Formation and study of thin films of *tert*-butyl-substituted thiopyrylium dyes

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The formation of thin films of symmetrical and asymmetrical thiopyrylium dyes, containing *tert*-butyl substituents, on glass supports was studied. The films were deposited by centrifugation of solutions of individual dyes or dye—polymer [poly(methyl methacrylate)] compositions. The dye : polymer ratios necessary for the formation of WORM recording layers based on these dyes were determined. The use of a polymeric matrix increases the film thickness and optical density but decreases its reflection power and does not allow crystallization of the dye on the support to be completely avoided. An increase in the number of *tert*-butyl groups in the dye molecule prevents crystallization of the recording layer in the case of symmetrical dye molecules, but does not prevent it for asymmetrical molecules. The data obtained were interpreted in terms of geometrical views on the interaction of dye molecules in thin layers.

Key words: thiopyrylium dyes, *tert*-butyl substituents, thin films; electronic absorption spectra; structure of layers; intermolecular interactions.

Thin films based on organic dyes are used in semiconductor devices for converting light energy into electric energy,[1] as layers for light conversion in nonlinear optics,[2] and as sensitive layers in optical disks of read-only memory (WORM).[3] In the latter case, semiconductor lasers and diodes emitting at wavelengths of 600—900 nm are used as the sources of radiation for information recording and reading-out in practical devices (read-only record accumulators). Dyes possessing intense absorption in the above-mentioned spectral range and relatively high thermal and photochemical stabilities are promising materials for this purpose.

The recording layers of optical disks are thin (50—200 nm), amorphous, time-invariant films with an optical-quality surface. The most technologically efficient way for depositing them onto a support is centrifugation of solutions of the dyes in organic solvents. One of the factors hampering the preparation of amorphous films is crystallization of the dye on the disk surface, which occurs upon evaporation of the solvent during the film deposition, when a supersaturation concentration is attained on the support surface. The microcrystals of the dye thus formed cause increased light scattering by the film and, hence, decrease the "signal-to-noise" ratio.[4,5]

Good properties in disk recording have been exhibited by pyrylo- and thiopyrylocyanines with relatively short polymethine chains which intensely absorb in the near IR region.[3] However, a drawback of these compounds is their poor solubility in organic media and tendency for crystallization. The introduction of bulky *tert*-butyl groups into molecules of these dyes could increase their solubility and facilitate the formation of recording layers by centrifugation.[3] In previous studies,[6,7] we synthesized a number of new dyes, 6-*tert*-butylthioflavylium derivatives, possessing intense absorption ($\varepsilon \sim 10^5$ mol^{-1} cm^{-1}) in the 680—880 nm range and good stability to light, and started an investigation of polymeric layers based on them.

In this work, we studied film formation and crystallization during the centrifugation of solutions of 1-benzothiopyrylium dyes, namely, symmetrical dyes 1a,b and styryl dyes 2a—d, containing different numbers (from 1 to 4) of *tert*-butyl groups in their molecules.

Experimental

Dye films were obtained on purified glass or silicon supports with dimensions 20×25 mm by centrifugation at rotation velocities of 1000—3000 min^{-1}. Silicon plates were used as supports to enhance the ellipsometric contrast (the ratio of the refraction indices of the support and the working layer) for the determination of the layer thickness by ellipsometry. The Langmuir—Blodgett films of dye **1b** were obtained by vertical transfer at 20 °C and a surface pressure of 16 nM m^{-1}. Deionized water served as the subphase.

The thicknesses (d) of thin films were measured by an LEF-2M ellipsometer and an MII-11 interferometer. To solve more correctly the reverse problem in order to determine d, the ellipsometric angles Δ and ψ were measured at three different angles of incidence of the 632.8 nm laser radiation (60°, 70°, 75°).[8,9] To carry out interferometeric measurements,

