Poly(Schiff's Bases)–Bifluorophores: Synthesis, Photophysical Properties, Nonradiational Transfer of Energy of Electronic Excitation

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ABSTRACT: A method of the synthesis of a new generation of polymers with intrinsic fluorescence—poly(Shiff's bases)-bifluorophores—was developed. These polymers contain two different fluorophores in each unit of the main polymer chain. One of the fluorescent fragments is a donor of electron excitation energy and the second one is an acceptor. The photophysical properties of poly(Shiff's bases)-bifluorophores were investigated. It was shown that in poly(Shiff's bases)-bifluorophores nonradiation energy transfer along the polymer chain in the solid and liquid solutions of polymers takes place. The influence of the disposition of fluorophores in the polymer chain and the distance between them on nonradiation energy transfer were investigated. It was shown that the maximum nonradiation energy transfer is realized in polymers-bifluorophores with a statistical distribution of the fluorophore fragment in the polymer chain. The influence of the distance between a donor and an acceptor of the electron excitation energy on the nonradiation energy transfer was investigated. It was established that nonradiation energy transfer is not observed if the distance between a donor and an acceptor of energy exceeds 10 nm. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 398-406, 2001

Key words: poly(Shiff's bases); fluorescence; polymers-bifluorophores; nonradiation electron excitation energy transfer

INTRODUCTION

Earlier,¹ for the first time, we synthesized poly-(Schiff's bases)–fluorophores by polycondensation of dialdehydes of dicarboxylic acids and diamines–fluorophores. It was shown that the solutions of these polymers have an abnormally high, for polymer solutions, quantum yield of fluorescence, reaching 80% at 20°C.

The next purpose of our study was the molecular

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design of a new class of polymers-bifluorophores poly(Schiff's bases)-bifluorophores, in which the non-radiational energy transfer of electronic excitation in polymeric chains was observed, detailed research of the photophysical processes occurring in polymers-bifluorophores at the absorption of light and establishment of the laws and mechanisms of radiational and nonradiational inside, and intermolecular energy transfer as the major opportunity of the energy dissipation.

The opportunity of the nonradiational energy transfer of electronic excitation in poly(Schiff's bases)-bifluorophores was determined by that the fluorophores-donors and fluorophores-acceptors are at a rather close distance (about 15 Å) and by the absence of conjugation between aldehyde and

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amine components of the polymer.² Poly(Schiff's bases)–bifluorophores were not described earlier.

The synthesis of polymers-bifluorophores is complicated enough and the study of the mechanism of energy transfer in polymers is connected with large difficulties from the viewpoint of the specificity of the macromolecule structure. Therefore, first, we developed methods of synthesis of the substances modeling elementary units of polymers-bifluorophores—azomethynes-bifluorophores.³ It was shown that in the case of azomethynes-bifluorophores nonradiational energy transfer takes place. The mechanism of nonradiational energy transfer was investigated. The obtained data were used as a basis for the development of methods of synthesis and research of poly(Schiff's bases)-bifluorophores.

The polymers were producted by polycondensation of the dialdehyde of terephthalic acid or dialdehyde of 5,5'-methylene-bis-salicylic acid and two diamines-fluorophores, where one is the donor of energy, and the other, the acceptor. The choice of mono- and diamines-fluorophores was determined by their spectral-fluorescent characteristics: just a degree of overlap of the radiation field of the amine donor of the energy of electronic excitation by the energy absorption field of the amine acceptor. On the basis of literary and experimental data, the following diamines-fluorophores were chosen:



2,8-diamine-3,7-dimethylacrydinehydrochloride (I)



9,9-bis(p-aminophenyl)anthracene (II)



5-amino-2-(4-aminophenyl)benzimidazol (III)



Safranine T (IY)



6-amino-l-iminophenalenhydrochloride (Y)

