INFLUENCE OF THE SIGN OF SOLVATOCHROMISM OF MEROCYANINES ON THEIR PHOTOELECTRIC PROPERTIES IN POLYMER FILMS

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It has been established that the intensities of the longwave, electron-absorption bands of merocyanine dyes differing in the sign of solvatochromism redistribute under the action of an external electric field. This is explained by the fact that the probability of vibronic transitions changes under the action of an electric field. It has been revealed that the photoconductivity of poly-N-epoxypropylcarbazole films doped with merocyanines increases with decrease in negative solvatochromism and increase in positive solvatochromism. It is suggested that the more bipolar structure of the excited state of the above-mentioned films in the first case as compared to the structure of these films in the second case is favorable for electron transfer from the poly-N-epoxypropylcarbazole molecules to the dye molecule and the formation of a carbazole cation-radical providing hole conduction in the polymer.

Keywords: vibronic interactions, merocyanine dyes, negative and positive solvatochromism, polymer, photocurrent.

Introduction. Photoconductive films based on poly-N-vinylcarbazole and poly-N-epoxypropylcarbazole with organic additions are widely used as media for recording and modulation of optical radiation [1-6]. Molecules of organic additions contained in the above-indicated films serve as centers of light absorption and photogeneration of charge carriers. As these additions, organic merocyanine dyes, which are among the intraionic compounds, can be used [7]. The end fragment D of their molecules possesses electron-donor properties and the end fragment A possesses electron-acceptor properties. In a molecule, the fragments D and A are linked by a polymethine chain and so the positive charge is partially localized on the fragment D and the negative charge is partially localized on the fragment A. When such a molecule absorbs a light quantum of energy hv, electrons are transferred from the fragment D, through the polymethine chain, to the fragment A. The electron-donor and electron-acceptor properties of the end fragments D and A can be changed by changing their chemical composition. This makes it possible to change the dipole moment of the merocyanine molecule in both the ground state S_0 and in the first excited state S_1 . If the dipole moment of a dye in the S_0 state is lower than that in the S_1 state, this dye possesses positive solvatochromism. This means that the longwave, electron-absorbtion band of the macrocyamine corresponding to the $\pi - \pi^{*}$ transition and polarized along the chain linking the fragments D and A undergoes a bathochromic shift when the solvent polarity increases. This shift is explained by the fact that, in a polar solvent, the state S_1 is more stable than the state S_0 and therefore the energy of the state S_1 decreases more significantly than the energy of the state S_0 . To the contrary, merocyanines, the dipole moment of which in the ground state is larger than that in the excited state, possess negative solvatochromism. Their longwave absorption band undergoes a bathochromic shift when the polarity of the medium increases. This is explained by the fact that, in a polar medium, the energy of the state S_0 decreases more significantly than the energy of the state S_1 . Merocyanines with positive solvatochromism are used to advantage as sensitizers of holographic recording media [6], and merocyanines with negative solvatochromism are used in photorefractive media [8, 9]. However, the de-

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pendence of the photoelectric properties of poly-*N*-vinylcarbazole and poly-*N*-epoxypropylcarbazole compounds containing merocyanines on the sign of solvatochromism of these dyes has not been revealed until the present time. This limits the possibility of selecting dyes for obtaining optical media with definite properties. Therefore, the aim of the present work is a comparative investigation of the electron-absorption spectra and the photoconduction of poly-*N*epoxypropylcarbazole films doped with merocyanine dyes possessing solvatochromism of opposite sign.

Objects, Samples, and Experimental Procedure. We investigated dyed films based on the photoconductive polymer poly-*N*-epoxypropylcarbazole and the nonconductive polymer polyvinylbutyral, containing the merocyanine dyes M1, M2, M3, or M4:



The samples studied were prepared in the form of structures containing a polymer film with a free surface: glass substrate — electrically conducting $SnO_2:In_2O_3$ layer — polymer film, or in the form of sandwich-type structures: glass substrate — electrically conducting $SnO_2:In_2O_3$ layer — polymer film — Al film. The polymer films based on poly-*N*-epoxypropylcarbazole and polyvinylbutyral contained 1 wt.% of the dye M1 or the dyes M2, M3, and M4 with respect to the polymer weight. They were obtained by drying of solutions of poly-*N*-epoxypropylcarbazole + 1 wt.% of (M1–M4) and polyvinyl butyral + 1 wt.% of (M1–M4) in 1,2-dichloroethane and deposited by the method of watering on the glass substrates with an electrically conducting $SnO_2:In_2O_3$ layer. The thickness of the dried films *L* was 1–3 µm. In the process of preparation of samples with a sandwich structure, Al films were deposited by the method of thermal sputtering in a vacuum chamber.

