ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 2, pp. 381–385. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © S.Yu. Marfin, E.V. Rumyantsev, S.L. Yutanova, E.V. Antina, 2013, published in Zhurnal Obshchei Khimii, 2013, Vol. 83, No. 2, pp. 326–330.

Spectral and Photophysical Properties, Photo and Heat Resistance of Dipyrrolylmethene Borofluoride Complex and Its Hybrid Material with Polymethylmethacrylate

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Received December 12, 2011

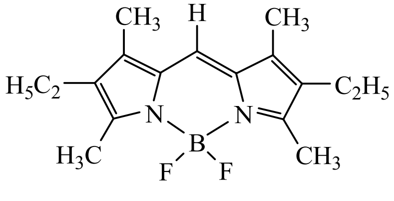
Abstract—A hybrid material based on polymethylmethacrylate with immobilized borofluoride dipyrrolylmethene complex. The inclusion of the chromophore in the polymer environment is shown to result in a reduced polarization due to the weakening of the forces of intermolecular interactions. Study of spectral properties, photo and thermal stability showed that inclusion of the complex in the polymer matrix can significantly increase the photo and thermal stability and mechanical strength of the material while preserving the spectral characteristics inherent to the individual compound.

DOI: 10.1134/S1070363213020242

Among the numerous dipyrrolylmethene derivatives and complexes, borfluoride complexes (Bodipy) are now actively studied. By spectral properties they are superior to the known dyes of the other chemical groups, due, among other, to the possibility of adjustment of their spectral characteristics by changing the intermolecular interaction nature and energy [1]. In this connection, the range of application of Bodipy is extremely wide: they are actively studied as restrictors of intense laser radiation, photosensitizers, fluorescent tags and sensors for cations and anions in analytical chemistry, high-intensity tags for the cancer cells, as well as precursors in the synthesis of functional supramolecular systems [2–4]. However, like most organic dyes, the compounds are not enough stable and undergo decomposition due to various physicochemical factors. The challenge to increase the stability of these chromophores in the compositions of the hybrid materials based on the matrices of organic or inorganic origin is very topical.

As a matrix for the hybrid materials inorganic and organic-inorganic polymer (silicon and titanium oxides and related derivatives) are used [5, 6]. In contrast to inorganic matrices, organic polymers are capable of providing extremely high optical homogeneity of the medium, transparency, and ease of processing the material [7]. At the present time thin films doped with dyes are used with better characteristics compared to solutions (nonvolatile, nonflammable, nontoxic, compact, mechanically strong) [8].

In this study we obtained hybrid materials based on poly(methylmetacrylate) and borfluoride complex of 2,4,8,10-tetramethyl-3,9-diethyldipyrrolylmethene-5,7 (Bodipy), investigated their spectroscopic and photophysical properties, as well as their photo and thermal stability.



Bodipy

The film type hybrid materials were prepared from polymethylmethacrylate and Bodipy by co-deposition from an organic solvent. To this end, 3 ml of Bodipy in benzene (concentration of dye was varied from 1×10^{-3}

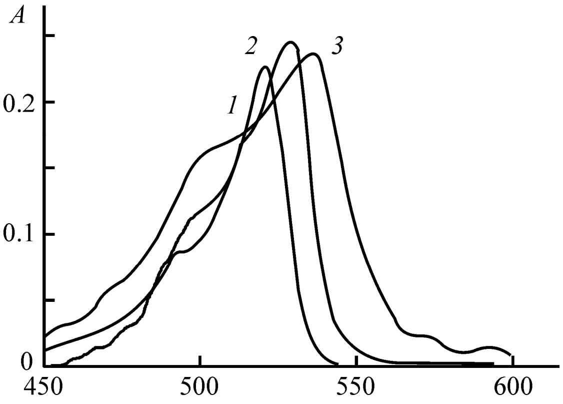


Fig. 1. EAS of Bodipy: (*1*) in a polymethylmethacrylate matrix, (*2*) in benzene, and (*3*) solid Bodipy.

