*Russian Journal of General Chemistry, Vol. 75, No. 10, 2005, pp. 1584–1593. Translated from Zhurnal Obshchei Khimii, Vol. 75, No. 10, 2005, pp. 1161–1170.*
*Original Russian Text Copyright © 2005 by Rtishchev, Nosova, Solovskaya, Romashkova, Kudryavtsev.*

# Formation of Exciplexes in Films of Polyimides, Polyamides, and Polyquinazolones Derived from Aromatic and Heteroaromatic Diamines

**N. I. Rtishchev*, G. I. Nosova**, N. A. Solovskaya**,
K. A. Romashkova**, and V. V. Kudryavtsev****

** St. Petersburg State Institute of Technology (Technical University), St. Petersburg, Russia*
*** Institute of Macromolecular Compounds, Russian Academy of Sciences, St. Petersburg, Russia*

Received October 28, 2004

**Abstract** — The emission bands exchibited by films of polyimides derived from 1,3-bis(3,4-dicarboxyphenoxy)benzene dianhydride, hexafluoroisopropylidenedibenzene-3,3',4,4'-tetracarboxylic dianhydride, and aromatic and heteroaromatic diamines, and also of polyamides and polyquinazolones derived from the same amines are exciplex bahnds. With polyamides, complexes in the ground state are formed. The fluorescence of the photoconductivity sensitizer Rhodamine 6G is quenched in films of these polymers by the exciplex mechanism.

Aromatic polyimides [1], polyamides [2], and poorly studied polyquinazolones [3] exhibit high heat resistance, high optical transparency, and good dielectric and film-forming properties; when modified with functional photosensitive fragments, they can be used in development of materials for optical technologies. Photosensitive polymers are of considerable interest from the viewpoint of their electronic, electrical, photoelectric, luminescence, and photophysical properties [4–6].

Previous studies revealed for the first time the high (without doping with dyes) intrinsic photoconductivity in the visible range of polyimides and polyquinazolones (integral photosensitivity $2 \times 10^{-5}$–$2.5 \times 10^{-4}$ cm$^2$ J$^{-1}$) whose polymeric chains contain in the diamine component of the repeating unit a quaternary carbon atom with various substituents or diamines of the heteroaromatic series [7–9]. The photoconductivity of the polyamides prepared from the same diamines is lower by two orders of magnitude [10].

The photoelectric properties of films are associated with the excitation of the electronic systems of these polymers. It is known that the major factor governing the photoelectric properties of polyimide films is the donor–acceptor (DA) interaction in the polymer molecule. The character and intensity of this interaction depend on the structure of the repeating monomeric unit, packing of the macrochains, and surrounding of the arising complexes in the solid polyimide [6]. Polyimide macromolecules can be considered as DA chains of the alternating structure [11] in which the diimide fragment is the electron acceptor (A) and the diamine residue, the electron donor (D). With strong A (high electron affinity) and D (low ionization potential), the charge transfer is realized even in the ground ($S_0$) state, with the formation of intrachain complex **1** [Scheme 1, Eq. (1a)] and interchain complex **2** [Scheme 1, Eq. (1b)].

**Scheme 1.**

$$\sim\!AD\!\sim \underset{}{\overset{h\nu_a}{\rightleftarrows}} \sim\!A^-D^+\!\sim \xrightarrow{h\nu_f} \sim\!(A^-D^+)^*\!\sim \longrightarrow \sim\!AD\!\sim, \tag{1a}$$

$$\begin{matrix}\sim\!AD\!\sim \longrightarrow \\ \sim\!AD\!\sim \longleftarrow\end{matrix} \begin{matrix}\sim \\ \sim A\end{matrix}\boxed{\begin{matrix}A^- \\ D^+\end{matrix}}\begin{matrix}D\!\sim \\ \sim\end{matrix} \xrightarrow{h\nu_a} \begin{matrix}\sim \\ \sim A\end{matrix}\boxed{\begin{matrix}A^- \\ D^+\end{matrix}}\begin{matrix}{}^*D\!\sim \\ \sim\end{matrix} \xrightarrow{h\nu_f} \begin{matrix}\sim\!AD\!\sim \\ \sim\!AD\!\sim\end{matrix}. \tag{1b}$$

Simultaneously, along with the overall absorption of D and A, a new long-wave band or shoulder appears in the electronic absorption spectrum, and the polymer films become colored [12]; also, a broad structureless fluorescence band appears. Its excitation spectrum reproduces the shape of the new absorption band. With a weak acceptor and/or donor, the electron transfer in the photoexcited state with formation of exciplexes becomes probable (Scheme 2).

**Scheme 2.**

$$\sim AD\sim \xrightarrow{h\nu_a} \sim AD^*\sim \xrightarrow{h\nu_f} \sim(A^-D^+)^*\sim \longrightarrow \sim AD\sim, \qquad (2a)$$

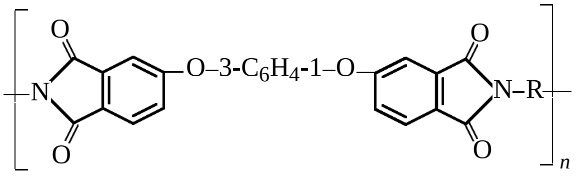
$$\left.\begin{matrix}\sim AD\sim\\ \sim AD\sim\end{matrix}\right] \xrightarrow{h\nu_a} \left.\begin{matrix}\sim AD\sim\\ \sim AD^*\sim\end{matrix}\right] \longrightarrow \begin{matrix}\sim\\ \sim A\end{matrix}\boxed{\begin{matrix}A^-\\ D^+\end{matrix}}\begin{matrix}{}^*D\sim\\ \sim\end{matrix} \xrightarrow{h\nu_f} \begin{matrix}\sim AD\sim\\ \sim AD\sim\end{matrix}. \qquad (2b)$$

The fluorescence excitation spectrum of the exciplex reproduces the overall curve of absorption of D and A, and the Stokes shift ($\Delta\nu_{Ss}$) is abnormally high (15 000–20 000 $cm^{-1}$) in contrast to the shift observed with complexes **1** and **2** ($\leq$6000 $cm^{-1}$) [6], although the exciplex emission band itself is similar in character to the emission bands of complexes **1** and **2**.

The character of the exciplex may change depending on the surrounding. In particular, addition of certain dyes to polyimide films leads to sensitized photogeneration of the charge carriers, accompanied by quenching of the dye fluorescence. The sensitization if due to formation of a nonfluorescent exciplex involving the dye and D in the initial polymer [5, 13].

