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CONDENSED-MATTER SPECTROSCOPY

Specific Features of the Radiative Relaxation of Excited States of Polymethine Dyes of Different Ionicity in Films of Photoconductive and Nonphotoconductive Polymers

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Abstract—The spectral and luminescent properties of film composites based on photoconductive poly-N-epoxipropylcarbazole and nonphotoconductive polyvinylbutyral with admixtures of cationic and anionic polymethine dyes, as well as the effect of an external magnetic field on these properties, are studied. It is found that the magnetic field affects the intensity and kinetics of the delayed fluorescence and recombination luminescence of the cationic dye in photoconductive films. This is explained by specific features of photogeneration of charge pairs, namely, by the participation of the singlet and triplet excited states of dye molecules in this process, as well as by the singlet–triplet conversion in dye molecules and photogenerated charge pairs.

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INTRODUCTION

Photosensitive polymer semiconductors are attracting attention due to the possibility of their practical use in creating electroluminescent devices [1, 2] and solar sells [3, 4], and well as for some other applications [5]. For these purposes, it is important to create materials with highly efficient generation and transport of charge carriers. One can consider photoconductive polymer films doped with ionic polymethine dyes (PDs) as promising materials [6, 7].

Investigations [6, 7] showed that the photogeneration of charge carriers in these colored polymer systems includes both the stage of photogeneration of electron–hole pairs (EHPs) and the stage of their dissociation into free charge carriers under the action of an external electric field [8]. The EHP formation and recombination occur with participation of excited electronic states of the dye molecule. An increase in the excited state lifetime leads to a higher probability of formation of charge carriers. In this connection, an important factor is the nature of the spin state of a dye molecule after its photoexcitation [9, 10]. In [7, 11], it has been shown that accumulation of dye molecules in the triplet state leads to an increase in the photocurrent density. However, the question of the influence of the triplet states of PDs on photoprocesses in photoconductive polymers has not been discussed in the literature.

The aim of the present work is to investigate the role played by triplet excited states of PDs of different ionicity in photogeneration of charge carriers in photoconductive films based on poly-N-epoxipropylcarbazole (PEPC) with hole conductivity compared to the films of nonphotoconductive polyvinylbutyral (PVB).

EXPERIMENTAL

We used cationic (PD1) and anionic (PD2) polymethine dyes as centers of photogeneration of charge carriers. PEPC and PVB were used as polymer matrices with photoconductive and nonphotoconductive properties. The structural formulas of PDs and monomer units of PEPC and PVB are given in Fig. 1. The concentration of dyes in PEPC and PVB films was 1% with respect to the polymer weight. The colored polymer films were obtained as a result of drying of ethanol solutions of PVB + 1 wt % PD1, PVB + 1 wt % PD2, PEPC + 1 wt % PD1, and PEPC + 1 wt % PD2 deposited on a glass surface.

The samples were photoexcited by the second harmonic of an LCS-DTL-374QT neodymium laser (the wavelength is $\lambda = 532$ nm, the pulse duration is $\tau = 7$ ns, and the pulse energy is 20 μJ). The spectral–kinetic characteristics were measured in the photon counting regime. Emission intensity I was measured 10 μs after switching off the exciting light. The signal

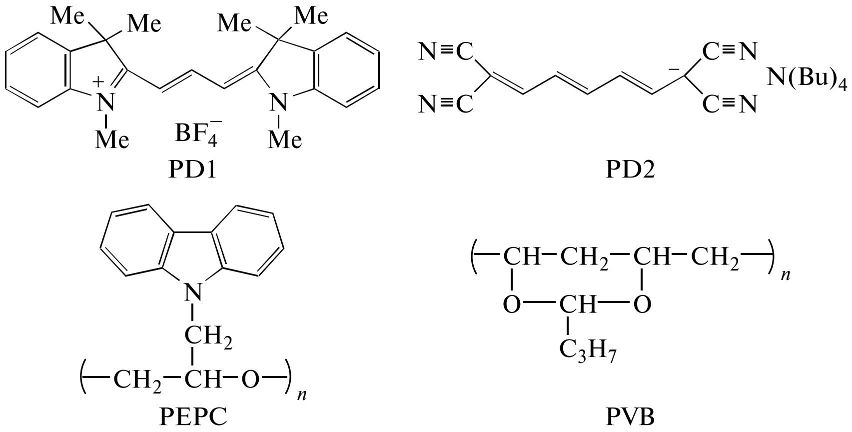

Fig. 1. Structural formulas of PD1 and PD2 molecules and PVB and PEPC monomer units.