1a,b

2a—d
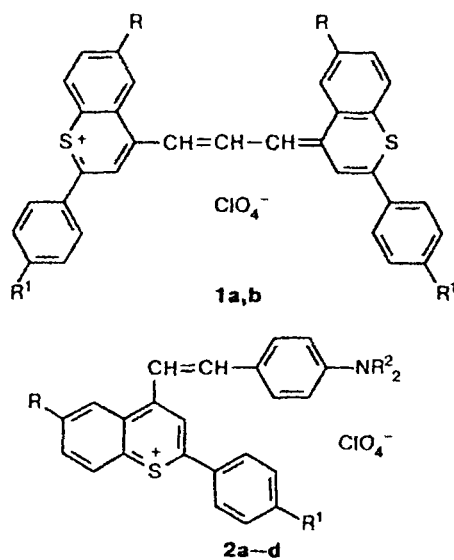
	R	R^1	R^2
Ia	Bu$^+$	H	
Ib	Bu$^+$	Bu$^+$	
2a	Bu$^+$	H	Me
2b	Bu$^+$	H	Et
2c	Bu$^+$	Bu$^+$	Me
2d	Bu$^+$	Bu$^+$	Et

a 600 Å-thick layer of aluminum was sprayed onto a dye film with paths drawn on it. The relative error of determination was 10%.

The formation of microcrystals in the film was monitored visually using an NU-E optical microscope (Karl Zeiss, Jena) at a magnification of 750 power. The absorption spectra of solutions of the dyes and dye films in the 350—800 nm range were recorded on a Specord-M40 spectrophotometer; those in the 800—1000 nm range were measured on an LSVU-12 spectral complex optically connected to a microscope. Thus, the measurements were carried out at the section of the film surface that was directly observed in the microscope. The reflection factors of films were measured in relation to the reflection of a 1000 Å-thick aluminum mirror sprayed onto a silicon plate.

Results and Discussion

One way of preventing crystallization of a dye in a film is introduction of a polymeric binding agent into the initial composition.[6] Polymer chains prevent the dye molecules from approaching one another, when the layer dries out, and stabilize the dye film. The efficiency of this method depends on the polymer : dye ratio. The introduction of a polymer into a composition increases the viscosity of the solution and results in thicker layers.[10]

The dependence of the layer thickness on the content of the polymer was elucidated for the Ib—poly(methyl methacrylate) (PMMA) composition by
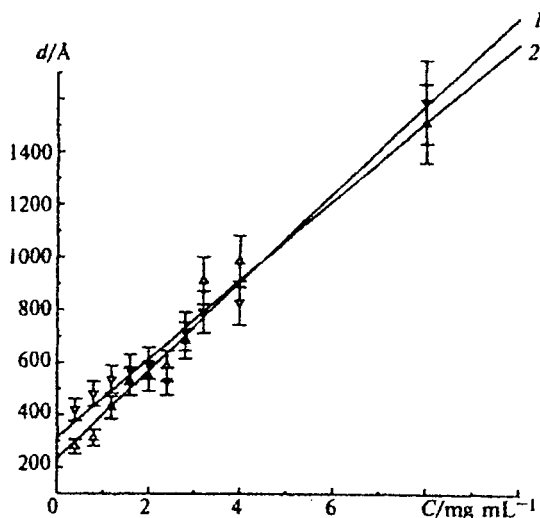
Fig. 1. Dependence of the thickness (*d*) of dye—polymer layers on glass (*1*) and silicon (*2*) supports on the polymer concentration at a constant dye concentration (4 mg mL^{-1}).

ellipsometric determination of the thicknesses of layers obtained with various concentrations of the polymer and an invariant concentration of the dye. The resulting dependences for glass- and silicon-supported films are presented in Fig. 1. It can be seen that the film thickness increases proportionally to the content of the polymer in the composition. The thickness of a working layer suitable for recording of information by a laser beam is restricted by the power input of the existing semicon-
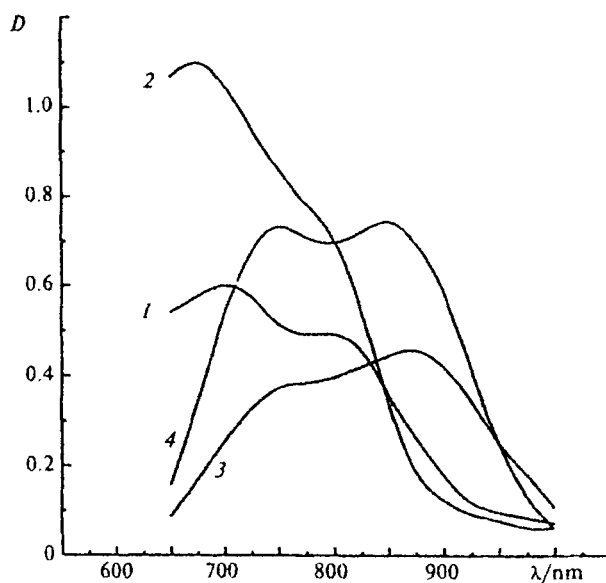