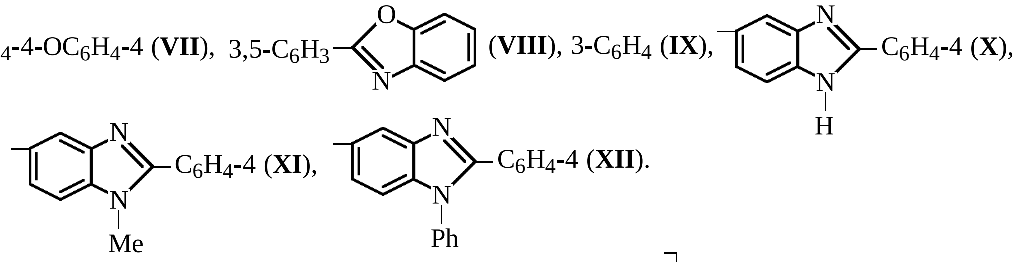
In this connection, it seems urgent to study how the structure of the monomeric unit (containing no fragments with pronounced donor properties) affects the polymer photophysics. In this study we examined the luminescence characteristics of the synthesized polyimides and polyquinazolones with various A and D, and also, for comparison, of certain polyamides that were not studied previously (**I**–**XXXI**).

*Polyimides*

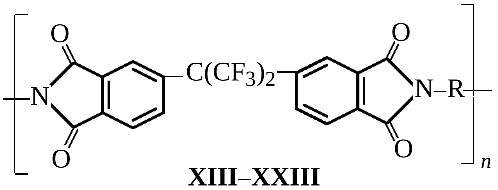


**I–XII**

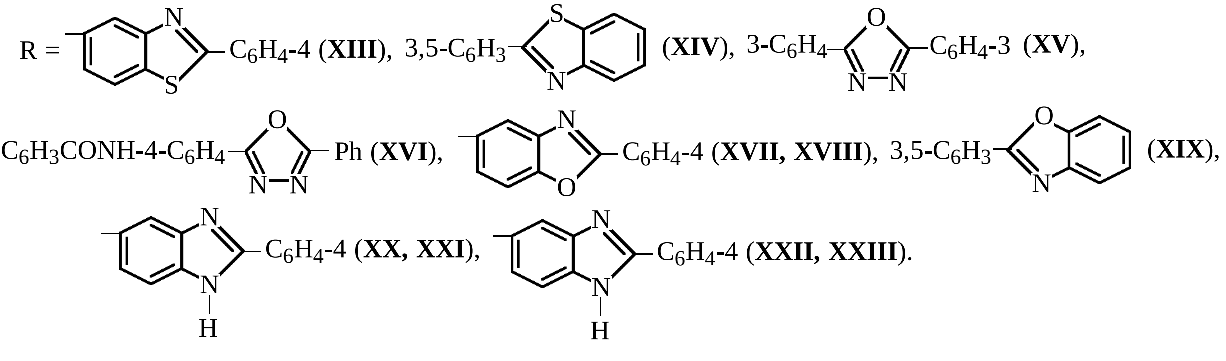
R = 4-$C_6H_4C(Me)_2C_6H_4$-4 (**I**), 4-$C_6H_4C(Me)(Ph)C_6H_4$-4 (**II**), 4-$C_6H_4C(Ph)_2C_6H_4$-4 (**III**), 4-$C_6H_4CH(Ph)C_6H_4$-4 (**IV**), 4-$C_6H_4O$-4-$C_6H_4C(Me)_2C_6H_4$-4-$OC_6H_4$-4 (**V**), 4-$C_6H_4O$-4-$C_6H_4C(Me)(Ph)C_6H_4$-4-$OC_6H_4$-4 (**VI**), 4-$C_6H_4O$-4-$C_6H_4C(Ph)_2C_6H_4$-4-$OC_6H_4$-4 (**VII**),



3,5-$C_6H_3$ (**VIII**), 3-$C_6H_4$ (**IX**), $C_6H_4$-4 (**X**), $C_6H_4$-4 (**XI**), $C_6H_4$-4 (**XII**).



**XIII–XXIII**

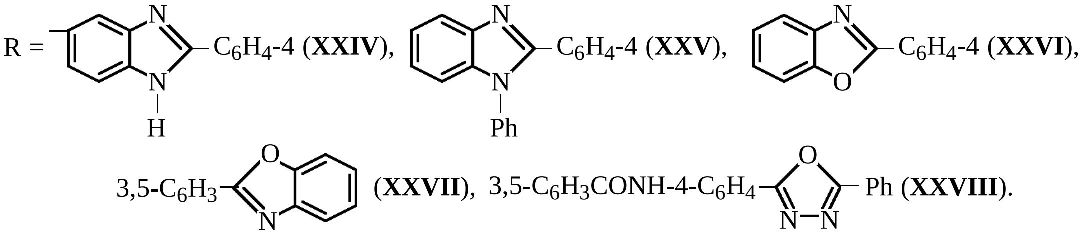


R = $C_6H_4$-4 (**XIII**), 3,5-$C_6H_3$ (**XIV**), 3-$C_6H_4$ $C_6H_4$-3 (**XV**), 3,5-$C_6H_3CONH$-4-$C_6H_4$ Ph (**XVI**), $C_6H_4$-4 (**XVII, XVIII**), 3,5-$C_6H_3$ (**XIX**), $C_6H_4$-4 (**XX, XXI**), $C_6H_4$-4 (**XXII, XXIII**).

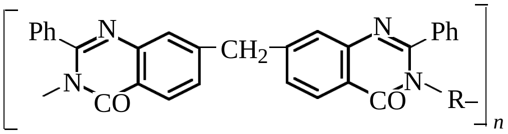
*Polyamides*

$$-\!\!\left[\mathrm{NHRNHCOC_6H_4\text{-}4\text{-}OC_6H_4\text{-}4\text{-}C(O)}\right]_n,$$

**XXIV–XXVIII**

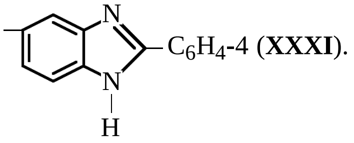


*Polyquinazolones*



**XXIX–XXXI**

R = 4-$C_6H_4$O-3-$C_6H_4$-1-O$C_6H_4$-4 (**XXIX**), 4-$C_6H_4$O-4-$C_6H_4$C(Me)$_2$$C_6H_4$O-4-$C_6H_4$-4 (**XXX**),



We estimated the capability of these polymers for sensitized photogeneration of charge carriers from the efficiency of quenching of the sensitizer fluorescence. Taking into account the highest efficiency of laser dyes [5], we chose Rhodamine 6G (Rh 6G).