At the initial stage of research, four polymersbifluorophores were synthesized:





where diamine **III** is the energy donor; diamines IY and Y, acceptors; and diamines I and II, donors or acceptors depending on the structure of the polymer. For the production of polymers-bifluorophores, intermonomer dialdehyde was gradually added into the solution of an eqimolar mixture of two diamines at 120°C, kept for several hours until the disappearance of the monomers, and then heated to 140°C and kept for 4-5 h. Because of such a method of polymers-bifluorophores synthesis, it is possible to produce both a regular and the statistical distribution of the fluorescent fragments in a polymeric chain, which is largely determined by the basicity of the diamines. Below, this aspect of the problem will be considered on the example of the polycondensation of the dialdehyde of terephthalic acid with 2,8-diamine-3,7-dimethylacrydine hydrochloride and 2-(4-amino-phenyl)-6-aminobenzimidazol. Since in the initial stage of reaction an interaction of the dialdehyde of terephthalic acid with diamines occurs, the formation of substances of the following structures take place:





В

It is possible to suppose that diamines can react with the dialdehyde of terephthalic acid in various sequences depending on the basicity of their amino groups.

For an estimation of the reactionary ability of amino groups, the calculation of charges on the atoms of nitrogen and the specification of the geometry of both molecules was made by the half-empirical quantum-chemical method AI1 with use of the software package MOPAC. The data on the geometry of the molecules were used for the calculation of the virtual bands inside the heterocycles (see structures \mathbf{A} and \mathbf{B}). The angles, given in the Table I, are additional to the valency angles.

From the table, one can see that the size of the charge on the nitrogen atom of the amino group in substance **B** is higher than is the size of the charge on the nitrogen atom of the amino group in substance **A**. Besides this, the nucleophilicy of the amino group in substance **A** is reduced because the methyl group in the *o*-position to the amino group creates a sterical obstacle to the interaction of the aldehyde and amino groups. As follows from the above, the statistical distribution of fluorescent fragments in the polymeric chain is the most probable.

Table IGeometrical Parameters of MoleculesA and B and Charges on the Nitrogen Atoms

Molecule	Charge	Band	Length (Å)	Angle, Degree
Α	-0.3341	1-4 4-5 5-3 3-6 6-9	1.39 7.32 1.39 1.28 5.72	$\begin{array}{c} 1-4-5,\ 32\\ 4-5-3,\ 32\\ 5-3-6,\ 50.1\\ 3-6-7,\ 48.2\end{array}$
В	-0.4154	1-5 5-6 6-3 3-8 8-11	$1.39 \\ 4.56 \\ 5.70 \\ 1.29 \\ 5.72$	$\begin{array}{c} 1-5-6,\ 20.6\\ 5-6-7,\ 7.8\\ 7-3-8,\ 50.1\\ 3-8-9,\ 48.2\end{array}$

EXPERIMENTAL

Synthesis of Polymer 1

The solution of 6-amino-1-iminophenalen hydrochloride (0.4594 g, 0.002 mol) in 8 cm³ of N-methylpyrrolidone and the solution of 2,8-diamine-3,7dimethylacrydine hydrochloride (0.5471 g. 0.02 mol) in 10 cm^3 of N-methylpyrrolidone were placed in a four-necked flask fitted with a condenser, a capillary for argon supply, a thermometer, and a drop funnel and heated to 130°C under argon. The solution of terephthaloyl dialdehyde (0.5364 g, 0.004 mol) in 4 cm² of the mixture of N-methylpyrrolidone:p-xylene = 3 : 1 vol was placed in a drop funnel and added dropwise for 3 h to the mixture of the diamine solution, kept at this temperature for 5 h, heated to 180°C for N-methylpyrrolidone distillation, and cooled to room temperature. The beads were filtered off, washed with methanol, extracted by ethanol for 24 h, and dried in a vacuum for 24 h. The mass of beads was 1.24 g (91.2%). $\eta_{\rm red}$ of a 5% solution of the polymer in N-methylpyrrolidone was 0.35 dL/g.