Fig. 2. Variation of the absorption spectra of films of dyes **2b** (*1*, *2*) and **Ib** (*3*, *4*) upon the addition of PMMA: *1*, *3*, films of an individual dye; *2*, *4*, dye **2b** : PMMA = 1 : 0.5 and dye **Ib** : PMMA = 1 : 1 films.

ductor lasers and lies in the 60—150 nm range with an optimal value of 120 nm.[11] In this particular case, the acceptable thickness range corresponds to a polymer concentration of 2—8 mg mL^{-1}; this leads to dye : polymer working ratios of 1 : 1—1 : 0.5 for typical values of solubility of the dye. When the concentration of the polymer increases, the optical density of the layer does not increase, since the dye is proportionally diluted with the polymer; however, it is still higher than the optical density of a film of pure dye obtained from a solution of the same concentration (Fig. 2).

When the polymer is added to the initial dye solution, the reflection power of the film decreases (Fig. 3). Dilution of the dye with the polymer decreases the refraction index of the material at the film—air interface compared to a film of the pure dye, resulting in a decrease in the reflection factor of the working layer. Since addition of the polymer increases the layer thickness [for example, to obtain a dye : polymer = 1 : 1 ratio, the addition of the polymer (4 mg mL^{-1}) increases the film thickness 5-fold and narrows down the absorption spectrum (see Fig. 2) due to the increase in the concentration of the monomeric form of the dye] the optical density of the film measured at the absorption maximum of the monomeric dye increases. This influence of a polymer added on the reflection and absorption spectra is manifested for films of both symmetrical (see Fig. 2 and 3, spectra *1, 2*) and asymmetrical (see Fig. 2 and 3, spectra *3, 4*) dye molecules.

For films of other dyes obtained without a polymer, the reflection factor at the spectral maximum is ~30% in the absence of crystallization. To perform recording and
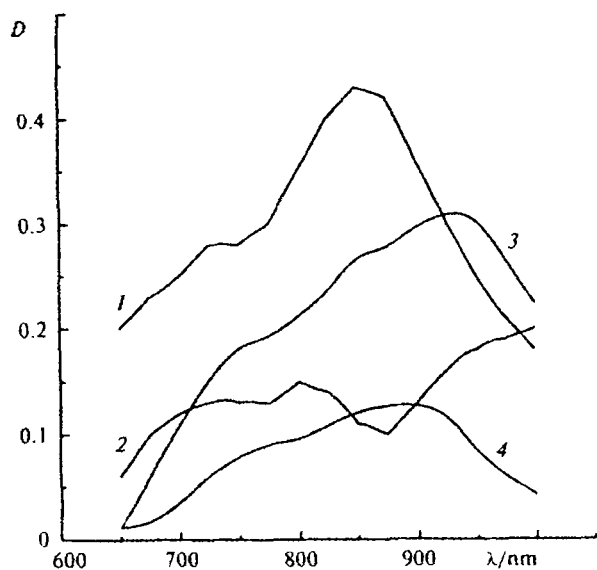

Fig. 3. Variation of the reflection spectra of films of dyes 2b (*1, 2*) and 1b (*3, 4*) upon the addition of PMMA: *1, 2*, films of an individual dye; *2, 4*, dye 2b : PMMA = 1 : 0.5 and dye 1b : PMMA = 1 : 1 films.

reading out of information, the reflection factor should be 30—40%, because focusing of the laser beam in the working layer is accomplished by tracing the light signals reflected from the surface of the disk. The decrease in the reflection factor of the recording medium to 10% following the addition of the polymer results in unstable operation of the recording—reading out device.

Moreover, experiments showed that the addition of a polymer can stabilize the film only on the threshold of crystallization. When this threshold for easily crystallizable dyes has been surpassed, this method is inefficient. For example, when a chloroform solution of dye 1a with a concentration of 6 mg mL^{-1} is subjected to centrifugation, its crystallization on the support occurs in the same way, no matter whether or not the polymer has been added to it.