**Luminescence properties of polymers.** The spectral characteristics of the polymers studied are given in Table 1 and Figs. 1–3. The long-wave absorption band of the polymers $\nu_a$ is observed in the range $(40.4–29.6) \times 10^3$ $cm^{-1}$ (248–338 nm) depending on the structure of components A and D of the repeating monomeric unit. Excitation in the range $\lambda \le 366$ nm always gave rise to a broad ($\Delta\nu_{1/2}$ 7000–10 000 $cm^{-1}$) fluorescence band in the range $(26.0–12.0) \times 10^3$ $cm^{-1}$ with a very large Stokes shift. This shift depends on the position of the bands of the components; the number of the bands (one to three) is determined by the structure of the amine component of the repeating unit. This is indicated by the results of measuring the fluorescence excited with polarized light (Figs. 1–3).

The degree of the fluorescence polarization (*P*) for the majority of the films is not constant within the band and, as a rule, changes stepwise, decreasing in going to the red region. Thus, the overall emission spectrum consists of several components differing in *P* (from 36 to 2%, Table 2). Exceptions are polyimides **I**–**IV** containing diphenylmethane units in the amine fragment. In this case, one-component fluorescence is observed with the band maximum at $\nu_f \sim 18 \times 10^3$ $cm^{-1}$ and Stokes shift of $\sim 22 \times 10^3$ $cm^{-1}$; on replacement of the phenyl radical with the diphenyl oxide group (polyimides **V**–**VII**), an additional band appears with $\nu_f \sim 20 \times 10^3$ $cm^{-1}$. A similar pattern is observed upon introducing into the diamine moiety various heterocycles (e.g., 2-phenylbenzoxazole, 2,5-diphenyloxadiazole, polyimides **XIII**–**XXIII**). For these substances, the parameters of the short- and long-wave components are $\nu_f \sim 20 \times 10^3$ and $(14–18) \times 10^3$, $\Delta\nu_{Ss}$ $(12–14) \times 10^3$ and $(13–17) \times 10^3$ $cm^{-1}$, respectively. The structure of the phthalimide (initially dianhydride) component in the repeating unit of the polyimide affects the position of the overall fluorescence band insignificantly (cf. **VIII** and **XIX**, Table 1). However, in going from **I**–**XII** to **XIII**–**XXIII**, the low-frequency maximum shifts bathoflorically by 500 $cm^{-1}$, and the Stokes shift of both components increases by 2100 and 2700 $cm^{-1}$. In addition, the polyimides with benzimidazole substituents (polymers **X**–**XII**) do not exhibit the short-wave component, in contrast to polyimides **XX**–**XXIII**.

The contour and position of the overall fluorescence band of polyimides **XIII**–**XXIII** are determined by the structure of the heterocycle, position of the 2-phenylbenzazole group in the macromolecular chain

**Table 1.** Spectral characteristics of polymer films

| Comp. no. | $\nu_a \times 10^{-3}$, cm$^{-1}$ | $\nu_f \times 10^{-3}$, cm$^{-1}$ | $\Delta\nu_{Ss}$ | $\varphi_{ref}/\varphi_x$ |
|---|---|---|---|---|
| **I** | 40.5 | 17.8 | 22.7 | 1.2 |
| **II** | 40.5 | 18.0 | 22.5 | 1.3 |
| **III** | 40.4 | 17.8 | 22.6 | 1.3 |
| **IV** | 40.5 | 18.0 | 22.5 | 1.5 |
| **V** | 43.0 | 19.6 sh, 17.9 | 23.4, 25.1 | 1.6 |
| **VI** | 43.0 | 20.0 sh, 17.9 | 23.0, 25.1 | 1.1 |
| **VII** | 43.0 | 19.6 sh, 17.8 | 23.4, 25.2 | 2.0 |
| **VIII** | 34.0 | 20.1, 18.1 | 13.9, 15.9 | 2.1 |
| **IX** | 40.8 | 20.0, 18.3 | 20.8, 22.5 | 2.0 |
| **X** | 31.3 | 17.8 | 13.5 | 1.9 |
| **XI** | 31.2 | 17.8 | 13.4 | 2.1 |
| **XII** | 32.2 | 17.7 | 14.5 | 2.8 |
| **XIII** | 32.0 | 19.6 sh, 17.3 | 12.4, 14.7 | 3.1 |
| **XIV** | 32.5 | 20.0 sh, 18.6 | 12.5, 13.9 | 1.5 |
| **XV** | 34.0 | 19.1, 16.6 sh | 14.9, 17.4 | 0.8 |
| **XVI** | 32.4 | 19.6 sh, 16.4 | 12.8, 16.0 | 7.4 |
| **XVII** | 32.4 | 19.6 sh, 17.3 | 12.8, 15.1 | 1.5 |
| **XVIII** | 32.8 | 19.6 sh, 17.3 | 13.2, 15.5 | 16 |
| **XIX** | 31.8 | 20.0 sh, 18.6 | 11.8, 13.2 | 1.3 |
| **XX** | 32.2 | 20.0 sh, 17.6 | 12.2, 14.6 | 2.1 |
| **XXI** | 32.0 | 20.0 sh, 16.4 | 12.0, 15.6 | 6.0 |
| **XXII** | 32.0 | 20.0 sh, 17.6 | 12.0, 14.4 | 1.2 |
| **XXIII** | 32.0 | 20.0 sh, 17.2 | 12.0, 14.8 | 1.8 |
| **XXIV** | 29.6 | 20.4, 19.4 sh | 9.2, 10.2 | 46 |
| **XXV** | 30.4 | 21.3, 18.0 sh | 9.1, 12.4 | 3.5 |
| **XXVI** | 29.8 | 21.3, 18.0 sh | 8.5, 11.8 | 1.7 |
| **XXVII** | 34.6, 27.0 sh | 21.0 sh, 18.4 | 6.0, 16.2 | 4.6 |
| **XXVIII** | 33.1, 27.0 sh | 20.8, 19.3 | 6.0, 13.8 | 6.7 |
| **XXIX** | 35.7 | 23.3, 17.5 | 12.4, 18.2 | 3.8 |
| **XXX** | 35.0 | 23.2, 19.0 sh | 11.8, 16.0 | 5.0 |
| **XXXI** | 32.2 | 23.3, 20.4, 18.5 | 8.9, 11.8, 13.7 | 106 |

**Table 2.** Limiting degrees of fluorescence polarization for polyimide, polyamide, and polyquinazolone films, *P*, % ($\lambda_{exc}$ 334, 365 nm)

| Comp. no. | *P*, % | Comp. no. | *P*, % | Comp. no. | *P*, % |
|---|---|---|---|---|---|
| **VIII** | 17, 3 | **XXII** | 34, 23 | **XXVIII** | 17, 11 |
| **XIII** | 12, 4 | **XXIV** | 11, 8 | **XXIX** | 14, 21 |
| **XIV** | 17, 3 | **XXV** | 13, 3 | **XXX** | 28, 16 |
| **XVII** | 17, 10 | **XXVI** | 7, 5 | **XXXI** | 13, 6, 2 |
| **XXI** | 36, 17 | **XXVII** | 19, 11 | | |