Synthesis of Polymer II

A solution of 5-amino-2-(4-aminophenyl)benzimidazol (0.4256 g, 0.0019 mol) in 1.5 cm² of *N*methylpyrrolidone and a solution of 2,8-diamine-3,7-dimethylacrydine hydrochloride (0.4503 g, 0.0019 mol) in 10 cm³ of *N*-methylpyrrolidone were placed in a four-necked flask fitted with a condenser, a capillary for argon supply, a thermometer, and a drop funnel and heated to 130°C under argon. The solution of terephthaloyl dialdehyde (0.5092 g, 0.0038 mol) in 4 cm² of the mixture of *N*-methylpyrrolidone : *p*-xylene = 3 : 1 vol was placed in a drop funnel and added dropwise for 5 h to the mixture of the diamine solution, kept at this temperature for 5 h, heated to 180°C for *N*-methylpyrrolidone distillation, cooled to 50°C, and poured out in 50 cm³ of methanol. The beads were filtered off, washed with methanol, reprecipitated from *N*-methylpyrrolidone to methanol, and dried in a vacuum for 24 h. The mass of the beads was 0.51 g (40.86%). The $\eta_{\rm red}$ of the 5% solution of the polymer in *N*-methylpyrrolidone was 0.41 dL/g.

Synthesis of Polymer III

A solution of 5-amino-2-(4-aminophenyl)benzimidazol (0.202 g, 0.009 mol) in 1.5 cm² of N-methylpyrrolidone and a solution of 9,9-bis(p-aminophenyl)anthracene (0.325 g, 0.009 mol) in 5 cm³ of N-methylpyrrolidone were placed in a fournecked flask fitted with a condenser, a capillary for argon supply, a thermometer, and a drop funnel and heated to 130°C. The solution of terephthaloyl dialdehyde (0.242 g, 0.0018 mol) in 4 cm² of the mixture of *N*-methylpyrrolidone : *p*-xylene = 3:1 vol was placed in a drop funnel and added dropwise for 3 h to the mixture of the diamine solution, kept at this temperature for 5 h, heated to 180°C for the distillation of 5 cm³ of N-methylpyrrolidone, cooled to 50°C, and poured out in 50 cm^3 of methanol. The beads were filtered off, washed with methanol, reprecipitated from Nmethylpyrrolidone to methanol, and dried in a vacuum for 24 h. The mass of beads was 0.52 g (74.07%). The $\eta_{\rm red}$ of the 5% solution of the polymer in N-methylpyrrolidone was 0.28 dL/g.

Synthesis of Polymer IV

A solution of safranine T (0.3505 g, 0.001 mol) in 10 cm^2 of *N*-methylpyrrolidone and a solution of 9,9-bis(p-aminophenyl)anthracene (0.36 g, 0.001 mol) in 5 cm³ of N-methylpyrrolidone were placed in a four-necked flask fitted with a condenser, a capillary for argon supply, a thermometer, and a drop funnel and heated to 130°C. The solution of 5.5'-methylene-bis-salicylic dialdehyde (0.512 g, 0.002 mol) in 8 cm² of the mixture of N-methylpyrrolidone : p-xylene = 3 : 1 vol was placed in a drop funnel and added dropwise for 3 h to the mixture of the diamine solution, kept at this temperature for 5 h, heated to 180°C for the distillation of 15 cm^3 of N-methylpyrrolidone, cooled to 50°C, and poured out in 50 cm³ of methanol. The beads were filtered off, washed with methanol,

reprecipitated from *N*-methylpyrrolidone to methanol twice, and dried in a vacuum for 24 h. The mass of beads was 0.71 g (79.3%). The $\eta_{\rm red}$ of the 5% solution of the polymer in *N*-methylpyrrolidone was 0.39 dL/g.

Synthesis of Polymer V

Synthesis of Oligomer with Dialdehyde End Groups on the Base of 5-Amino-2-(4-aminophenyl)benzimidazol

A solution of terephthaloyl dialdehyde (0.536 g, 0.04 mol) in 50 cm³ of ethanol and a solution of 5-amino-2-(4-aminophenyl)benzimidazol (2.37 g, 0.01 mol) in 50 cm³ of ethanol placed in a three-necked flask was fitted with a condenser, a capillary for argon supply, and a thermometer, heated to 78°C, kept at this temperature for 3 h, and cooled to 20°C. The beads were filtered off, washed with methanol, and dried in a vacuum for 24 h. The mass of beads was 1.81 g (49.41%).