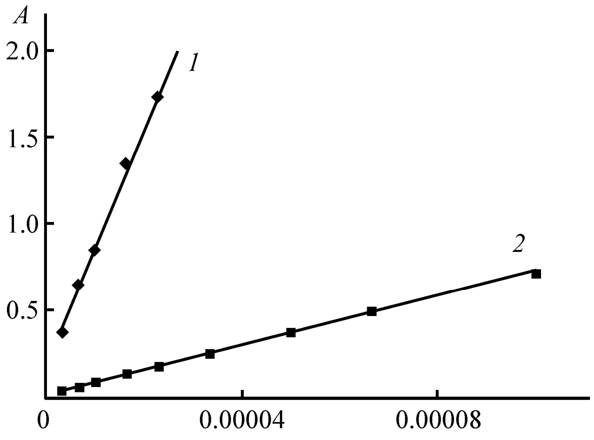


Fig. 2. The dependence of optical density of the hybrid material on the Bodipy concentration: (*1*) at the wavelength 524 nm (R^2 = 0.997), (*2*) at the wavelength 373 nm (R^2 = 0.999).

to 3.33×10^{-6} M) was added to 0.01 g of polymethylmethacrylate, and the mixture was heated at permanent stirring until a complete dissolution. The mixture was applied onto a glass substrate, dried first for 1 h at room temperature and then at 80ºC in a vacuum. The materials obtained are uniformly colored thin films.

The electron absorption spectra (EAS) of the Bodipy solutions in benzene (Fig. 1, Table 1) contain a strong peak at ~530 nm (log ε = 4.95) corresponding to the S_0–S_1 electron transfer, and a low-intensity band in the near-UV region at ~370 nm (log ε = 3.90) corresponding to the charge transfer [1]. The Bodipy film based on polymethylmethacrylate and individual Bodipy film obtained by deposition on a glass substrate from the solution show similar EAS, but changes in the position of the maxima are observed. The long-wavelength absorption maximum of the hybrid material based on polymethylmethacrylate suffered a blue shift by 10 nm compared with the benzene solution, and by 13 nm compared with the solid substance. Thus, the incorporation of Bodipy chromophore in the polymeric environment leads to a decrease in the polarization, that is, to weakening of intermolecular interactions.

Table 1. Spectral characteristics of Bodipy and 2,4,6,8,10-pentamethyl-3,9-diethyldipyrrolylmetenate-5,7 boron(III) difluoride (RM567)

System	λ_{abs}, nm	λ_{fl}, nm	Δλ, nm[a]
Bodipy/benzene	534	540	6
RM567/benzene[b]	522.7	536.4	13.7
Bodipy/polymethylmethacrylate	524	538	14
RM567/polymethylmethacrylate[b]	518.5	543.2	24.7

[a] Hypsochromic shift of the absorption maximum. [b] [11].

We have determined the concentration dependence of the absorption and fluorescence characteristics of the hybrid materials. The nature of EAS of the films does not vary at varying the dye content from 1×10^{-3} to 1.67×10^{-6} M (in the original mixture before drying). We observed a linear dependence of the optical density at the absorption maximum on the Bodipy concentration (Fig. 2), which indicates the existence of only one chemical form of the compound in this range, as well as the uniform distribution of the dye in the bulk polymer matrix. It should be noted that the association of organic dye of rhodamine group is observed at 4×10^{-5} M [9], which leads to quenching of fluorescence in concentrated solutions. Thus, for Bodipy this range is extended to higher concentrations of dye in the solution.