Thus, the introduction of the polymer in acceptable concentrations does not prevent crystallization of films of organic dyes, and tackling this problem by chemical modification of a film-forming molecule remains a challenging problem. Therefore, we studied the formation of films by individual dyes of type 1 and 2, containing different numbers of *tert*-butyl substituents, by depositing them onto glass supports by centrifugation of solutions.

The selection of solvents was based not only on their dissolving capacity but also on the effect on the quality of films formed upon their evaporation. We used the following solvents: acetonitrile, chloroform, and dichloroethane, which differ in boiling points, viscosities, and polarities.

To determine crystallization thresholds, we studied the variation of the optical density of the films at the absorption maximum as a function of the concentration of the dye in the solution. The weight concentrations of the solutions varied from 1 to 30 mg mL^{-1} (M ~ 10^{-3}—10^{-2}).

Figure 4 shows the dependences of the optical density of films of styryl dyes 2b and 2d on the dye concentration in various solvents. Unlike films of dye 2b, for which an increase in the concentration leads in all cases to an increase in the optical density, the films of dye 2d, which contains twice as many *tert*-butyl groups, exhibit this type of behavior only in chloroform and dichloroethane; the crystallization threshold for a film of dye 2b deposited from chloroform or acetonitrile occurs at a higher concentration than that for 2d.

Similar results were also obtained for the pair of styryl dyes 2a and 2c (see Fig. 4, *b*). In both cases, dye layers with an optical density of 0.8 can be obtained from dichloroethane. Films of both dyes deposited from chloroform are characterized by low crystallization thresholds (< 10 mg mL^{-1}), while films from acetonitrile are formed up to a concentration of 20 mg mL^{-1} for dye 2a and crystallize at 7.5 mg mL^{-1} in the case of dye 2c.

Thus, the introduction of an additional *tert*-butyl substituent into a molecule of asymmetrical thio-
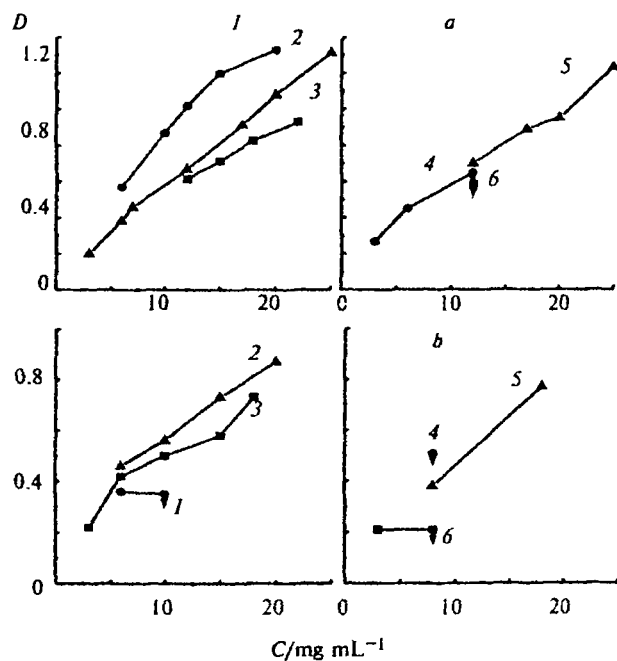
Fig. 4. Dependence of the optical density (*D*) of films on the concentration (*C*) of dyes: *a*, **2b** (*1—3*) and **2d** (*4—6*); *b*, **2a** (*1—3*) and **2c** (*4—6*) in a composition for CHCl₃ (*1*, *4*), C₂H₄Cl₃ (*2*, 5), and MeCN (*3*, *6*). Here and below, the arrow marks the formation of observable microcrystals (crystallization threshold).

pyrylocyanine dye does not diminish crystallization and, in some cases, for example, when the film is deposited from an acetonitrile solution, causes the opposite effect.

