PL spectra are shown in Fig. 2. With a decrease in the pore diameter, the emission band shifts to shorter wavelengths. The blue shift for the sample with d = 1 nm, as compared to the sample with d = 14 nm, is as high as $\Delta\lambda \approx 20$ nm. Since this effect is observed for pore diameters close to 1 nm, it may have a quantum-mechanical nature, as in the case of porous Si [13]. Unfortunately, the set of porous matrices we have to date is insufficiently complete to investigate more carefully the PL shift as a function of the pore diameter.



Fig. 2. (1) Time-resolved and (2–4) stationary fluorescence spectra of porous glasses with different pore diameters *d* at T = 300 K. (1) d = 1, 4, 14 nm; $t_d = 1$ ns; (2) d = 1 nm; (3) d = 4 nm; (4) d = 14 nm.

The time-resolved PL spectra of porous matrices measured with a short delay ($t_d = 1$ ns) were almost independent of the pore diameter (Fig. 2, curve 1). A band peaked at 410 nm is pronounced. The PL lifetime at the maximum of this band is 2.5 ns. This lifetime somewhat increases at long PL wavelengths, due to which the stationary PL spectra (Fig. 2, curves 2–4) shift to longer wavelengths.

Absorption and PL Spectra of a BMAOB Layer

Figure 3 (curve 1) shows the absorption spectrum of a BMAOB LC layer 1 µm thick in an optical quartz cell. A strong band at 345 nm is pronounced. Under UV irradiation ($\lambda = 365$ nm), a decrease in the intensity of this band is observed with the simultaneous appearance of a band peaked at 275 nm and an increase in the absorption in the long-wavelength wing of the spectrum (Fig. 3, curves 2, 3). Such changes are in good agreement with the mechanism of *trans-cis* isomerization, which is the main photochemical mechanism for azoxybenzene derivatives [14, 15]. As in the case of other materials of this class, the band at 345 nm can be assigned to the $\pi\pi^*$ absorption of BMAOB *trans* isomers, which dominate at room temperature. At the same time, the band at 275 nm is due to the $\pi\pi^*$ absorption of *cis* isomers. The increase in the absorption in the wing of the spectrum is related to the increase in the $n\pi^*$ absorption band of the *cis* isomers, which are characterized by a stronger absorption in this spectral region in comparison with *trans* isomers. The absence of fine structure in the long-wavelength absorption region is related to the strong overlap of the $n\pi^*$ bands of the *trans* and *cis* isomers.

Due to the high efficiency of *trans-cis* photoisomerization, the PL quantum yield of azo derivatives is



Fig. 3. UV absorption spectra of a BMAOB LC layer (*I*) before and (2, 3) after irradiation with UV light with $\lambda = 365$ nm. Parameters of irradiation: (2) 10 mW/cm², 10 min; (3) 50 mW/cm², 25 min.

rather low. However, in the case under study, it was sufficient to carry out measurements. Apparently, during nonradiative relaxation, an excited BMAOB molecule passes to the lowest state ${}^{1}(n,\pi^{*})$, from which (with a certain probability) emission occurs. The measurements of the stationary PL spectra (with a nanosecond time resolution) and the PL kinetics showed that the radiative processes in the samples under investigation occur in nano- and subnanosecond time intervals.

The PL spectra of BMAOB in an optical cell 6 um thick are shown in Fig. 4. Spectra 1-3 and 5 correspond to the LC state at 300 K and spectrum 4 corresponds to a solid crystalline state at 77 K. In the stationary PL spectrum (curve 1), which covers the entire emission time, a wide band peaked at 475 nm and a weak shoulder at 500 nm are observed. When measured at the maximum of the band at 475 nm, the PL lifetime is 1.1 ns. In recording of spectra with different time resolution, the position of the PL peaks changes. With an increase in t_d from 0.7 (curve 2) to 4 ns (curve 3), the spectrum extends to longer wavelengths. In the stationary spectrum, the PL maximum is at 475 nm, as compared with 460 nm for the spectra recorded with $t_d = 0.7$ ns. The PL spectra of BMAOB molecules in the solid crystalline state, both stationary (curve 4) and measured with nanosecond resolution, contain a new band at 503 nm, which is not observed in the LC phase. This band can be attributed to the luminescence of *trans* isomers since, in the solid crystalline state, *trans-cis* transitions are spatially hindered at low temperatures and the concentration of *cis* isomers is negligible. As can be seen from Fig. 4, the PL intensity in the solid crystalline state is higher than in the LC phase. We may suggest that BMAOB trans isomers have a flattened form at 77 K, as do azobenzene molecules [15]. Due to the spa-