The Bodipy fluorescence spectra are "mirror" reflections of their absorption spectra (Fig. 3). The spectra do not depend on the wavelength of the excitation light, that is, the fluorescence occurs from the lowest vibrational sublevel of the S_1 excited state. The spectra depend on the Bodipy concentration in the solutions: an increase in concentration leads to a shift of the emission maximum to longer wavelengths with a simultaneous decrease in intensity. This relationship is different in the cases of solution and polymer film. At low chromophore concentration the red shift is

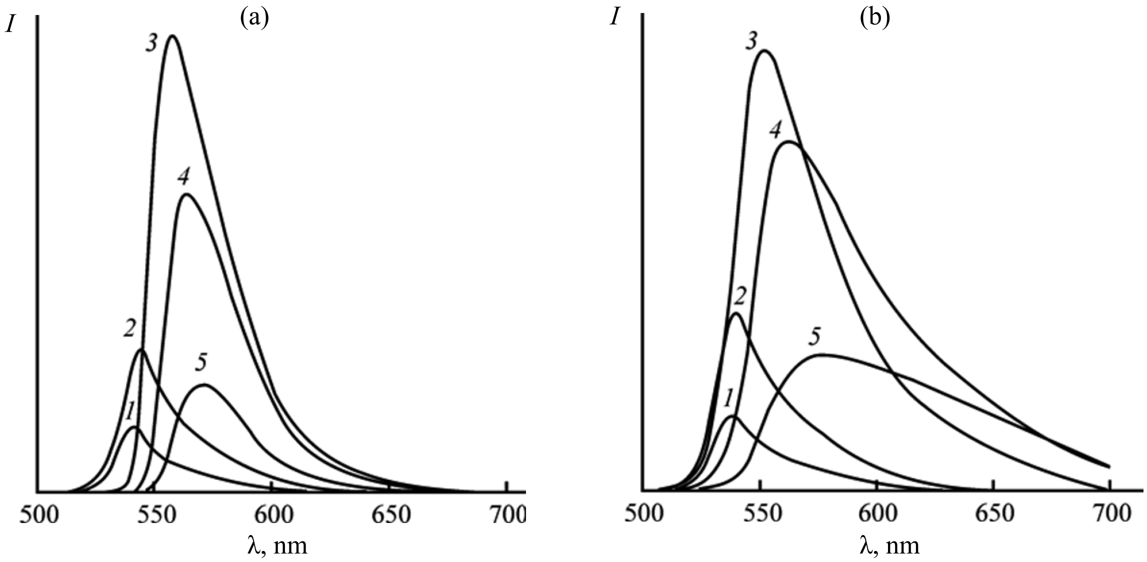


Fig. 3. The fluorescence spectra of the Bodipy: (a) solutions in benzene, (b) polymethylmethacrylate film (b), *c*, M: 3.33×10^{-6} (*1*), 1×10^{-5} (*2*), 1×10^{-4} (*3*), 3.33×10^{-4} (*4*), 6.67×10^{-4} (*5*).