at each time interval was accumulated as the number of electronic pulses arrived from the photomultiplier. To obtain a satisfactory kinetic signal from a sample, the number of accumulated pulses was no less than 500 (on average, 1000). The spectral–kinetic measurements were performed at different temperatures T both with and without a magnetic field. For measurements at different temperatures, the sample under study was placed in a vacuum optical cryostat. The temperature was controlled using a copper–constantan thermocouple. External magnetic field strength B was changed within the range of 0–0.5 T. The magnetic effect was estimated as a relative change in the emission intensity in the magnetic field with respect to the case without magnetic field by the formula $g(B) = (I_B - I_0)/I_0$, where I_B and I_0 are the long-lived fluorescence intensities in the presence and absence of field, respectively.

Quantum-mechanical calculations were performed by the DFT/B3LYP method with the 6-31G(d,p) basis set using the PC Gamess/Firefly program package.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 shows the absorption and fluorescence spectra of PD1 and PD2 ethanol solutions. The characteristics of the absorption and fluorescence spectra of these dyes in ethanol and PVB and PEPC polymer matrices are given in Table 1.

The absorption and fluorescence bands of the dyes in polymer films are shifted to longer wavelengths with respect to the spectra in ethanol. The largest shift is observed for PEPC.

PVB and PEPC films doped with PD1 and PD2 exhibit delayed fluorescence (DF) under excitation by laser pulses at a wavelength of 532 nm. The DF spectra coincide with the corresponding fluorescence spectra of dyes in polymers under steady-state photoexcitation. Figure 3 presents the DF decay curves of dyes in polymer films. By comparing curves *1* and *2* in Fig. 3, one can see that the DF of cationic PD1 in PEPC decays more slowly than in PVB. The lifetime calculated from the long-lived region of the kinetic curves is 1.5 and 2.5 ms for PVB and PEPC, respectively. The fluorescence duration of anionic PD2 in PVB and PEPC is almost identical, ~0.6 ms.

To understand why the DF lifetimes of PD1 and PD2 are different in different polymer films, we performed quantum-mechanical calculations of PD1 and PD2 molecules and of N-methylcarbazole (Cz-NMe) as a model PEPC monomer. The calculated energies of the highest occupied molecular orbital (HOMO) for Cz-NMe, PD1, and PD2 are –5.328, –8.093, and –2.22 eV, respectively. Since the PD1 HOMO energy is lower than the energy of the Cz-NMe HOMO, an electron can be easily transferred from the Cz-NME HOMO to the incompletely occupied HOMO of the excited PD1 molecule. This electron transition results in the formation of an EHP, the cation–radical of the carbazole fragment and the electrically neutral radical of PD1. Conversely, the energy of the PD2 HOMO is much higher than the energy of Cz-NMe HOMO, because of which the electron transition from Cz-

Table 1. Maxima of the absorption ($\lambda_{\max}^{\text{abs}}$) and fluorescence ($\lambda_{\max}^{\text{fl}}$) spectra of polymethine dyes in ethanol solution and polymers

Dye	Medium	$\lambda_{\max}^{\text{abs}}$, nm	$\lambda_{\max}^{\text{fl}}$, nm
PD1	Ethanol	545	565
	PVB	555	585
	PEPC	563	600
PD2	Ethanol	535	570
	PVB	550	605
	PEPC	577	615