Found: C, 72.59%; H, 4.47%; N, 14.39%. Calcd for $C_{71}H_{12}N_{48}O_2\cdot 4H_2O;$ C, 72.70%; H, 4.78%; N, 14.33%.

Synthesis of Polymer

A solution of an oligomer (0.7032 g, 0.0006 mol) in 6 cm³ of *N*-methylpyrrolidone-2 and a solution of 2,8 diamine-3,7-dimethylacrydine hydrochloride (0.1641 g, 0.0006 mol) in a mixture of 3 cm³ of *N*-methylpyrrolidone-2 and 2 cm³ of *p*-xylene were placed in a three-necked flask fitted with a condenser, a capillary for argon supply, and a thermometer, heated to 160°C, kept at this temperature for 6 h, cooled to 20°C, and poured out in 50 cm³ of methanol. The beads were filtered off, washed with methanol, reprecipitated from *N*methylpyrrolidone to methanol twice, and dried in a vacuum for 24 h. The mass of beads was 0.21 g (24.83%). The $\eta_{\rm red}$ of a 5% solution of the polymer in *N*-methylpyrrolidone was 0.28 dL/g.

Synthesis of Polymer VI

Synthesis of Oligomer with Dialdehyde End Groups on the Base of 2,8-Diamine-3,7dimethylacrydine Hydrochloride

A solution of terephthaloyl dialdehyde (2.68 g, 0.02 mol) in 50 cm³ of DMF and a solution of 2,8-diamine-3,7-dimethylacrydine hydrochloride (1.275 g, 0.0047 mol) in 100 cm³ of DMF were placed in a three-necked flask fitted with a condenser, a capillary for argon supply, and a thermometer, heated to 50°C, kept at this tempera-

ture for 8 h, distilled to 120 cm^3 of DMF, cooled to 20° C, and poured out in acetone. The beads were filtered off, washed with acetone, and dried in a vacuum for 24 h. The mass of beads was 0.86 g (44.01%).

Found: C, 75.26%; H, 5.25%; N, 10.18%. Calcd for $C_{77}H_{57}N_9O_2\cdot 5H_2O$: C, 75.18%; H, 5.45%; N, 10.25%.

Synthesis of the Polymer

A solution of the oligomer (0.3687 g, 0.0003 mol) in 4 cm³ of *N*-methylpyrrolidone-2 and a solution of 5-amino-2-(4-aminophenyl)benzimidazol (0.0672 g, 0.0003 mol) in a mixture of 1 cm³ of N-methylpyrrolidone-2 and 0.5 cm^3 of *p*-xylene was placed in a three-necked flask fitted with a condenser, a capillary for argon supply, and a thermometer, heated to 150°C, kept at this temperature for 6 h, cooled to 20°C, and poured out in 50 cm³ of methanol. The beads were filtered off, washed with methanol, reprecipitated from N-methylpyrrolidone to methanol twice, and dried in a vacuum for 24 h. The mass of beads was 0.15 g (35.29%). The $\eta_{
m red}$ of the 5% solution of the polymer in N-methylpyrrolidone was 0.28 dL/g. The molecular masses all of polymers, determined by the method of ultracentrifugation, are about 10,000.

The UR spectra were recorded on a UR-20 instrument. The absorption spectra of the solutions of all investigated polymers in N-methylpyrrolidone were recorded at room temperature on a Specord M-40 instrument and the spectra of fluorescence and the excitation of fluorescence on a Jobin Yvon 3CS instrument, ensuring automatic correction of the spectra. The quantum yields of the fluorescence were determined by a relative method.⁴ The solution of 7-amino-4-methylcoumarin with a quantum yield of fluorescence of 0.61 (ref. 5) was used as the standard. For determination of the quantum yield of the fluorescence for donor and acceptor fragments in bifluorophores, their spectra of absorption and fluorescence were resolved into separate bands by the method of Alentsev-Fok.⁶