(backbone or pendant chain), and procedure of the polymer synthesis. Replacement of the thiazole core (polyimides **XIII**, **XIV)** with the oxazole core (**XVII**, **XIX**) only weakly affects $\nu_f$ of both maxima (18600, 17300 cm$^{-1}$, Table 1) and their intensity, irrespective of the position of the heterocycle in the molecular chain, whereas introduction of the benzimidazole ring (polyimide **XX**) considerably enhances the intensity of the first band. In the polymer containing the oxadiazole ring (polyimides **XV**, **XVI**), $\nu_f$ of the low-frequency component is minimal in this series of polymers, $16 \times 10^3$ cm$^{-1}$. In going from polyimides **XIII** and **XVII** with the 2-phenylbenzazole group in the backbone to polyimides **XIV** and **XIX** with the same group in the pendant chain, the second maximum is blue-shifted (by 1300 cm$^{-1}$), and the position of the first maximum remains unchanged. Note that the synthesis procedure mainly affects the position of the second fluorescence maximum of the polyimides containing imidazole structures. For example, when the polyamido acid cyclization is performed in an *N*-methylpyrrolidone solution (polyimide **XXI**), the maximum is red-shifted by 1200 cm$^{-1}$ relative to the same polymer prepared by chemical condensation of the polyamido acid (polyimide **XX**, Table 1). The emission spectra of polyimides **I**–**XXIII**, recorded from the films frozen to 77 K, are identical to the spectra of the polymers in solution ($CHCl_3$, dimethylacetamide). The fluorescence excitation spectra recorded for some of them (Fig. 1, spectrum *2*; Fig. 2a, spectrum *2*), irrespective of $\nu_f$, reproduce the shape of the absorption curves, showing no new long-wave maxima, except an ill-defined “tail” (Fig. 1, spectra *1*–*3*) for polyimides **VIII**, **IX**, and **XII**. Assignment of this absorption to complexes **1** or **2** (Scheme 1) seems improbable, because at varied $\lambda_{exc}$ (313, 366, 406 nm) the shape of the overall luminescence band remains constant.

Taking into account the aforesaid and data from [6, 11, 14], we can assign the emission of the polymers to the fluorescence of short-lived exciplexes formed by Scheme 2 [Eqs. (2a), (2b)]. Participation of excimers (or excited dimers) [15] seems doubtful because of the positive value of *P*. It is known that, for an excimer, *P* is negative [16]. At present, it is difficult to identify the exciplexes formed in the polyimides. We may only assume the presence of several local centers in the polymer molecule, required for the exciplex formation. Since a change in the dipole orientation in the $S_1$ state is restricted by the lifetime $\tau_s$, this quantity and *P* vary in the same direction. Therefore, we can state that the “red” component in the emission spectra of the polyimides with the maximum in the range $(18.0–16.4) \times 10^3$ cm$^{-1}$ (Table 1), whose degree of polarization is the lowest (Table 2; Figs. 1, 2a), is the most short-lived.

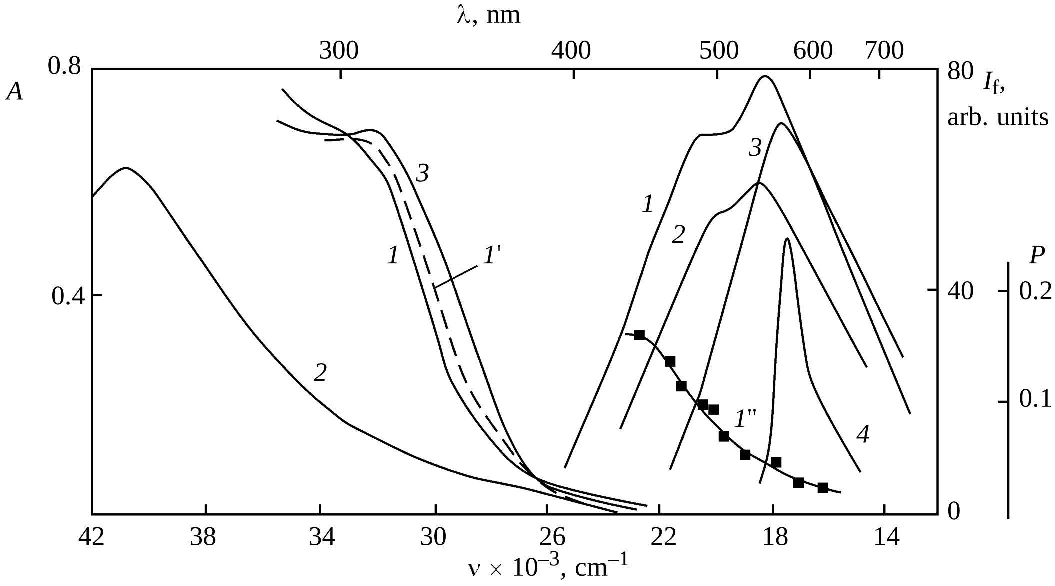


**Fig. 1.** Long-wave absorption (left) and fluorescence (right) band of films (295 K) of polyimides (*1*) **VIII**, (*2*) **IX**, and (*3*) **XII** ($\lambda_{exc}$ 313, 366 nm); (*4*) fluorescence of Rh 6G in polymethacrylate ($\lambda_{exc}$ 546 nm); (*1*') fluorescence excitation spectrum ($\lambda_f$ 450, 550 nm) and (*1*'') fluorescence polarization spectrum ($\lambda_{exc}$ 334 nm) of polyimide **VIII**.