Fundamentally different results have been obtained in a study of film formation by symmetrical thiopyrylocyanines **1a** (two *tert*-butyl groups) and **1b** (four *tert*-butyl groups). For dye **1a**, the crystallization threshold corresponds to a concentration of the dye in dichloroethane of 6 mg mL⁻¹; above this concentration, numerous microcrystals are formed in the film. In this
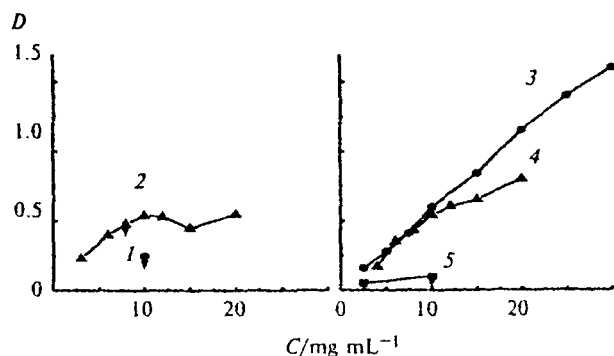

Fig. 5. Dependence of the optical density (*D*) of films on the concentration (*C*) of dyes **1a** (*1*, *2*) and **1b** (*3—5*) in a composition for CHCl₃ (*1*, *3*), C₂H₄Cl₃ (*2*, 4), and MeCN (*5*).

case, no increase in the optical density, proportional to the concentration of the solution, is observed, and the *D* = 0.8 value needed to accomplish the photothermal information recording by a laser beam cannot be attained in the absorption maximum (Fig. 5, curves *1*, *2*). However, in the case of dye **1b**, the formation of microcrystals was observed only for film deposition from acetonitrile. When chloroform or dichloroethane solutions are subjected to centrifugation, the films do not crystallize even when saturated solutions with concentrations of 30 and 20 mg mL⁻¹, respectively, prepared at elevated temperatures, are used (see Fig. 5, curves *3—5*). For this dye, an optical density of the working layer greater than 1 can be attained. Thus, the introduction of additional *tert*-butyl groups into the molecule of a symmetrical thiopyrylocyanine of type **1** results in efficient suppression of crystallization and gives films with a high-quality surface. Since films of this dye possess high reflection factors (30%) and high optical densities at the wavelength of radiation of a semiconductor laser (*D* ~1), this dye can be recommended as a material suitable for the preparation of layers for laser information recording without using a stabilizing polymer.

The obtained results can be interpreted based on the views on the spatial structures of the dyes in question and their aggregated forms. As model structures, we used Langmuir—Blodgett (LB) films of dye **1b** with a controlled number of monolayers (34). From the relationship between the thickness of the LB film, found by ellipsometry, and the number of deposited layers, the thickness per monolayer was determined for the dye film. To estimate the arrangement of molecules in a layer, the structure of dye **1b** was studied by molecular mechanics with geometry optimization using MM⁺ force field parameters (corrected MM2 force field[12]).
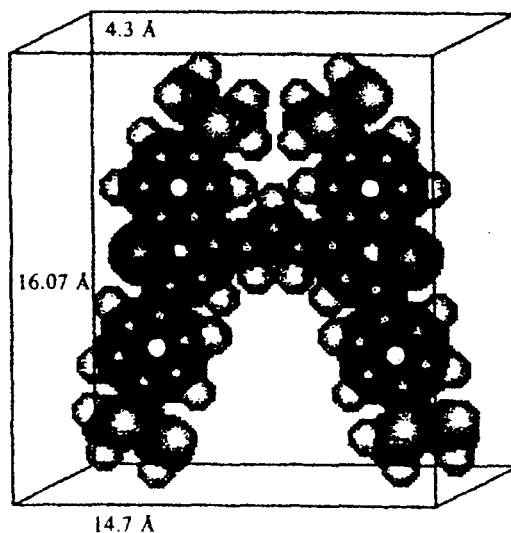

Fig. 6. Model of the molecule of dye **1b**.

In a first approximation, the aromatic moiety of the dye molecule is planar, and the structure of the molecule corresponds to the model shown in Fig. 6. Dye **1b** can be represented in a simplified form as a parallelepiped with dimensions 16.07×14.7×4.3 Å.

The thickness of dye **1b** films, prepared by centrifugation of 1—7 mg mL^{-1} chloroform solutions, varies in the 200—1000 Å range. In this range, the optical density of the layer depends linearly on the thickness and is 1.5 times larger than the optical density of an equally thick LB film (Fig. 7). The height of one monolayer of the dye in the LB film is 16.15 Å, which corresponds to the perpendicular arrangement of the dye molecules in the layer with respect to the support. Dye films prepared by various methods exhibit similar absorption spectra (Fig. 8). The different absorbances might be due to different orientations of the dye molecules with respect to the support in the case of LB films and films prepared by centrifugation. For LB films of dyes, the intensity of absorption by the layer is known to vary as a function of the angle of incidence of light on the support and the orientation of the deposited molecules.[13] Based on the data obtained, it can be suggested that dye films obtained by centrifugation are characterized by close packing rather than by a loose structure and that the dye molecules in these films can form dimers or other associates including ordered ones.