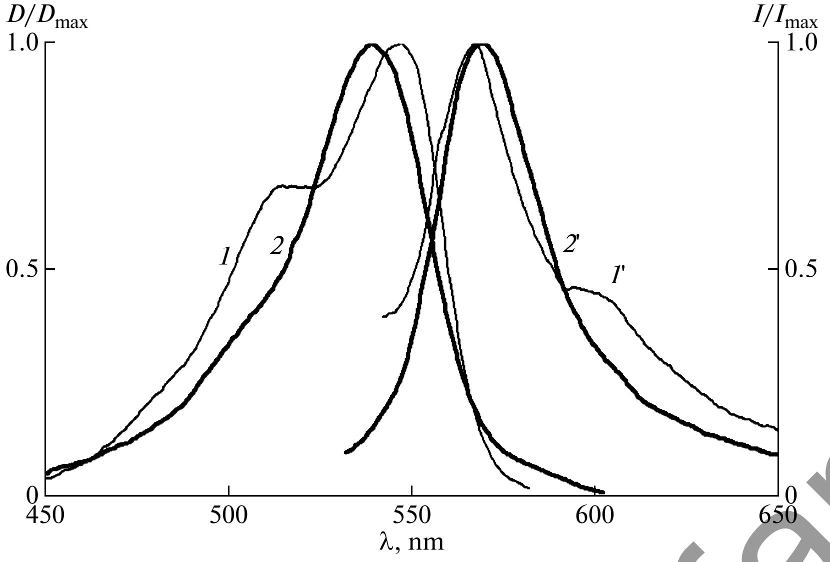

Fig. 2. Absorption (*1*, *2*) and fluorescence (*1'*, *2'*) spectra of ethanol solutions of PD1 (*1*, *1'*) and PD2 (*2*, *2'*). The concentration of dyes is 10^{-5} mol/L.

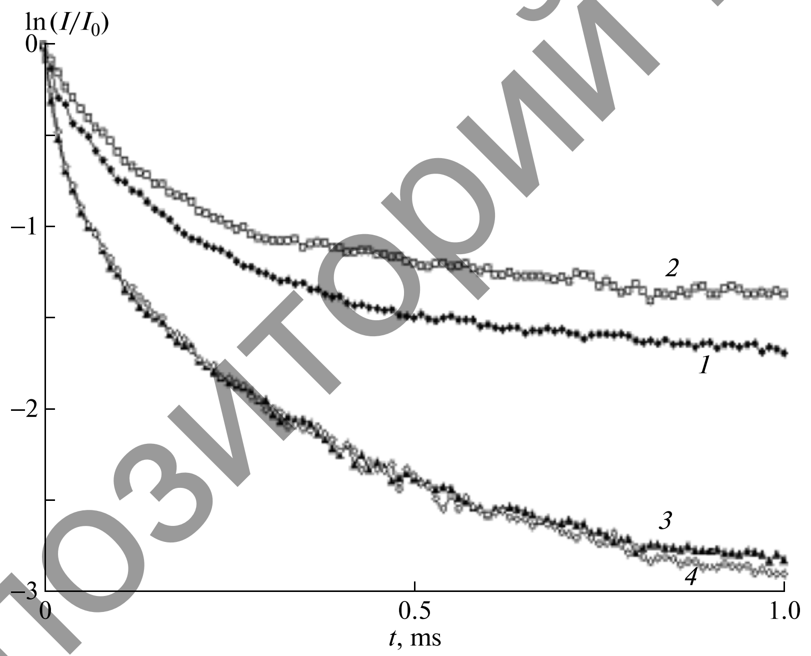

Fig. 3. DF decay kinetics of PD1 (*1*, *2*) and PD2 (*3*, *4*) in PVB (*1*, *3*) and PEPC (*2*, *4*) films.

NMe to the excited PD2 molecule is impossible. Therefore, there is no photogeneration of EHPs in this case. Thus, the difference in the DF lifetimes of anionic PD2 in PEPC and PDV films is caused by the possibility of EHP photogeneration in PEPC films and the absence of such a possibility in PVB films. The equivalence of the DF lifetimes of anionic PD2 in PVB and PEPC films can be explained by the absence of EHP photogeneration. However, it should be noted that the DF lifetime in films with PD1 and PD2 considerably exceeds the lifetime of singlet excited states of organic dyes. Therefore, to clarify the reasons for the delay of PD1 and PD2 excitation relaxation, we performed more detailed investigations.

Let us assume that the long-lived fluorescence of PD1 and PD2 involves triplet excited states. However, the triplet state quantum yield in polymethine dyes is low [12, 13]. To understand the nature of the long-lived fluorescence observed in PEPC and PVB films with cationic PD1 and anionic PD2, we studied long-lived fluorescence in colored PVB films with an admixture of KI salt. It was found that PD1 and PD2 in PVB with KI exhibit both DF and phosphorescence. The maxima of the PD1 and PD2 phosphorescence spectra are given in Table 2. The phosphorescence duration calculated from the exponent of the long-time tail ($t > 0.5$ ms) of the kinetic curve for PD1 in PVB is 0.43 ms, which is close to the 0.52-ms phosphorescence lifetime for this dye reported in [13].

We may assume that the complex shape of the phosphorescence kinetic curve is caused by inhomogeneous broadening of the triplet levels of dyes, which is typical for inhomogeneous solids [14]. The DF kinetic curves of dyes in PVB with KI are close in shape to the phosphorescence curves. The DF and phosphorescence lifetimes in dyes almost coincide. This allows us to conclude that the DF of dyes in polymers relates to the reverse intersystem crossing from the T_1 to the S_1 state. The probability of this process is rather high, since the S_1–T_1 splitting energy calculated from the peaks of the DF and phosphorescence spectra is about 5000 cm^{-1} [15].