The absorption coefficient κ of the polymer films in the samples with a free surface (free of an Al film) and the change in it were determined with the use of a KSVIP-23 spectral-computational complex. The absorption coefficient of a polymer film in the absence of an external electric field was determined by measuring the intensity of light passing through samples with polymer films of various thickness. In these experiments, samples were alternately positioned behind the exit slit of a monochromator before the entrance window of a photomultiplier such that the plane of their glass substrate was exactly perpendicular to the direction of the incident light. Since samples with polymer films of various thickness were used, the light scattering on their surface was not taken into account. For the purpose of determining the absorption coefficient of a film exposed to an external electric field κ_E , a sample containing a polymer film with a free surface was also positioned between the exit slit of the monochromator and the entrance window of the photomultiplier; however, in the process of recording the intensity of light of a definite wavelength λ passing through the sample, an external electric field was induced in the polymer film by its charging in a corona discharge with the use of a special electron device [6, 10] developed and used for recording holograms by the photothermoplastic method. The strength of the electric field in the film $E = 10^8$ V/m was determined by the free-surface potential measured relative to the potential of the electrically conducting SnO₂:In₂O₃ layer. The change in the absorption coefficient $\Delta \kappa = \kappa_E - \kappa$ of a film under the action of an electric field was determined by comparison of the intensities of light passing through it before and after the electric field was switched on. The monochromator was controlled, the intensity of light passing through the sample was recorded, and the measurement data were processed with the use of a computer forming a part of the KSVIP-23 complex. The relative error in the measurement of the light intensity was $\sim 10^{-5}$. The value of $\Delta \kappa$ at each wavelength of light passing through a sample was determined by averaging the data of ten measurements. The measurements were carried out with the use of an unpolarized and linearly polarized light. In the last-mentioned case, a polarizer with a variable polarization direction was positioned before the entrance slit of

Compound	Solvent	λ ^a _{max} , nm	$\epsilon \cdot 10^{-5}$, liter/(mole·cm)
M1	МС	600	0.839
	DMFA	622	1.066
M2	МС	653	1.260
	DMFA	662	1.493
M3	МС	638	2.199
	DMFA	630	1.544
M4	MC	656	1.682
	DMFA	643	0.947

TABLE 1. Characteristics of Longwave Electron-Absorption Bands of M1-M4 Merocyanine Solutions.

the monochromator in the path of the light beam obtained from a light source and passing though another polarizer and the sample studied. The values of κ and $\Delta \kappa$ were calculated for the light with wavelengths 400–1000 nm corresponding to the longwave absorption bands of the dyes M1–M4 at which poly-*N*-epoxypropyl carbazole and polyvinylbutyral do not absorb light.

For the purpose of measurement of the photocurrent density j_{ph} in the samples with a sandwich structure in the regime of photoresistance, they were exposed, on the SnO₂:In₂O₃ electrode side, to light with $\lambda = 650$ nm corresponding to the absorption band of the dyes M1–M4. The value of j_{ph} was determined as an addition to the density of the dark current experienced by the sample when a voltage is applied across the Al and SnO₂:In₂O₃ contacts. The light intensity I = 0.2-10.0 W/m² was changed with the use of neutral light filters. The electric field strength in the samples with a sandwich structure was changed in the range of $E = 2 \cdot 10^7 - 2 \cdot 10^8$ V/m. The measurements were taken at the temperature T = 293 K at which poly-*N*-epoxypropylcarbazole films can be used as recording media.