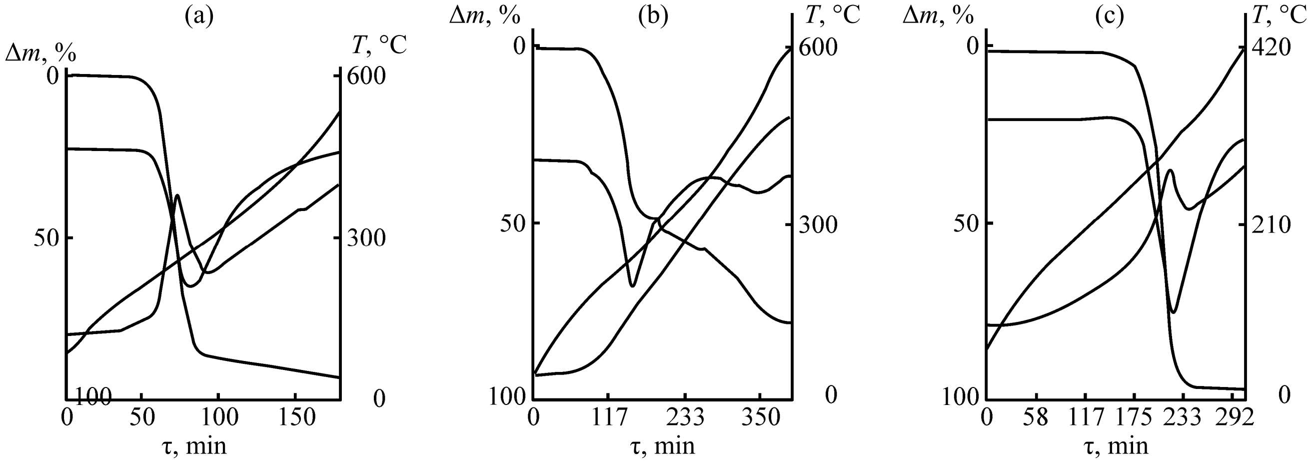


Fig. 4. Derivatograms of the samples: (a) polymethylmethacrylate film, (b) Bodipy film; (c) Film of Bodipy in polymethylmethacrylate, $c = 1\times10^{-3}$ M.

more pronounced in the solution, but at higher concentrations the same occurs in the polymer film. The increased contribution of long-wavelength emission is due to the light reabsorption [10], that is, repeated absorption of a quantum of light emitted by the molecule. With increasing concentration of the solutions the area of overlapping absorption and fluorescence spectra increases, and this effect becomes more pronounced. It should be noted that the effect of reabsorption of light is more pronounced in the case of the hybrid material compared with the solution in benzene.

The analyzed changes in the spectral characteristics of hybrid materials in comparison with individual Bodipy are in good agreement with literature data [11] (Table 1).

The results of differential thermal analysis in the atmospheric air showed a significant increase in thermal stability of hybrid materials in comparison with the individual components. The onset temperature of the thermal degradation of the hybrid material containing 1×10^{-5} M of Bodipy is by 36 and 49°C higher compared with the individual polymethyl-

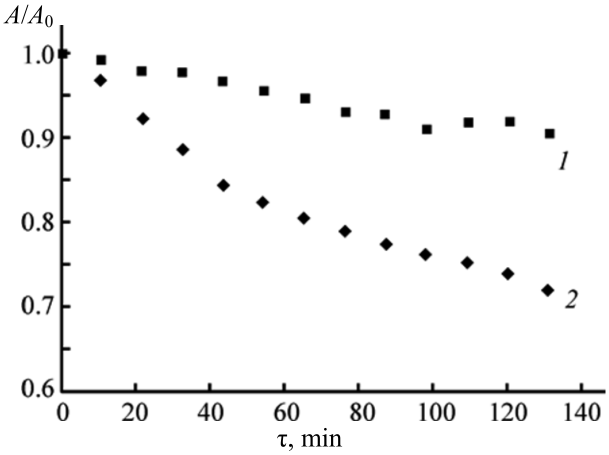


Fig. 5. The dependence of the reduced optical density of the Bodipy solution at 534 (524) nm in the polymethylmethacrylate matrix (*1*) and benzene (*2*) on the irradiation time.

methacrylate and Bodipy, respectively (Fig. 4, Table. 2). The maximum increase in thermal stability exhibits the material with maximum content of Bodipy. With decreasing content of Bodipy the thermal stability of materials is reduced. Apparently, the increase in the Bodipy concentration in the polymethylmethacrylate matrix increases the onset temperature of thermal degradation, which appears to be associated with the strengthening of the spatial structural organization of the hybrid material. For all studied samples of polymer films the thermooxidative destruction proceeds in one stage with the release or absorption of heat till the complete loss of the sample weight [12]. The stages of degradation of polymethylmethacrylate and Bodipy are indistinguishable in the derivatograms, which indicates a high structural strength of the material.