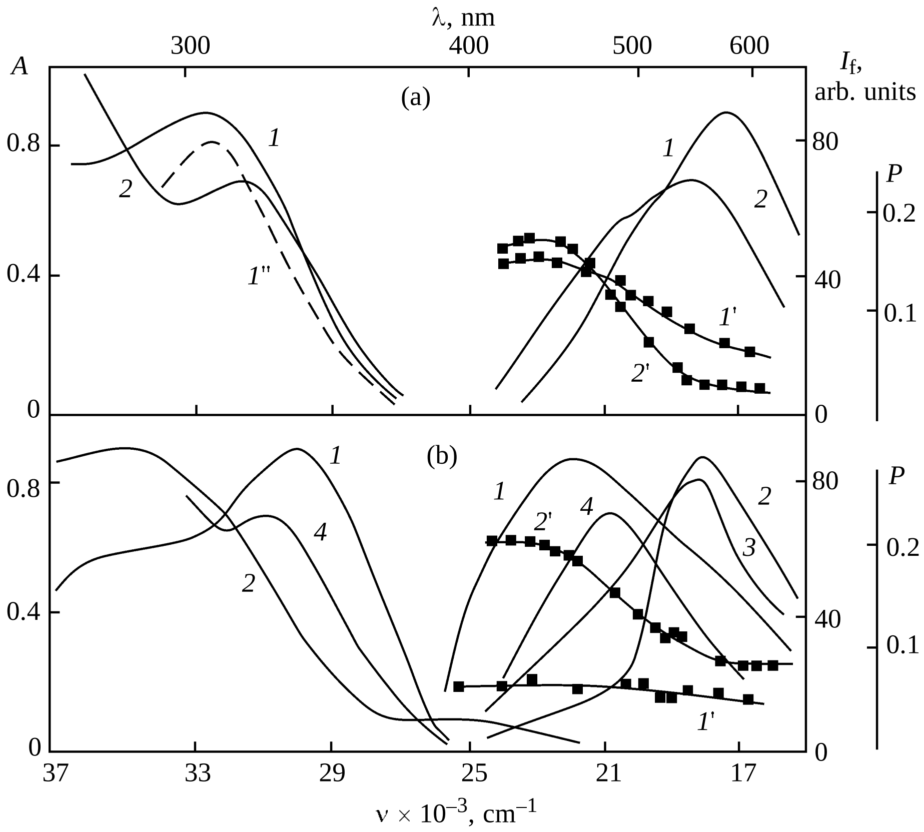


**Fig. 2.** Spectral characteristics (295 K) of (a) polyimide films and (b) polyamides and 5-amino-2-(4-aminophenyl)benzoxazole in chloroform. Absorption (left) and fluorescence (right) spectra: (a) polyimides (*1*) **XVII** and (*2*) **XIX**; (b) polyamides (*1*) **XXVI** ($\lambda_{exc}$ 313, 366 nm) and (*2*, *3*) **XXVII** ($\lambda_{exc}$ 313 and 366 nm, respectively); (*4*) 5-amino-2-(4-aminophenyl)benzoxazole ($\lambda_{exc}$ 365 nm). Fluorescence polarization spectra: (a) polyimides (*1*') **XVII** and (*2*') **XIX** ($\lambda_{exc}$ 334 nm); (b) polyamides (*1*') **XXVI** and (*2*') **XXVII** ($\lambda_{exc}$ 366 nm); (*1*'') excitation spectrum of polyimide **XVII** ($\lambda_f$ 540 nm).

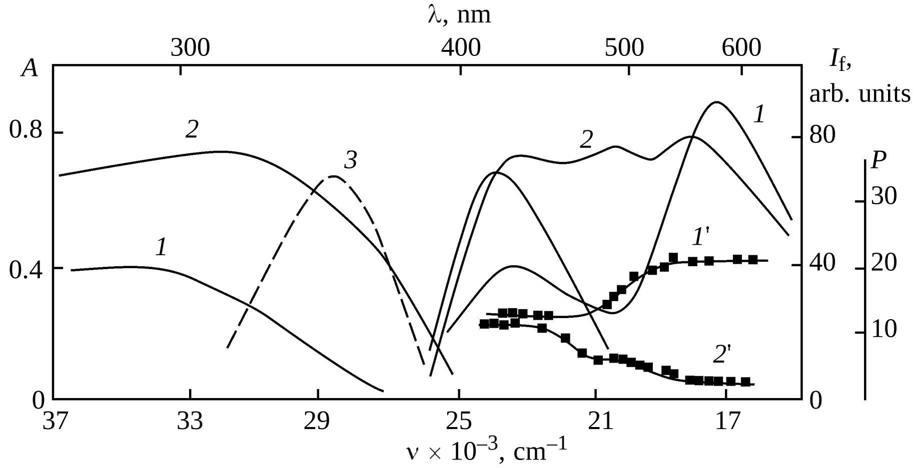


**Fig. 3.** Absorption and luminescence of films of (*1*) polyquinazolone **XXIX**, (*2*) polyquinazolone **XXXI**, and (*3*) 5-amino-2-(4-aminophenyl)benzimidazole in dimethylacetamide. $\lambda_{exc}$, nm: (*1*) 313 and (*2, 3*) 366. Fluorescence polarization spectra of polyquinazolones (*1*') **XXIX** ($\lambda_{exc}$ 334 nm) and (*2*') **XXXI** ($\lambda_{exc}$ 366 nm).

In the case of polyamides containing the same diamine fragments as polyimides **XIII**–**XXIII** (polymers **XXIV**–**XXVIII**, Table 1), we also observed two fluorescence bands, one of which was shifted hypsoflorically relative to the corresponding component in the spectrum of the polyimide: $\nu_f$ (20–21) × $10^3$ and (18–19) × $10^3$ $cm^{-1}$; $\Delta\nu_{Ss}$ (6–9) × $10^3$ and (10–16) × $10^3$ $cm^{-1}$. Considerably smaller $\Delta\nu_{Ss}$ of the "blue" component is apparently due to a different nature of the emission center. A strong influence on the luminescence characteristics of the polyamide is exerted by the position of the 2-phenylbenzazole fragment: in the backbone or pendant chain of the macromolecule. Figure 2 shows the spectral characteristics of (a) polyimides and (b) polyamides that were prepared from the same diamines containing the 2-phenylbenzoxazole fragment in the backbone (**XVII**, **XXVI**) and pendant chain (**XIX**, **XXVII**). In the series **XVII** → **XIX**, the absorption maximum ($\nu_a$) is slightly red-shifted (by 600 $cm^{-1}$), and the general shape of the emission band does not change; only a high-frequency shift of the "red" component (by 1300 $cm^{-1}$) is observed (see above; Fig. 2a, spectra *1, 2*).

Polyamide **XXVI** exhibits a broad, weakly structured luminescence band with $\nu_f$ 21 300 $cm^{-1}$, asymmetric to the long-wave absorption band with $\nu_a$ 29 800 $cm^{-1}$ (Fig. 2b, spectra *1*). Taking into account the overlap of both bands and similarity of their characteristics to those of the starting diamine, 5-amino-2-(4-aminophenyl)benzoxazole (Fig. 2b, spectra *4*), we can assign the observed emission primarily to an intramolecular transition with a significant contribution of the charge transfer from the amine nitrogen atom to the heterocyclic core [17]. The structure similar to that of the starting amine can be realized in the case of formation of the intermolecular hydrogen bond NH···OC, decreasing the electron-withdrawing effect of the carbonyl group in the polyamide macromolecule. Broadening of the emission band from the long-wave side is caused by the presence of a weak "red" component (a shoulder at about 18 000 $cm^{-1}$; apparently, exciplex emission). The fact that the position and shape of the fluorescence band are independent of $\nu_{exc}$ (313, 366 nm) indicates that complexes **1** and **2** are not formed, or that the probability of their formation is low. The polyamide containing the heterocycle in the pendant chain (polymer **XXVII**), like its analog **XXVI**, exhibits two-component fluorescence, but, in contrast to **XXVI**, its major component is the exciplex emission at ν 18 400 $cm^{-1}$, and the short-wave component is minor (shoulder at 21 000 $cm^{-1}$). The absorption spectrum of **XVII** contains, along with the major maximum at 34 600 $cm^{-1}$ characterizing the absorption of 2-phenylbenzoxazole, also a long-wave shoulder at $\nu_a$ ~27 000 $cm^{-1}$, significantly overlapping with the high-frequency component of the fluorescence; the relative intensity of the high-frequency fluorescence band grows with an increase in $\lambda_{exc}$ from 313 to 366 nm (Fig. 2b, spectra *2, 3*). This fact suggests that polymer **XXVII** can form, along with exciplexes (Scheme 2), also complexes **1** and **2** (Scheme 1). Presumably, the role of acceptor A in the charge transfer is played by the benzoylamide or benzoyldiphenyl oxide group of the polymer.