The merocyanine M1 was obtained by the reaction of malonodinitrile with hemicyanine 1,3,3-trimethyl-2-[(1E,3E,5E)-6-methyl(phenyl)carboxamido-1,3,5-hexatrienyl)]-3H-indole perchlorate [11] in acetic anhydride medium in the presence of sodium acetate. For the purpose of obtaining barbiturates of M2 and M4, we have synthesized a new hemicyanine ____ *N*-phenyl-*N*-[(1E,3E)-5-(1,3-dimethyl-2,4,6-trioxohexahydro-5-pyrimidinylidene)]-1,3-pentadienyl]acetamide — as a result of interaction of equimolar amounts of dimethylbarbituric acid with N-[(1E,3E)-5phenylimino-1,3-pentadienyl]aniline hydrochloride in acetic anhydride medium. The yield was 53% at $T_{\text{melt}} = 230^{\circ}$. The hemicyanine used for obtaining the dye M3 was synthesized by the reaction of malonodinitrile with N-[(1E,3E)-5-phenylimino-1,3-pentadienyl]aniline hydrochloride in acetic anhydride medium with a yield of 62% at $T_{melt} = 146-$ 147°. The merocyanines M2–M4 were obtained by the reaction of the corresponding hemicyanines with quaternary salts (1,2,3,3-tetramethylindole tetrafluoroborate for M2 and 2-methyl-1,3-dephenylbenzimidazole chloride for M3 and M4) in dehydrated ethanol medium in the presence of triethylamine. The yields (%) of the merocyanines M1-M4 and their T_{melt} (°C) were respectively 24 and 194–195, 36 and 190–191, 18 and 208–210, and 19 and 217–219. The structures of all the compounds are supported by their ¹H NMR spectra. The dyes obtained were carefully purified by chromatography in alumina oxide. The purity was controlled by the method of thin-layer chromatography. The maxima λ_{max}^{a} and the molar extinction ratios ϵ of the longwave, electron-absorption bands of the merocyanines M1–M4 in the low-polar methylene chloride and the high-polar dimethyl formamide are presented in Table 1.

Experimental Results. The absorption of poly-*N*-epoxypropylcarbazole and polyvinylbutyral film containing 1 wt.% of the dyes M1–M4 was determined by the electron absorption of the dyes (Table 1). One absorption band was detected for each merocyanine considered. It has been revealed that the intensities of the shortwave and longwave regions of the absorption bands of the dyes M1–M4 in the absorption spectra of the dyed films of both photoconductive poly-*N*-epoxypropylcarbazole and nonphotoconductive polyvinylbutyral redistribute under the action of an external electric field, with the result that positive and negative maxima appear on the dependence $\Delta \kappa(\lambda)$ (Fig. 1). After the electric field is switched off, the intensity of light passing through a sample with a polymer film and, consequently, its absorption spectrum was restored. It is significant that the dependences $\Delta \kappa(\lambda)$ of the polymer films containing merocyanines with positive solvatochromism and polymer films containing microcyanines with negative solvatochromism differ markedly. In the absorption band of the dyes M1 and M2 possessing positive solvatochromism, the intensity of the short-



Fig. 1. Electron-absorption spectra of poly-*N*-epoxypropylcarbazole films with 1 wt.% of M1 (1) and 1 wt.% of M4 (2) and change in spectra 1 (3) and 2 (4) under the action of an electric field.

Fig. 2. Dependence of log $j_{\rm ph}$ on $E^{1/2}$ in Al — poly-*N*-epoxypropylcarbazole samples with 1 wt.% of M1 — SnO₂:In₂O₃ (1) and 1 wt.% of M4 — SnO₂:In₂O₃ (2), I = 10 W/m².

wave region decreases and the intensity of the longwave region increases under the action of an electric field. This effect is more pronounced for M1 than for M2. It should be noted that the absorption spectrum of M1 undergoes a larger bathochromic shift (its solvatochromism volume is larger) as compared to that of M2 (Table 1). When passing from the dyes M1 and M2 to the dyes M3 and M4 possessing negative solvatochromism, the order in which maxima and minima on the dependence $\Delta \kappa (\lambda)$ alternate changes. The intensity of the shortwave region of the absorption band of the dyes M3 and M4 increases and the intensity of the longwave region decreases under the action of an electric field. This affect is also directly proportional to the increase in the solvatochromism volume when passing from M3 to M4. An electric field exerts the strongest influence on merocyanine M1 whose solvatochromism is highest and the weakest influence on dye M3 whose solvatochromism is lowest.

The spectral effects manifested by films with merocyanines M1–M4 under the action of an electric field were observed for both polarized and unpolarized light. The intensity of light passing through a sample with a polymer film changes when the plane of the polarizer or of the analyzer rotate; however, the relative value of this change is independent of the electric field applied to the sample. This effect was observed when the angle between the plane of the sample and the direction of the incident light changed from 0 to 45°. When an external electric field was switched on and switched off, the time of change in the intensity of light passing through a plane sample with a polymer film in the direction of the field lines was the same for all the samples studied with poly-*N*-epoxypropylcarbazole or poly-vinylbutyral films with dyes M1–M4. This points to the fact that the effects detected depend weakly on the geometric size of the dye molecule and the viscosity of the polymer.