Fig. 4. PL spectra of a BMAOB layer: (1) stationary spectrum at T = 300 K, (2) time-resolved ($t_d = 0.7$ ns) spectrum at T = 300 K, (3) time-resolved ($t_d = 4$ ns) spectrum at T = 300 K, (4) stationary spectrum at T = 77 K, and (5) stationary spectrum after UV irradiation ($\lambda = 365$ nm, I = 8 mW/cm²).





Fig. 5. Stationary PL spectra of BMAOB in porous glasses with different pore diameters. T = (1-4) 300 and (5) 77 K. d = (1) 44, (2) 14, (3) 4, (4) 1, and (5) 4 nm.

tial hindrance in the solid crystalline phase, the form of the molecules should not change significantly upon excitation. Therefore, it is most likely that the band at 503 nm is due to the luminescence of flattened *trans* isomers from the lowest ${}^{1}(n,\pi^{*})$ state. The band at 475 nm, which manifests itself as a weak shoulder at 77 K and is the main emission band in the LC phase, is, apparently, due to the intermediate conformation of excited *trans* isomers. To measure the PL spectrum of *cis* isomers, the BMAOB LC layer was exposed to UV irradiation at the wavelength $\lambda = 365$ nm for 0.5 h. A DRSh-500 mercury lamp equipped with a filter was used as a UV source. Only the band at 440 nm was observed in the PL spectrum of the irradiated LC layer (Fig. 4, curve 5). Since, according to Fig. 3, long-term irradiation at $\lambda = 365$ nm leads to the transition of almost all BMAOB molecules from the *trans* to the *cis* form, it is more reasonable to attribute the PL band at 400 nm to the luminescence of *cis* isomers from the ¹(n,π^*) state. After the irradiation, the PL lifetime in the band at 440 nm is shorter than 0.1 ns. Thus, the lifetime of the excited state of *cis* isomers (1.1 ns).

PL Spectra of BMAOB in Porous Glasses

The PL spectra of BMAOB in porous glasses are shown in Fig. 5. The spectrum of BMAOB in a porous glass with a pore diameter of 44 nm (curve 1) almost coincides with the spectrum of a BMAOB layer (Fig. 4, curve 1). The same situation is observed for BMAOB in porous glasses with a pore diameter of 14 nm (curve 2). The PL lifetime in the strongest band, at 475 nm, is 1.9 ns, which is comparable with the corresponding value for a BMAOB layer. This result indicates that BMAOB retains its bulk properties in pores larger than 10 nm in diameter. In contrast to this, the band at 475 nm is almost suppressed and a new strong band at 550 nm arises in the PL spectrum of the samples with a pore diameter of 1 nm (curve 4). The spectrum of the samples with a pore diameter of 4 nm is intermediate: the PL spectrum contains both the band at 475 nm and the band at 550 nm (curve 3). The significant difference between the PL spectrum of the LC BMAOB in pores of small diameter ($d \le 4$ nm) and the spectrum of the LC in a macroscopic volume may be caused by the suppression of the LC phase. This may occur due to the increase in the fraction of LC molecules that are in contact with pore walls. Efficient interaction with the matrix, for example, due to the formation of hydrogen bonds [16], may lead to freezing of molecular motions and transition of the LC to a qualitatively different thermodynamic state. Calorimetric investigations performed for other LCs in this range of pore diameters showed that the transition of the first kind from a nematic to an isotropic liquid is suppressed. Instead of this, a diffuse transition is observed (similar to a vitrification transition), which accounts for the evolution of the local orientational order [4, 5].