Thus, the spectral and kinetic measurements show that the long-lived emission of PVB and PEPC films doped with PD1 and PD2 is associated with the intersystem crossing from the triplet T_1 state to the lowest excited singlet S_1 state followed by the emission of a photon. A slower emission decay of PD1 in PEPC than in PVB (Fig. 3) can be explained by the formation and recombination of EHPs in PEPC films [6]. The identity of the emission decay curves of PD2 in PEPC and PVB films (Fig. 3) confirms that the anionic dye is the center of EHP photogeneration neither in the PEPC polymer film with the hole conductivity nor in the nonphotoconductive PVB polymer matrix. This means that the emission of the PD1 dye in PEPC contains a contribution of the EHP recombination luminescence (RL).

The RL characteristics for cationic PD1 in PEPC were studied below room temperature. A decrease in temperature slows down the EHP recombination to a rate corresponding to the time resolution of our system of luminescence excitation and recording. In addition, according to [15], a decrease in temperature should reduce the contribution of thermally activated DF to the total emission intensity.

To determine the role played by the triplet state in the EHP formation and recombination in PEPC films with PD1, we studied the RL decay kinetics in comparison with the phosphorescence decay kinetics. Figure 4 shows the decay curves of both emission types of cationic PD1 in PEPC with admixture of a heavy atom (KI salt). Analysis of the curves shows that, in the time interval 0–0.6 ms, the RL decays with a lower rate than does the phosphorescence.

It is known that an external magnetic field does not affect the thermally activated DF from T_1 to S_1 [16]. Investigations of the long-lived emission of cationic PD1 and anionic PD2 in a magnetic field showed that the magnetic field exerts no effect on the DF of these dyes in PVB. An effect of magnetic field on the DF in PEPC films with anionic PD2 was not observed either. However, this effect manifested itself in PEPC films with cationic PD1.

Table 2. Phosphorescence maxima ($\lambda_{\max}^{\mathrm{fl}}$) and phosphorescence ($\tau_{\mathrm{ph}}$) and DF ($\tau_{\mathrm{DF}}$) lifetimes, as well as energy difference between the lowest excited singlet and triplet states ($\Delta E_{S_1-T_1}$), for PD1 and PD2 polymethine dyes in PVB films

Dye	$\lambda_{\max}^{\mathrm{fl}}$, nm	τ_{ph}, ms	τ_{DF}, ms	$\Delta E_{S_1-T_1}$, cm^{-1}
PD1	755	0.43	0.35	4685
PD2	735	0.39	0.37	4510

Figure 5a presents dependences $g(B)$ in PEPC samples with cationic PD1 at a temperature of 100 K. We observed a negative magnetic field effect, $g = 26\%$ for $B \sim 0.5$ T. At recording times $t_{\mathrm{rec}} > 0.25$ ms, the magnetic effect does not depend on the time of signal recording. Because of this, to determine $g(B)$, we used instantaneous long-lived luminescence intensities at 0.5 ms after the laser pulse termination. At shorter times, value $g(B)$ depends on t_{rec}. Figure 5b shows an enhancement of the magnetic effect with increasing t_{rec} in the initial kinetic curve region.

The magnetic field effect in PEPC films with cationic PD1 depends on temperature. Figure 6 shows the temperature dependences of the RL intensity and $g(B)$ measured at $B = 0.47$ T. The magnetic field effect becomes weaker with increasing T. In the presence of a heavy atom, parameter $g(B)$ decreases, but its temperature dependence has qualitatively the same behavior. Curve *2* in Fig. 5b shows the time dependence of the magnetic field effect in films PEPC + 1 wt % PD1 with a heavy atom. This dependence has a complex shape. In the range of a fast phosphorescence and RL decay, the magnetic field effect is positive. At $t = 0.05$ ms, $g(B)$ changes its sign and the maximum value of the negative magnetic effect is observed at $t = 0.6$ ms. Then, $g(B)$ begins to decrease. It should be noted that the magnetic effect decreases in the presence of a heavy atom. For example, the maximum value of the negative magnetic effect is 26%, while this value in the presence of a heavy atom is 6%.