A photocurrent was detected in samples of sandwich structure with poly-*N*-epoxypropylcarbazole films containing 1 wt.% of (M1–M4), unlike samples with polyvinyl butyral films containing 1 wt.% of (M1–M4). The dependences $j_{ph}(E)$ are linear in log $j_{ph}-E^{1/2}$ coordinates (Fig. 2). The slope of these dependences is the same for all the samples studied. This allows us to suggest that, for poly-*N*-epoxypropylcarbazole films with M1–M4, the dependence $j_{ph}(E)$ can be represented in analytical form as $j_{ph}(E) \sim \exp(-(W_{0ph} - \beta E^{1/2})(T^{-1} - T_0^{-1})/k)$. This expression defines the process of photogeneration of charge carriers in photogeneration centers in poly-*N*-epoxypropylcarbazole [10, 12]. Here, W_{0ph} is the photogenerated electron-hole pair, *k* is the Boltzmann constant, and T_0 is the characteristic temperature, which is equal to 490 ± 20 K for films based on poly-*N*-epoxypropylcarbazole [10]. The coefficient β calculated from graphs $j_{ph}(E)$ in coordinates log $j_{ph}-E^{1/2}$ is equal to $(4.3 \pm 0.1)\cdot10^{-5} \text{ eV}\cdot(\text{V/m})^{-1/2}$; this value is close to the theoretical value of the Pool–Frenkel constant [10, 11]. However, the value of j_{ph} regularly decreases at constant values of *E*, *L*, and *I* when passing from samples with M1 to samples with M2–M4 in the same sequence in which the positive solvatochromism (dyes M1 and M2) decreases and the negative solvatochromism (M3 and M4) increases. The largest difference in photocurrent has been revealed for samples with poly-*N*-epoxypropylcarbazole films containing 1 wt.% of M1 or 1 wt.% of M4 (Fig. 2), for which the largest solvatochromic shifts opposite in sign have been detected. The independence of $\Delta \kappa(\lambda)$ on the light polarization and the angle between the light propagation direction and the external electric field lines points to the fact that the effect of an electric field on the absorption spectra of the compounds studied is not due to intermolecular orientation processes of the type of Kerr or Freedericksz effects [13] but due to intramolecular processes of electron-density redistribution, because an electric field causes analogous changes in the absorption spectrum of poly-*N*-epoxypropylcarbazole capable of photogeneration and charge transfer and in the spectrum of polyvinylbutyral in which photoconduction is absent. To analyze the changes in the electron structure of merocyanines under the action of an external electric field and of a solvent, we will use the scheme of neutral D–A and bipolar D^+-A^- boundary structures. A charged structure should interact with molecules of a polar solvent more strongly than a neutral one. Therefore, the energy of that state in which this structure prevails will decrease more significantly than the energy of the state with a larger contribution of the neutral structure. The positive solvatochromism of the compounds M1 and M2 points to the fact that their structure in the ground state is close to the D–A structure (formulas M1 and M2) and their structure in the excited state is close to the D⁺–A⁻ structure (formulas M1a and M2a):



Therefore, the energy of the ground state of these compounds decreases more significantly than the energy of the excited state under the action of a polar medium. The reverse situation was observed for merocyanines M3 and M4 possessing negative solvatochromism. The structures of these compounds in the ground state correspond to formulas M3a and M4a, and, in the excited state, to formulas M3 and M4.

A dye molecule exposed to an external electric field is found between the positive and negative electrodes. This should lead to a shift of the electron density in the chromophore from the fragment D to the fragment A. It may be suggested that the ground state of M1 and M2 molecules is polarized in the field and, because of the shit of the electron density in the molecules, will become, at least, partially bipolar. Consequently, it will approach the excited state of these molecules with a boundary structure. Therefore, the equilibrium internuclear distances in merocyanines with positive solvatochromism (M1 and M2) increase under the action of an external electric field as a result of excitation of their molecules. As a consequence, the probability of vibronic transitions to higher vibrational levels in these molecules decreases and the probability of 0–0 transitions increases, and, in the experimental spectra, the intensity of the shortwave edge of the absorption band decreases and the intensity of the longwave edge increases.

The conclusion that an external electric field changes the charge distribution in a dye in the ground state was made on the basis of the fact that the value of $\Delta \kappa$ is independent of the field if this field is applied simultaneously with illumination of the sample by light or immediately before the illumination and the measurement of $\Delta \kappa$ and κ .