The significant bathochromic shift of the PL band can be explained by several reasons. First, this may be related to the formation of complexes with charge transfer between the BMAOB molecules adsorbed by the pore walls and unabsorbed BMAOB molecules. However, this process should also manifest itself in a significant bathochromic shift of the absorption spectrum of BMAOB in pores, which is not observed experimentally. Second, the appearance of a band in the longwavelength region may be related to excimer lumines-



Fig. 6. Stationary fluorescence spectra of the LC BMAOB in a porous glass with d = 1 nm (1, 2) and in a layer (3, 4) before (1, 3) and after (2, 4) UV irradiation $(\lambda = 365$ nm, I = 8 mW/cm²).

cence [17]. Indeed, the close packing of BMAOB molecules in pores with partial overlap of benzene rings may result in the formation of predimer states, excitation of which gives rise to excimer PL. The suppression of the band at 475 nm may be related to the presence of a potential barrier between the monomeric and excimer states, due to which the luminescence occurs predominantly from the excimer state.

Figure 5 (curve 5) also shows the PL spectrum of BMAOB in pores with a diameter of 4 nm at T = 77 K. It almost coincides with the spectrum of a BMAOB layer at the same temperature (Fig. 4, curve 5). This indicates that the location of BMAOB in pores does not prevent it from crystallization, which is accompanied by transitions of BMAOB molecules to a more flattened conformation.

In summary, we should note that the luminescence band of porous glass (Fig. 2) in the samples filled with BMAOB was observed very poorly if at all. The PL quenching in a porous matrix may be due to efficient energy transfer from the matrix to BMAOB molecules.

PL Spectra of BMAOB in Porous Glasses after UV Irradiation

Figure 6 shows the spectra of BMAOB in a porous glass (d = 1 nm) before (curve 1) and after (curve 2) UV irradiation. Irradiation by a mercury lamp (365 nm) and a nitrogen laser (337.1 nm) led to the same spectral changes. For comparison, the PL spectrum of a BMAOB layer before (curve 3) and after (curve 4) irradiation is also shown in Fig. 6. The results show the difference in the character of the spectral changes in macroscopic volumes and nanovolumes of BMAOB. A hypsochromic shift is observed in a macroscopic vol-

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ume, which, as was noted above, can be explained by the trans-cis isomerization of BMAOB molecules. At the same time, a bathochromic shift of the PL band is observed in a nanovolume. This shift is accompanied by a pronounced photochromic effect, which makes it possible to implement nonlinear optical recording in such media [18, 19]. The results of measurement of the PL of BMAOB in porous glasses indicate that the efficiency of *trans-cis* isomerization in pores of small diameter may be weak due to the decrease in the free volume [7, 8]. The efficiency of *trans-cis* photoisomerization in pores can also be reduced by other photochemical reactions. In our opinion, the most likely is photodestruction caused by the interaction of BMAOB molecules with the oxygen and water bound in pores [20].

CONCLUSIONS

The obtained results demonstrate the efficiency of the PL method for comparative analysis of the properties of LCs in macroscopic volumes and nanovolumes. The results obtained by this method are in good agreement with the results of calorimetric [4, 5, 21], NMR [5], dielectric [22], and other measurements indicating qualitative changes in the properties of LCs on going to volumes smaller than 10 nm in size. Such a transition, as well as the transient region, manifests itself in the occurrence of a new PL band at longer wavelengths. This band may be related to excimer luminescence, which arises due to the freezing of molecular motions and the formation of predimer states. The PL measurements confirm the earlier conclusion [18, 19] that the main mechanism of phototransformations in pores differs from the *trans-cis* isomerization (which is dominant in macroscopic volumes). Most likely, this mechanism is photodestruction.

As in the case of porous Si [13], intrinsic luminescence of porous glasses is revealed. Its intensity is much lower than that of porous Si but is comparable with the luminescence intensity of BMAOB molecules. A nanosize effect is found, which consists in a hypsochromic shift of the PL band of a porous glass with a decrease in the pore diameter.

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