The occurrence of long-lived RL in PEPC films with cationic PD1 testifies to the participation of triplet dye molecules in the EHP formation. In these films, the EHP recombination rate is lower than the decay rate of the triplet states of the PD1 molecule. This is especially pronounced at the initial stage of the RL decay kinetics. The EHP formation and recombination is also evidenced by the magnetic field effect on the RL properties. The magneto-sensitive stage is the

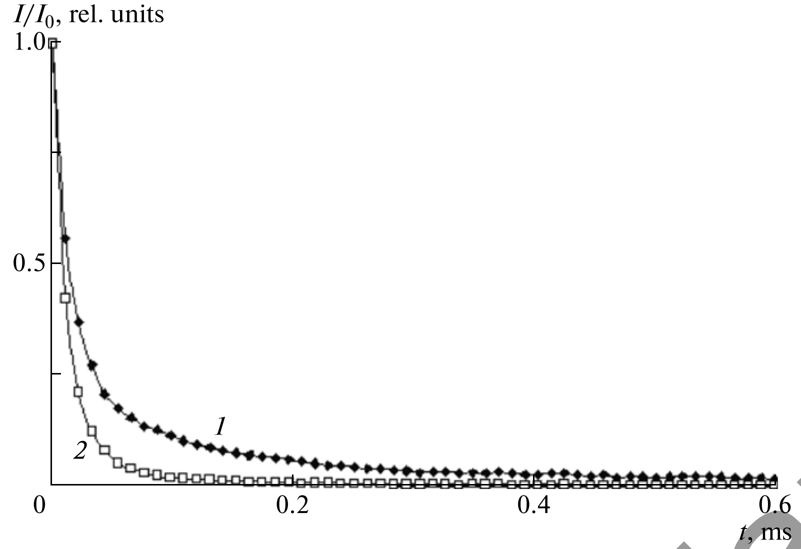

Fig. 4. RL (*1*) and phosphorescence (*2*) intensities of a PEPC + 1 wt % PD1 film with a heavy atom at a temperature of 100 K.

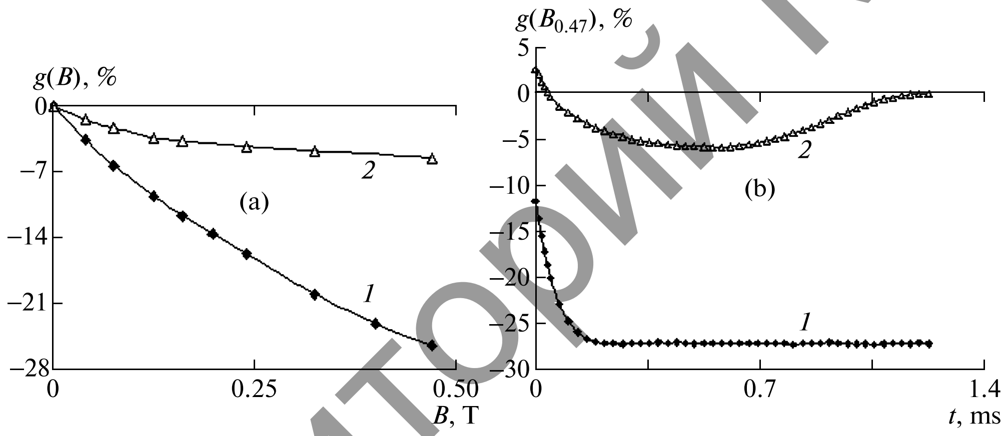

Fig. 5. (a) Effect of a magnetic field on the long-lived luminescence and (b) time dependence of magnetic effect (b) in PEPC + 1 wt % PD1 films (*1*) without and (*2*) with a heavy atom.

singlet–triplet conversion of EHPs. The decrease in the RL intensity shows that EHPs are formed mainly through the triplet channel ($S_1 \longrightarrow T_1 \longrightarrow T_{\mathrm{EHP}}$). The magnetic field decreases the probability of recombination of triplet EHPs and increases the probability of their dissociation to free charge carriers. The absence of RL and magnetic field effect in PEPC films with anionic PD2, as well an in PVB films with cationic PD1 and anionic PD2, indicates that all radiative processes in these films are determined only by intramolecular transitions in dye molecules.

The time dependence of the magnetic effect at the initial stage of the luminescence decay kinetics in PEPC films with cationic PD1 can be caused by the participation of EHPs formed by dye molecules in the S_1 state. At a strong quenching of triplet states by molecular oxygen, we observed an increase in the fluorescence intensity of PD1 in PEPC in a magnetic field. Similar data were obtained in [8]. Along with the S_1 molecules that appeared as a direct result of light absorption, the EHP formation may involve molecules that undergo the intersystem crossing transition from the T_1 state. The competition between the positive and negative magnetic effects leads to the time dependence of $g(B)$.