In the merocyanines with negative solvatochromism (dyes M3 and M4), an external electric field polarizes the ground state of the molecules and, in doing so, enhances their bipolar structure. This, in turn, increases the difference between the structure of the molecules in this state and the neutral, boundary structure of these molecule in the excited state. As a result, the equilibrium, internuclear distances increase under excitation, which enhances vibronic interactions and, therefore, unlike dyes M1 and M2, increases the probability of transitions to higher vibrational levels and decreases the probability of purely electron transitions. As a consequence, the intensity of the shortwave region of the absorption band increases and the intensity of the longwave region decreases.

The above-described approach to the interpretation of changes in the absorption spectra of compounds under the action of a solvent and an electric field can also be used for explaining the decrease in the photoconduction of

Dye	НОМО	LUMO
M1	-8.095	-1.427
M2	-8.111	-1.585
M3	-7.946	-1.348
M4	-7.921	-1.419

TABLE 2. Energies (eV) of the HOMOs and LUMOs of Merocyanines M1-M4 Calculated by the AM1 Method.

poly-*N*-epoxypropylcarbazole films when M2–M4 are used in them, instead of M1, as the photogeneration centers. The electron density in a dye molecule redistributes when this molecule absorbs a light quantum of energy $h\nu$. A merocy-anine molecule becomes more reactive and can capture an electron from a poly-*N*-epoxypropylcarbazole molecule and, in doing so, form an electron-hole pair. The process of photogeneration of electron-hole pairs in poly-*N*-epoxypropylcarbazole films with M1–M4 involves intermolecular reactions with electron transfer:

$$Cz + (D - A) \xrightarrow{hv} Cz + (D^{+} - A^{-})^{*} \longrightarrow Cz^{+\bullet} + (D - A)^{-\bullet}, \qquad (1)$$

$$Cz + (D^{+} - A^{-}) \xrightarrow{hv} Cz + (D - A)^{*} \longrightarrow Cz^{+\bullet} + (D - A)^{-\bullet}, \qquad (2)$$

where Cz is the carbazole ring of poly-*N*-epoxypropylcarbazole; $(D^+-A^-)^*$ and $(D-A)^*$ are excited dye molecules; $Cz^{+\bullet}$ and $(D-A)^{+\bullet}$ are a carbazole cation-radical and a dye anion-radical which form an electron-hole pair. An electron-hole pair is formed as a result of the transition of an electron from the highest occupied molecular orbital (HOMO) of Cz to the HOMO of $(D^+-A^-)^*$ or $(D-A)^*$ of the merocyanine. The energies of the HOMOs of dyes M1– M4 differ insignificantly, which is seen from Table 2, in which the results of our calculations of the energies of the HOMO and the lowest unoccupied MO (LUMO) of the merocyanines M1-M4 by the AM1 method [14] are presented. This means that the decrease in j_{ph} , when passing from samples with dye M1 to the samples with dye M4, is not due to the change in the potential barrier to the electron transition between the HOMOs of Cz and the dye [10]. At the same time, reactions (1) and (2) of these dyes differ significantly at the stage of formation of C $\stackrel{+\bullet}{Z}$. In reaction (1), $Cz^{+\bullet}$ is formed as a result of the transition of an electron from Cz to a positively charged electron-donor pair $(D^+ - A^-)^*$, and in reaction (2) it is formed as a result of the transition of an electron from Cz to a practically neutral electrondonor pair (D-A)*. Therefore, it may be suggested that, due to the electrostatic attraction of an electron to the positively charged fragment D^+ of the merocyanine, the probability of formation of $Cz^{+\bullet}$ in reaction (1) is higher than in reaction (2). Since C $\stackrel{+\bullet}{2}$ is a hole charge carrier and these carriers are mobile in poly-N-vinylcarbazole and poly-Nepoxypropylcarbazole films and create a photocurrent in them [10, 12], the photoconduction increases with increase in the probability of formation of $Cz^{+\bullet}$.

Conclusion. An external, constant electric field of strength 10^8 V/m causes an intramolecular redistribution of the electron density in an organic dye in the ground state, with the result that its polarizability and the probability of vibronic transitions in the case of absorption by it of light quanta changes. Therefore, it may be suggested that in organic dyes exposed to an electric field of fairly high strength there can arise nonlinear optical effects even at low intensities of the absorbed light. In this respect, merocyanines appear to have considerable promise since they are highly sensitive to an external electric field, including the microsurrounding field. These factors also influence the intermolecular processes of electron phototransfer, giving birth to change carriers moving in dyed photoconductive polymers. In deciding on the effective photogeneration centers from among intraionic compounds, preference should be given to merocyanines with positive solvatochromism since they can serve to increase the photogeneration of electron-hole pairs.

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