Polyamides **XXIV**, **XXV**, and **XXVIII** behave similarly, showing well-defined exciplex fluorescence (Table 1).

Polyquinazolones **XXIX**–**XXXI** have a broad structureless long-wave absorption band apparently including several $\pi \to \pi^*$ and $n \to \pi^*$ transitions. Replacement of bis(1,3-phenoxy)benzene (polymer **XXIX**) with 2-phenylbenzimidazole (**XXXI**) leads to a low-frequency shift of the band maximum by 3500 $\mathrm{cm}^{-1}$ and of the red edge by 2400 $\mathrm{cm}^{-1}$ (Fig. 3, spectra *1*, *2*). Taking into account the short-wave absorption of the heterocyclic fragment (~33 000 $\mathrm{cm}^{-1}$) [18], we can assume appearance of a new $la \to \pi^*$ transition involving the amine nitrogen atom of the quinazolone ring and the π system of substituent R. Such a transition may be realized in other polyquinazolones also. Significant overlap of the first (short-wave) fluorescence band of **XXXI** (23 300 $\mathrm{cm}^{-1}$) with the long-wave absorption band suggests that the first band is an autonomous molecular $\pi^* \to \pi$ transition with a significant contribution of charge transfer, similar in nature to the corresponding transition in 5(6)-amino-2(4-aminophenyl)benzimidazole molecules [19] with $\Delta\nu_{\mathrm{Ss}}$ ~4500 $\mathrm{cm}^{-1}$ (Fig. 3, spectra *2*, *3*). The other two components in the fluorescence spectrum of this polymer (20 400 and 18 500 $\mathrm{cm}^{-1}$) are due, apparently, to the exciplex emission, like both bands in the spectra of **XXIX** and **XXX** (Table 1; Fig. 1, spectrum *1*).

**Quenching of photosensitizer luminescence.** The majority of polymers (Table 1) do not quench the fluorescence of Rhodamine 6G dye or quench it weakly: $\varphi_{\mathrm{ref}}/\varphi_x = 1–2$ {$\varphi_{\mathrm{ref}}$ and $\varphi_x$ are the quantum efficiencies of the sensitizer fluorescence in an inert reference polymer [poly(methyl methacrylate)] and in the given polymer, respectively}. The other polymers can be subdivided into two groups with respect to $\varphi_{\mathrm{ref}}/\varphi_x$: $\varphi_{\mathrm{ref}}/\varphi_x = 3–7$: **XIII** < **XXV** < **XXIX** < **XXVII** < **XXX** < **XXI** < **XXVIII** < **XVII**; $\varphi_{\mathrm{ref}}/\varphi_x =$ 16–106: **XVIII** < **XXIV** < **XXXI**.

Minor changes in the optical parameters of the dye in the films (absorption, $\lambda_a$ 542 ± 5 nm; fluorescence, $\lambda_f$ 560–575 nm) are apparently due to the macro- and microeffects of the polymer matrix.

It is known that the sensitizer luminescence can be quenched either by nonradiative energy transfer and by electron transfer [5, 13]. In the first case, the necessary condition is the overlap of the fluorescence spectrum of the dye (S) with the absorption spectrum of the polymer (complexes **1** and **2**). As follows from Figs. 1–3, this condition is not met: The energy deficiency is 4000–9000 $\mathrm{cm}^{-1}$. A reasonable alternative is an exciplex mechanism [13, 20] involving interaction of the excited sensitizer (S) molecule with the donor fragment (D) of the polymer chain. A nonfluorescing or weakly fluorescing exciplex is presumably formed; it subsequently transforms into a radical ion pair, which is followed by formation of free charge carriers (Scheme 3).

**Scheme 3.**

$$\begin{tikzcd}
\mathrm{S} \arrow[r, "h\nu_{\mathrm{a}}"] & \mathrm{S}^* \arrow[r, "\mathrm{D}"] \arrow[d, "h\nu_{\mathrm{f}}"'] & (\mathrm{S}^-\mathrm{D}^+)^* \arrow[r] & (\mathrm{S}^-\cdots\mathrm{D}^+) \arrow[r] & \mathrm{S}^- + \mathrm{D}^+ \\
& \mathrm{S} & & &
\end{tikzcd}$$

The fluorescence quenching increases in going to films of polymers containing heterocyclic structures in the diamine component of the repeating unit; the process is the most intense with the benzimidazole component. This result is consistent with our previous data on the sensitized photoconductivity [7–10]: On introducing Rhodamine 6G into films of the benzimidazole polyimide, the photoconductivity increased by an order of magnitude compared to the other polymers.

To summarize the results obtained, we can make the following conclusions. We confirmed our previous assumption [11] that all aromatic polyimides form exciplexes in films. Complexes of this type are also formed by heterocyclic polyimides and by polyamides and other polymers in which the AD interaction is realized. The relative lifetime of the exciplexes can be estimated from the degree of polarization of the film luminescence within the given band. Polyamides derived from 2-phenylbenzazole derivatives as diamine components can form, along with exciplexes, also various complexes in the ground state.

## EXPERIMENTAL

The $^1$H NMR spectra were recorded on a Bruker AC-200 spectrometer (200 MHz) in DMSO-$d_6$ relative to the solvent signal. The absorption spectra were measured on a Specord M-40 spectrophotometer. The apparatus and procedure of the luminescence measurements were described elsewhere [21]. The luminescence of films was measured in the frontal mode, and that of solutions, at an angle of 90°. In low-temperature (77 K) measurements, the polymer solution in chloroform was applied as a thin layer on the front wall of a cylindrical quartz cell; after thorough drying at 40–50°C, the resulting film was frozen. The polarization measurements were performed using film polaroids. The degree of the fluorescence polarization *P* was determined as follows:

$$P = [I_{\parallel} - I_{\perp}/(T_{\perp}/100)]/[I_{\parallel} + I_{\perp}/(T_{\perp}/100)],$$

where $I_{\parallel}$ and $I_{\perp}$ are the intensities of the fluorescence components (at a given frequency ν) parallel and perpindicular to the polarized excitation beam, respectively; $T_\perp$ is the transmission by the monochromator-analyzer of the perpendicular component, which was determined in a separate experiment [22].