In general, ionic cyanine dyes, in particular thiopyrylocyanines, are characterized by dipole—dipole attraction resulting in the formation of ion associates of various types.[14,15] The mutual orientation of the associated dye molecules corresponds to a parallel arrangement of the planes of aromatic nuclei. It is assumed that
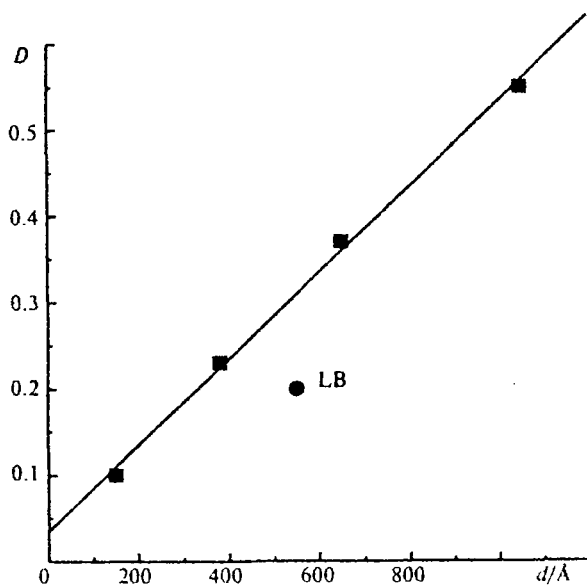
Fig. 8. Absorption spectra of dye **1b** films: *1*, LB films and *2, 3*, films deposited by centrifugation at concentrations of 2 and 6 mg mL^{-1}, respectively.

the van der Waals radius for the interacting aromatic rings in the stacks of molecules amounts to 3.4—3.2 Å.[16] A close interplanar distance (3.4 Å) has been reported for closely packed dimeric H-aggregates of merocyanine dyes.[17] In the crystalline state, pyrylocyanine dyes form a close packing of molecules located at distances limited by the van der Waals radius between the planes. The possible character of intermolecular contacts arising when the dye molecules approach one another during crystallization can be conveniently considered using their dimers as an example.

The structure of the dimer of the symmetrical thioflavylium dye **1b** is shown in Fig. 9, *a*. The bulky *tert*-butyl groups prevent the aromatic planes of the molecules in the dimer from coming to one another within a distance of less than 4.3 Å and create an energy barrier to the formation of a crystalline structure. A closer association of molecules of dye **1b** is hampered by geometric restrictions, and no additional bands typical of ordered dye associates appear in the absorption spectra of films formed by dye **1b** molecules as the concentration of the dye increases up to the solubility limit. For molecules of symmetrical dye **1a** with two *tert*-butyl groups, the steric restrictions are eliminated in the case of opposite orientations of the planes of interacting

Fig. 7. Dependence of the optical density (*D*) on the thickness (*d*) for a dye **1b** film deposited by centrifugation and for an LB film (34 monolayers).
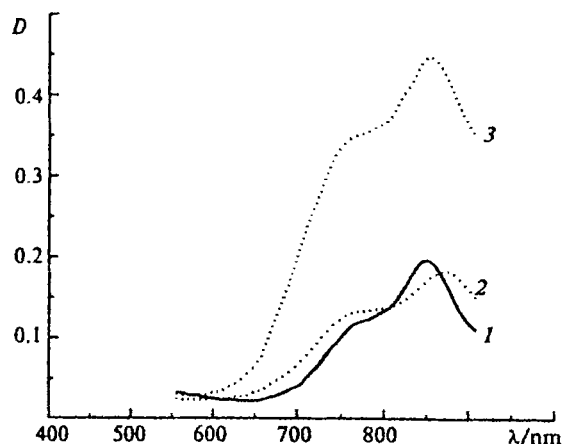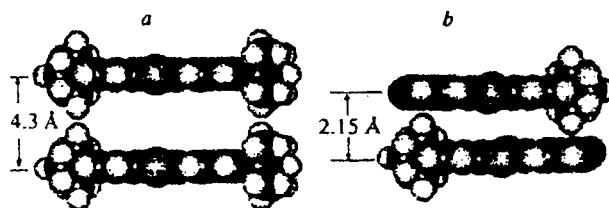
Fig. 9. Assumed structure of the dimer of dyes **1b** (*a*) and **1a** (*b*).
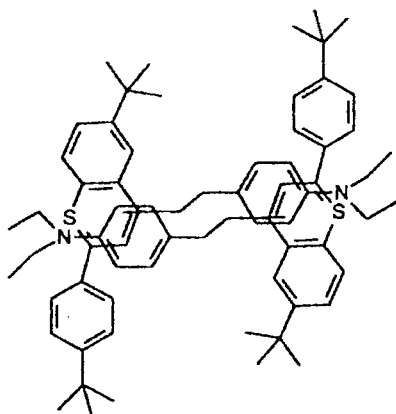
Fig. 10. Assumed structure of the dimer of dye **2d**.