RESULTS AND DISCUSSION

In Figure 1, the absorption (1,3) and fluorescence (2,4) spectra of the solutions of diamine I (energy donor) and **Y** (energy acceptor) in *N*-methylpyrrolidone-2 are given. From Figure 1, one can see that the field of radiation of diamine I is partially overlapped by the field of absorption of diamine **Y**,



Figure 1 Spectral fluorescent characteristics of solutions of diamines I and Y in N-methylpyrrolidone-2: (1) absorption spectra of diamine I; (2) fluorescence spectra of diamine I (excitation at 410 nm); (3) absorption spectra of diamine Y; (4) fluorescence spectra of diamine Y (excitation at 500 nm).

which confirms the opportunity of nonradiational energy transfer from diamine **I** to diamine **Y**.

In Figure 2, the absorption and fluorescence spectra of the solution of polymer 1 in N-methylpyrrolidone-2 are given. From Figure 2, one can see that in the absorption spectra there are absorption bands of both initial diamines. In the fluorescence spectra of the polymer obtained by excitation at the absorption band of diamine **I**, there are an intensive peak of fluorescence of diamine **I** and a slight intensive peak of fluorescence of the diamine acceptor, which is explained by the rather small field of overlap of the radiation field of the energy donor by the absorption field of the energy acceptor.



Figure 2 Spectral fluorescent characteristics of the solution of polymer 1 in *N*-methylpyrrolidone-2: (1) absorption spectra; (2) fluorescence spectra (excitation at 410 nm).



Figure 3 Spectral fluorescent characteristics of the solutions of diamines III and I in *N*-methylpyrrolidone-2: (1) absorption spectra of diamine III; (2) fluorescence spectra of diamine III (excitation at 348 nm); (3) absorption spectra of diamine I; (4) fluorescence spectra of diamine I (excitation at 410 nm).

In Figure 3, the absorption (1,3) and fluorescence (2,4) spectra of the solutions of diamines **I** and **III** in *N*-methylpyrrolidone-2 are given. From Figure 3, one can see that the field of radiation of the diamine **III** energy donor is almost completely overlapped by the field of absorption of the diamine **I** energy acceptor.

In Figure 4, the absorption and fluorescence spectra of the solution of polymer 2 in N-methylpyrrolidone-2 are given. As follows from the figure, in the case of excitation in the absorption band of the energy donor (diamine **III**), 348 nm in the fluorescence spectra of the polymer solution, an intensive peak of fluorescence of the energy acceptor (500 nm) and a slight intensive peak of



Figure 4 Spectral fluorescent characteristics of the solution of polymer **2** in *N*-methylpyrrolidone-2: (1) absorption spectra; (2) fluorescence spectra (excitation at 348 nm).



Figure 5 Spectral fluorescent characteristics of solutions of diamines III and II in *N*-methylpyrrolidone-2: (1) absorption spectra of diamine III; (2) fluorescence spectra of diamine III (excitation at 348 nm); (3) absorption spectra of diamine II; (4) fluorescence spectra of diamine II (excitation at 410).

fluorescence of the energy donor (420 nm) are observed. It testifies to the effective nonradiational energy transfer in polymer **2**.

In Figure 5, the absorption (1,3) and fluorescence (2,4) spectra of the solutions of diamine III (energy donor) and diamine II (energy acceptor) in *N*-methylpyrrolidone-2 are given. From Figure 5, one can see that the field of radiation of diamine III is largely overlapped by the field of absorption of diamine II, which confirms the correct selection of the initial diamines-fluorophores for the synthesis of polymer 2.

In Figure 6, the absorption and fluorescence spectra of the solution of polymer 3 in N-meth-



Figure 6 Spectral fluorescent characteristics of solution of polymer **3** in *N*-methylpyrrolidone-2: (1) spectrum of absorption; (2) spectrum of fluorescence (excitation at 348 nm).