The optical sensitizer of the photoconductivity, Rhodamine 6G dye, was introduced both in each film of the polymer and into an inert reference polymer, poly(methyl methacrylate).

The fluorescence quenching was measured at an excitation wavelength of 546 nm and was calculated by the formula

$$\varphi_{\mathrm{ref}}/\varphi_x = I_{\mathrm{ref}}(100 - T_x)/I_x(100 - T_{\mathrm{ref}}),$$

where $\varphi_{\mathrm{ref}}$ and $\varphi_x$ are the quantum efficiencies of the dye fluorescence in the standard and given polymers, respectively; $I_{\mathrm{ref}}$ and $I_x$ are the fluorescence intensities in the band maximum (λ 560–575 nm); and $T_{\mathrm{ref}}$ and $T_x$ are the transmissions of the corresponding films at λ 546 nm (70–90%). The relative measurement error was ±20%.

*N*-Methylpyrrolidone and *N*,*N*'-dimethylacetamide were dried over $CaH_2$ and vacuum-distilled.

1,3-Bis(3,4-dicarboxyphenoxy)benzene dianhydride and hexafluoroisopropylidenebisbenzene-3,3',4,4'-tetracarboxylic acid dianhydride were heated in a vacuum at 170–200°C to convert the hydrolyzed species into the anhydride. 6,6'-Methylenebis(2-phenyl-3,1-benzoxadiazin-4-one) was prepared according to [3].

Diamines of the diphenylmethane series were prepared according to [1], and the heterocyclic diamines (starting compounds for preparing polyimides **XI**–**XIII**, **XVII**, and **XX**), according to [23–25].

**2,5-Bis(3-aminophenyl)oxadiazole** was prepared by the reaction of 3-nitrobenzoyl chloride with hydrazine hydrate in *N*,*N*'-dimethylacetamide, followed by the cyclization of the resulting dinitro compound in thionyl chloride and reduction of the product in DMF on Raney nickel in the presence of hydrazine hydrate; yield 72%, mp 248–248.5°C (from dioxane). $^1H$ NMR spectrum (DMSO-$d_6$), δ, ppm: 5.50 s (4H, $NH_2$), 6.78–6.81 m (2H), 7.18–7.30 m (2H).

**2-(3,5-Diaminophenyl)benzoxazole.** To a solution of 5.45 g of 2-aminophenol in 60 ml of *N*,*N*'-dimethylacetamide, cooled to –15°C, we added 11.54 g of 3,5-dinitrobenzoyl chloride. Then the mixture was stirred for 1 h at 0°C and 2 h at 20°C. To the resulting solution we added 9.05 g of *p*-toluenesulfonic acid and 40 ml of *p*-xylene; the cyclization of the resulting dinitro compound was performed at 160°C for 6 h, with continuous removal of the released water. The precipitate was filtered off, washed with water, and recrystallized from aqueous DMF; yield 11.8 g (90%), mp 215–216°C. The dinitro compound was reduced with $SnCl_2 \cdot 7H_2O$ in concentrated HCl at 90–100°C for 2–3 h. The isolated diamine was sublimed in a vacuum (2 mm Hg) at 210°C; yield 7.5 g (80%), mp 228–229°C. $^1H$ NMR spectrum (DMSO-$d_6$), δ, ppm: 5.06 s (4H, $NH_2$), 6.03 s (1H), 6.69 s (2H), 7.33–7.38 m (2H), 7.69–7.72 m (2H).

**2-(3,5-Diaminophenyl)benzothiazole** was prepared similarly to 2-(3,5-diaminophenyl)benzoxazole, starting from 3,5-dinitrobenzoyl chloride and 2-aminothiophenol; yield 69%, mp 192–193°C (subl.). $^1H$ NMR spectrum (DMSO-$d_6$), δ, ppm: 5.06 s (4H, $NH_2$), 6.02 s (1H), 6.65 s (2H), 7.31–7.58 m (2H), 7.89–8.13 m (2H).

**3,5-Diamino-*N*-[4-(5-phenyloxadiazol-2-yl)phenyl]benzamide** was prepared similarly to 2,5-bis(3-aminophenyl)oxadiazole, starting from 3,5-dinitrobenzoyl chloride and 2-(4-aminophenyl)-5-phenyloxadiazole (synthesized from 4-nitrobenzoyl chloride and benzhydrazide); yield 67%, mp 244–245°C (from acetone–DMF). $^1H$ NMR spectrum (DMSO-$d_6$), δ, ppm: 4.96 s (4H, $NH_2$), 6.04 s (1H), 6.34 s (2H), 7.63–7.65 m (3H), 7.99–8.14 m (6H), 10.27 s (1H, NHCO).

**Polyimides I–XVII, XIX, XX, and XXIII.** A stoichiometric amount of the starting dianhydride was added to a solution of appropriate diamine in *N*-methylpyrrolidone. The viscous solution of the initially formed polyamido acid (25 wt %) was stirred for 8 h at room temperature and then diluted to a concentration of 5–8 wt %. After that, the imidizing mixture consisting of acetic anhydride and pyridine (volume ratio 2 : 1) was added in a fivefold excess relative to the polyimide monomeric units. Triethylamine (volume ratio to pyridine 1 : 10) was added to prevent formation of the isoimide. After stirring for 10 h, the solution was heated at 60°C for 2 h and slowly poured into methanol; the precipitate thus formed was filtered off, washed with methanol, and vacuum-dried at 60°C.

**Polyimides XVIII, XXI, and XXII.** Cyclodehydration of the intermediate polyamido acid was performed in a mixture of *N*-methylpyrrolidone with toluene at 170°C (the released water was removed by continuous azeotropic distillation). The resulting polyimides had high softening points, were soluble in amides and, in some cases, in chlorinated solvents, and form strong transparent films when applied onto substrates.

**Polyamides XXIV–XXVIII.** To a 15 wt % solution of appropriate diamine in *N*,*N*'-dimethylacetamide, cooled to –10°C, we added with stirring 4,4'-bis(chlorocarbonyl)diphenyl oxide. After stirring for 20 min, the mixture was warmed up to 20°C, and the stirring was continued for an additional 2 h. The released HCl was scavenged with propylene oxide. The polymer concentration was brought to 10 wt %, the viscous solution was poured into water, and the precipitate thus formed was washed with two portions of ethanol and vacuum-dried at 60°C.