Further the analysis was performed of the influence of the polymer environment on the quantitative characteristics of the Bodipy photostability. For this purpose the change in optical density was measured of benzene solution of Bodipy or hybrid material based on polymethylmethacrylate as a function of the irradiation time of the samples by the integrated light. The data obtained (Fig. 5) show increased photostability of Bodipy in the hybrid material: within 2 h the relative decrease in absorbance of a solution with Bodipy is 28%, and for the hybrid material, 10%. Thus, the inclusion of Bodipy in the polymer matrix increases the complex photostability. The photodecomposition process of both the Bodipy solution and the hybrid material based on it proceeds to the formation of monopyrrole products, as shows the increase in the intensity of the absorption bands in the far region of the UV spectrum [13].

Table 2. The results of differential thermal analysis of polymethylmethacrylate, Bodipy,and the hybrid materials based on them (t_{onset}, t_{end}, t_{eff} are the onset and end of destruction temperatures, and exo- or endothermic effects, respectively)

Образец	t±1.6°C		
	t_{onset}	t_{end}	t_{ef}
Polymethylmethacrylate	193.3	263.3	234.3
Bodipy	179.8	567.9	167.7
Polymethylmethacrylate–Bodipy (1×10^{-5} M)	228.9	310.5	275.7
Polymethylmethacrylate–Bodipy (1×10^{-4} M)	244.5	326.9	295.3
Polymethylmethacrylate–Bodipy (1×10^{-3} M)	250.9	326.6	275.7

The results obtained show a principal possibility of using hybrid materials based on Bodipy and organic polymer matrices for solving practical problems. The inclusion of the complex into the polymer matrix can significantly increase the photo and thermal stability, as well as the mechanical strength of the material while the spectral characteristics inherent to the individual compound are preserved.

EXPERIMENTAL

2,4,8,10-Tetramethyl-3,9-diethyldipyrrolylmetenate-5,7 boron(III) difluoride was synthesized, purified and identified according to the procedures given in [14].

The organic solvent, benzene of chemically pure grade, was purified by common procedure [15], the residual water content (< 0.02%) was determined by the method of Fisher.

Polymethylmethacrylate (molecular weight 3.5×10^4 g mol^{-1}), obtained by suspension polymerization, was purified by common methods [16].

The electron absorption spectra (EAS) were recorded in the range 350–800 nm on a SF-104 spectrophotometer (“Aquilon,” Russia) equipped with a holder for solid samples controlled with a PC using the software package “UVWin 5.1.” The fluorescence spectra were recorded in the ranges 500–700 nm, on a SM2230 spectrofluorimeter (“Solar,” Belarus), controlled with a PC. When registering the fluorescence spectra, the sample was illuminated at its center, the monochromator and detector (slit width 2.5 nm) were positioned at an angle of 45° relative to each other. To determine the fluorescence characteristics the light with a wavelength 480 nm was used.

Studies of the thermal stability were carried out on a 1000D derivatograph (MOM, Hungary) in a static air atmosphere, in a non-isothermal mode, the heating rate 1.25 deg min^{-1} in the range 21–600°C. The signals registered by the instrument (*T*, the temperature curve; TG, the curve of the change in the sample weight in time under the influence of temperature, DTG, the differential curve of the rate of change in weight, and DTA, the curve of differential thermal analysis of the sample) were processed with the software complex "PowerGraph."

The study of photodegradation of the dye was carried out by irradiating the hybrid material film or the dye solution with the integral polarized light from an incandescent lamp. The destruction of the complex was assessed by measuring the magnitude of the decrease in the optical density at a wavelength corresponding to the maximum absorption.

ACKNOWLEDGMENTS

This work was supported by the grant of the President of Russian Federation for young Russian scientists, Candidates of sciences (project MK-401.2011.3 number), and the Federal Target Program "Scientific and scientific-pedagogical personnel of innovative Russia" for 2009–2013 (State Contract no. 14.740.11.0617).

The study was supported by the Ministry of education and science of Russian Federation, project no. 14.132.21.1448.

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