Figure 7 Spectral fluorescent characteristics of solutions of diamines II and IY in *N*-methylpyrrolidone-2: (1) absorption spectra of diamine II; (2) fluorescence spectra of diamine II (excitation at 410 nm); (3) absorption spectra of diamine IY; (4) fluorescence spectra of diamine IY (excitation at 535 nm).

ylpyrrolidone-2 are given. From Figure 6, one can see that in the absorption spectra of the polymer there are bands of the energy donor and acceptor, which confirms the structure of polymer **3**. The fluorescence spectra of the solution of polymer **3** in *N*-methylpyrrolidone confirms the presence of nonradiational energy transfer in this polymer. For the establishment of the influence of the structure of the intermonomer on the process of energy transfer, 5,5'-methylene-bis-salicylic dialdehyde was used as an intermonomer for the synthesis of polymer **4**.

In Figure 7, the absorption and fluorescence spectra of 9,9-bis(*p*-aminophenyl)anthracene and



Figure 8 Spectral fluorescent characteristics of solution of polymer 4 in N-methylpyrrolidone-2: (1) absorption spectra; (2) fluorescence spectra (excitation at 410 nm).

cafranine T are given. From Figure 7, one can see, that the overlap of the field of fluorescence of 9,9-bis(p-aminophenyl)anthracene by the field of absorption of safranine T is rather great. Because of this, it was possible to expect that in the polymer, on the basis of these diamines (polymer 4), nonradiational energy transfer must have occurred. But it is provided that, even though in the absorption spectrum of the polymer the absorption bands of both diamines are observed, there is only the radiation band of the energy donor in the fluorescence spectra (Fig. 8). Thus, in polymer **4**, nonradiational energy transfer is not observed. It must be connected with the large distance between the centers of fluorescence.

For the study of the influence of the disposition of fluorescent fragments in a polymeric chain on nonradiational energy transfer, the method of polymer synthesis by polycondensation of the oligomer on the basis of the energy donor (diamine **III**) and the diamine energy acceptor (diamine **I**) was developed (polymer **5**):



Then, the synthesis method of the polymer on the basis of the diamine energy donor (diamine **III**) and the oligomer on the basis of the diamine

energy acceptor (diamine I) was carried out (polymer 6). The dialdehyde of terephthalic acid was used as the intermonomer:



(16)

In Figures 9 and 10, the fluorescence spectra of polymers 5 and 6 (where one of the initial substances is an oligomer) and 2 (with statistical disposition of the diamines-fluorophores in the polymer chain) are given. From Figure 10, one can see that in the fluorescence spectra of polymer 5 an intensive band of emission of the energy donor is observed, while a band of emission of the energy acceptor is practically absent. In the radiation spectra of polymer 6, the weak fluorescence bands of the energy acceptor are observed only. So, the most intensive fluorescence band of the

energy acceptor at excitation at an absorption band of the energy donor is observed in the polymer with a statistical distribution of diamines– fluorophores.

Thus, for the first time, poly(Schiff's bases)bifluorophores were synthesized. It was shown that in these polymers nonradiational energy transfer of the electron excitation is realized.

The results of the study will be used for the developing of scientific bases of the synthesis of polymers-bifluorophores, where the selective process of nonradiational energy transfer of electron excitation in the solid and liquid states of polymers is possible. So, the new approach to the decision of one of the fundamental problems of photophysics, the development of methods of the management of processes of energy conversation, will be thus carried out.

The polymers-fluorophores and bifluorophores are prospective for use as active components for liquid and solid lasers and scintillators, especially for the indication of hard radiation, for transformation of short-wave radiation to a long-wave one for transfer of the information on optical fiber communication lines, for increase of capacity of



Figure 9 Absorption spectra of polymer solutions in *N*-methylpyrrolidone-2: (1) polymer **5**; (2) polymer **2**; (3) polymer **6**.

solar batteries, for protection of valuable papers, for manufacturing publicity boards, etc.



Figure 10 Fluorescence spectra of polymer solutions in *N*-methylpyrrolidone-2 (excitation at 348 nm): (1) polymer **5**; (2) polymer **2**; (3) polymer **6**.

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