**Polyquinazolones XXIX**–**XXXI.** To a solution of appropriate diamine in *m*-cresol, we added a stoichiometric amount of 6,6'-methylenebis(2-phenyl-3,1-benzoxazin-4-one) at 20°C (25 wt % monomers) and $P_2O_5$ as dehydrating agent (70 mol % relative to the diamine). The oil bath temperature was raised to 150°C over a period of 1 h, the mixture was stirred at this temperature for 2 h, after which it was further heated to 180°C over a period of 1 h and stirred at this temperature for an additional 6 h. The cooled viscous solution of the polymer was poured into ethanol, and the precipitate thus formed was washed. After drying, the polymer was dissolved in *N*,*N*'-dimethylacetamide. The solution was filtered and again poured into ethanol; the precipitate thus formed was washed with ethanol. Polyquinazolones were dried in a vacuum at a temperature gradually raised from 60 to 100°C.

Films were applied onto glass supports by centrifugation from a 2% solution of a polymer in chloroform or *N*,*N*'-dimethylacetamide. The coating was dried at 60°C and then at 80–100°C in a vacuum to constant weight. The polymer layer thickness was 1–2 μm. If necessary, Rhodamine 6G (chemically pure grade) was added into the initial polymer solution in an amount of 1 wt % relative to the polymer.

## ACKNOWLEDGMENTS

The study was financially supported by the President of the Russian Federation (project no. NSh-1824.2003.3).

## REFERENCES

1. Bessonov, M.I., Koton, M.M., Kudryavtsev, V.V., and Laius, L.A., *Poliimidy – klass termostoikikh polimerov* (Polyimides: a Class of Heat-Resistant Polymers), Leningrad: Nauka, 1983.
2. Sokolov, L.B., *Termostoikie aromaticheskie poliamidy* (Heat-Resistant Aromatic Polyamides), Moscow: Khimiya, 1975.
3. Kulota, S., Moriwaki, T., Ando, T., Eton, S., and Fukami, A., *J. Polym. Sci., Polym. Chem. Ed.*, 1986, vol. 24, no. 9, p. 2047.
4. *Fizicheskaya khimiya: Sovremennye problemy* (Physical Chemistry: Modern Problems), Kolotyrkin, Ya.M., Ed., Moscow: Khimiya, 1987, p. 165.
5. Rumyantsev, B.M., Berendyaev, V.I., Vasilenko, N.A., Malengo, S.V., and Kotov, B.V., *Vysokomol. Soedin., Ser.* A, 1997, vol. 39, no. 4, p. 720.
6. Hasegawa, M. and Horie, K., *Prog. Polym. Sci.*, 2001, vol. 26, no. 1, p. 259.
7. Aleksandrova, E.L., Nosova, G.I., Solovskaya, N.A., Romashkova, K.A., Luk’yashina, V.A., Konozobko, E.V., and Kudryavtsev, V.V., *Fiz. Tekh. Poluprov.*, 2004, vol. 38, no. 6, p. 678.
8. Aleksandrova, E.L., Nosova, G.I., Romashkova, K.A., Galaktionova, E.F., and Kudryavtsev, V.V., *Opt. Zh.*, 2002, vol. 69, no. 10, p. 10.
9. Aleksandrova, E.L., Solovskaya, N.A., Nosova, G.I., Romashkova, K.A., Luk’yashina, V.A., and Kudryavtsev, V.V., Abstracts of Papers, *III Mezhdunarodnaya konferentsiya “Amorfnye i mikrokristallicheskie poluprovodniki”* (III Int. Conf. “Amorphous and Microcrystalline Semiconductors”), St. Petersburg, 2002, p. 103.
10. Nosova, G.I., Aleksandrova, E.L., Solovskaya, N.A., Romashkova, K.A., Gofman, I.V., Luk’yashina, V.A., Zhukova, E.V., and Kudryavtsev, V.V., *Vysokomol. Soedin., Ser. A*, 2005, vol. 47, no. 9.
11. Kotov, B.V., *Zh. Fiz. Khim.*, 1988, vol. 62, no. 10, p. 2709.
12. Lamskaya, E.V. and Kotov, B.V., *Dokl. Akad. Nauk SSSR*, 1987, vol. 296, no. 6, p. 1397.
13. Rumyantsev, B.M., Berendyaev, V.I., and Kotov, B.V., *Vysokomol. Soedin., Ser. A*, 1998, vol. 40, no. 11, p. 1787.
14. Kapustin, G.V., Rumyantsev, B.M., Pebalk, D.V., and Kotov, B.V., *Vysokomol. Soedin., Ser. A*, 1996, vol. 38, no. 8, p. 1343.
15. Guillet, J., *Polymer Photophysics and Photochemistry: An Introduction to the Study of Photoprocesses in Macromolecules*, New York: Cambridge Univ. Press, 1985.
16. Ghosh, A.S., Gupta, D., and Basi, S., *J. Photochem.*, 1975, vol. 4, no. 3, p. 227.
17. Rtishchev, N.I., Lebedeva, G.K., Kvitko, I.Ya., and El’tsov, A.V., *Zh. Obshch. Khim.*, 1988, vol. 58, no. 9, p. 2148.
18. Cernani, A. and Passerini, R., *J. Chem. Soc.*, 1954, p. 2261; Lostovskii, I.Ya., Pushkina, L.N., and Mazalov, S.P., *Zh. Obshch. Khim.*, 1962, vol. 32, no. 11, p. 2617.
19. Rtishchev, N.I., Kvitko, I.Ya., Nagorskaya, L.P., and El’tsov, A.V., *Zh. Obshch. Khim.*, 1993, vol. 63, no. 2, p. 429.

20. Rumyantsev, B.M., Balabanov, E.I., Semenova, L.V., Yudina, G.I., and Mel’nichuk, L.A., *Usp. Nauchn. Fotogr.*, 1984, vol. 22, p. 161.

21. Rtishchev, N.I., El’tsov, A.V., Kvitko, I.Ya., and Alam, L.B., *Zh. Obshch. Khim.*, 1980, vol. 50, no. 9, p. 2070.

22. Parker, C.A., *Photoluminescence of Solutions. With Applications to Photochemistry and Analytical Chemistry*, Amsterdam: Elsevier, 1968.

23. Preston, J., De Winter, W.E., and Hofferbert, W.L., *J. Heterocyclic Chem.*, 1969, vol. 6, no. 1, p. 119.

24. Kym, O., *Chem. Ber.*, 1899, vol. 32, no. 9, p. 2178.

25. Smolenkova, L.A., Rudaya, L.I., Kvitko, I.Ya., and El’tsov, A.V., USSR Inventor’s Certificate no. 486 018, 1973, *Buyll. Izobret.*, 1976, no. 36.