It is known that an external heavy atom increases the possibility of intersystem crossing transitions between singlet and triplet states [17]. In the presence of a heavy atom, the number of S_1 molecules returning from the T_1 state increases, which leads to the positive magnetic effect in the initial part of the RL kinetic curve in PEPC films with cationic PD1 (Fig. 5b, curve *2*). The strong positive magnetic effect in the presence of a heavy atom increases the time for which the negative magnetic effect reaches its maximum in comparison with the case without the external heavy atom effect. A

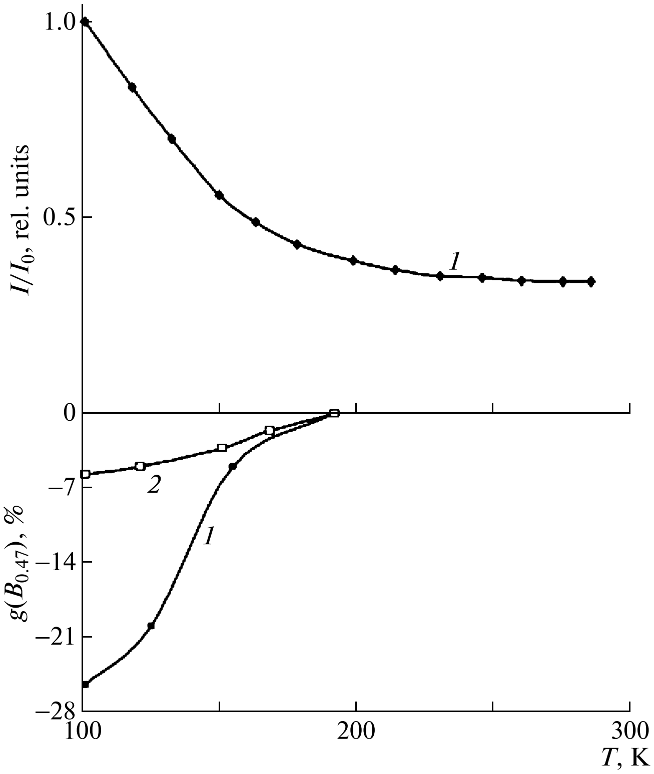

Fig. 6. Temperature dependences of the magnetic effect at $B = 0.47$ T and of the RL intensity in PEPC + 1 wt % PD1 films (*1*) without and (*2*) with a heavy atom.

decrease in $g(B)$ that is observed in 0.6 ms is obviously related to weakening of RL on the background of the thermally activated DF.

The observed temperature dependence of the RL intensity and the magnetic effect points to the different roles of singlet ($S_1 \longrightarrow S_{\mathrm{EHP}}$) and triplet ($S_1 \longrightarrow T_1 \longrightarrow T_{\mathrm{EHP}}$) channels in the EHP formation and recombination. An increase in temperature can lead to an enhancement of the triplet channel of EHP recombination due to an increase in the probability of the nonradiative process $T_1 \rightsquigarrow S_1$. In addition, an increase in temperature can lead to nonradiative degradation of triplet EHPs.

CONCLUSIONS

In PVB and PEPC films doped with cationic and anionic polymethine dyes, photoexcitation into the absorption band of dyes leads to the appearance of DF related to the reverse intersystem crossing from the lowest triplet state to the excited singlet state. The polymer films with a heavy atom demonstrate time-dependent phosphorescence spectra.

The radiative relaxation of excited states of the polymethine dyes of different ionicity in the nonphotoconductive PVB films occurs with participation of intramolecular transitions alone. No effect of a magnetic field on the processes of radiative relaxation in these films was observed. In PEPC films with hole conductivity and cationic PD1, the EHP formation and recombination is an additional channel of relaxation of excited states, which manifests itself in RL contributing to the total emission intensity. In an external magnetic field, the RL intensity decreases. The maximum magnetic effect is 26% at a magnetic field induction of 0.47 T. The magnetic effect is time-dependent due to the competition between the singlet and triplet channels of EHP formation. The role of the singlet channel is enhanced in the presence of a heavy atom due to increasing rate of the triplet–singlet transitions in the dye molecules. In the PEPC films with anionic PD2, RL is not observed due to the impossibility of EHP formation. Because of this, as well as in PVB films with this dye, magnetic field exerts no effect on the radiative relaxation of the excited states of dye molecules.

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