molecules (see Fig. 9, *b*); therefore, a closer packing and a stronger interaction of the transition dipole moments of molecules in the aggregate during absorption of light are possible. This is manifested as changes in the absorption spectra of the films. Prior to the crystallization threshold, this dye forms an ordered aggregation state, characterized by its own absorption spectrum with a maximum at 960 nm.[6]

Asymmetrical pyrylium and thiopyrylium dyes tend to form dimers.[18,19] The absorption spectra of the dimers of dyes **2a** and **2b** undergo a hypsochromic shift compared to those of the monomers,[6] and dye and dye—polymer films consist essentially of the dimers. Due to the high polarizability of the conjugated molecular system of asymmetrical thioflavylium dyes and to the different natures of the donor ($-NR_2$) and acceptor ($-S^+=$) terminal groups in the ground state of these dyes, the electron density should be redistributed, in accordance with the mesomeric effects, toward the bipolar structure with a positive charge on the N atom.[20] Dimerization of this dye should occur most likely with opposite orientations of the interacting dipoles of the monomers. This arrangement of molecules in the dimer results in an additional symmetry element, a twofold rotation reflection axis (S_2). In this case, the presence of two tert-butyl groups in the molecule of an asymmetrical dye causes no steric hindrance preventing the molecules from approaching each other during dimerization to a distance of 3.2—3.4 Å (Fig. 10).

The bulky tert-butyl group requires additional energy for the formation of a cavity in the solvent and for an increase in the entropy of the surrounding polar solvent molecules due to hydrophobic interactions.[21] Therefore, further aggregation of the dimers of dyes containing an additional tert-butyl group can cause a more substantial decrease in the entropy factor than that for dyes without this group.

This effect should manifest itself for high-polarity solvents such as acetonitrile ($\mu = 3.92$ D, $\varepsilon = 36.2$).

Perhaps, this accounts for the fact that for film deposition from acetonitrile solutions, the crystallization threshold for dyes **2c** and **2d** is lower than that for **2a** and **2b**. The dipole moments and dielectric constants of dichloroethane ($\mu = 1.44$ D, $\varepsilon = 10.4$) and chloroform ($\mu = 1.87$ D, $\varepsilon = 4.7$) are smaller than those of acetonitrile, and the difference between the crystallization patterns of dye films deposited from these solvents cannot be unambiguously interpreted in terms of their polarity. At the qualitative level, it can be stated that in most of the cases studied, dye films formed from dichloroethane are characterized by smaller crystallization thresholds than those deposited from chloroform.

Thus, our studies showed that thiopyrylium dyes of type **1** and **2** form solid-state amorphous films on glass supports, which can be deposited from organic solvents, preferably from dichloroethane, by the centrifugation method. For several dyes **2a**, **2b**, **2d**, and **1b**, it is possible to prepare films whose optical density, thickness, and reflection coefficient are suitable for use in WORM disks. The preparation of high-quality films of dyes **1a** and **2c** is hampered by their crystallization on a support. The introduction of additional tert-butyl substituents into symmetrical dye **1a** completely suppresses the crystallization; however, this effect is not manifested when additional tert-butyl groups are introduced into the styryl type dyes studied. The experimental data obtained here were interpreted based on considerations concerning the geometry of the interaction of molecular structures during aggregation of the dyes.

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