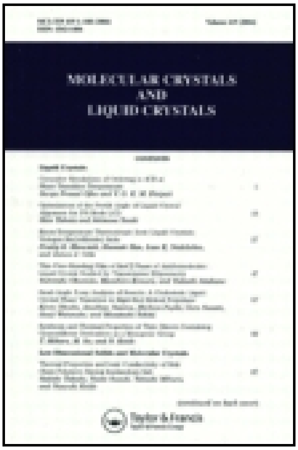

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THE STUDY OF THE PROPERTIES OF ORGANIC BULK MATERIALS BASED ON THE NEW KNOWLEDGE OF THEIR RADIOLUMINESCENCE MECHANISM

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Abstract The correlation between the radioluminescence characteristics of bulk organic materials and theirs structure features is discussed. It is shown, that using the results of the radioluminescence study, one can investigate not only the luminescent properties of a material, but the charge transport in it and its some structure features as well.

Keywords: radioluminescence, charge transport, organic crystal, ionizing

INTRODUCTION

For organic molecular system the radioluminescence is caused by luminescence of molecules excited in the recombination process of charge carriers generated by ionizing radiation. The luminescent process, which is going inside a track of ionizing particle is differ from that which is going outside it. The formation of the radioluminescence pulse is finished under the action of light - collection process. All these processes possess their own characteristic features. Therefore the latter process as well as the delayed and prompt radioluminescence needs the individual analysis.

The radioluminescence phenomenon usually was studied only as an aim of scientific or technical (certification of scintillation detector, for example) investigation. The material discussed allows not only to enunciate the radioluminescence theory of organic molecular solids, but to consider the radioluminescence study as the new method for investigation of structure features of organic bulk materials and the process of the charge transport in them as well.[5]

SOME GENERAL ASPECTS OF THE RADIOLUMINESCENCE PROCESS

The investigation of the radio- and photoluminescence spectra of organic single crystals (SC) of the stilbene, anthracene, p-terphenyl, plastic scintillators (PS) based on polystyrene, polyvinyltoluene, polyvinylxylene, liquid scintillators (LS) based on toluene, xylene, isopropyldiphenyl 1-methylnaphthalene has shown their identity. It proves that the radioluminescence phenomenon in molecular materials has a sensitized nature .[1] The effect of the ionizing radiation on the molecules of a chemical component of an i-type is proportional to the electronic fraction of this component. Owing to the fact, that the number of electrons in solvent - solute molecules is not essentially differ for the systems under discussion, the probability of interaction of ionizing particle with molecules of an i-type is proportional to theirs mole fraction. Thus the main processes (i.e. the ionizing energy transfer to the molecules of the material, a charge - state generation and recombination as well as a molecular excitation) mainly occur with the molecules of the base component. Nevertheless, the luminescence of the molecules of luminescent solutes is detected practically.

The plasmons and supperexcited states generation in organic bulk materials is the effect of ionizing energy.[2] These states decay results in charge-state generation. The charge carrier recombination can cause the appearance of singlet- (S) and triplet- (T) - excited molecules as well. The probability of the generation of T- excited molecules is high only in exchange interactions due to $S_0 \to T$ transition forbiddenness for single molecule, where S_0 is the ground state of the molecule. The exchange interactions of T-states result in T-T- annihilation process (Eq.(1)). The singlet channel of T - T- annihilation results in the formation of slow component of radioluminescence pulse

$$T + T_1 \Rightarrow \begin{cases} S_1 + S_0 \Rightarrow h\nu + 2\, S_0 \\ T_1 + S_0 \\ \cdots\cdots\cdots\cdots\cdots\cdots \end{cases} \qquad (1)$$

In Eq.(1) $h\nu$ is the delayed radioluminescence photon energy (the same one as for prompt radioluminescence photon), T_1 is the lowest T-excited state, S_1 the lowest S-excited one. A decay time of the delayed and prompt luminescence is the only difference between them. For the former process it is caused by the duration ($\sim 10^{-7}$- 10^{-6} s) of diffusion - controlled process (1), and for the latter by decay time ($\sim 10^{-10}$- 10^{-9} s) of $S_1 \to S_0$ transition. During the propagation of the light through the bulk material the radioluminescence pulse shape and intensity are changed due to the light scattering, reflection and reabsorption. Having taken into account that the different parameters of the radioluminescence pulse are defined by the different properties of the luminescent object[5] it is not difficult to simplify the problem.

PROMPT RADIOLUMINESCENCE

In contrast to liquids, for organic solids the additional delay of the moments of photon emission is observed.[5,6] It is described by the following function

$$f(t) \sim \exp(-(t-3\sigma)^2/\,2\sigma^2) \qquad (2)$$

where t is the time after excitation, σ is the time constant. For the SC $\sigma \simeq 0.18 - 0.38$ ns, for the PS $\sigma \simeq 0.20$ ns (PS based on polyvinyltoluene or polyvinylxylene) and 0.26 ns (PS based on polystyrene). The σ - value grows with SC structure perfection increase. The shape of the radioluminescence fast component is described by

$$i(t) \sim f(t) * \exp(-t/\tau) \equiv \int_0^t f(t-\beta)\exp(-\beta/\tau)d\tau \qquad (3)$$

where * is the sign of convolution, τ is the decay time constant of the radioluminescence fast component.

As follows from the form of the convolution equation (3), the Gaussian function (2) describes the influence on the shape of the scintillation pulse rise of all the processes those occur after the scintillator was hit by an initial particle and result in excitation of luminescence centers. Such processes take place when the molecules are in higher energy states, both excited and charged ones. It should be noted, that the Gaussian form of function (2) only testifies to the statistical nature of the processes described, which follows from the central limit theorem. The analysis of the situation discussed has shown that the Gaussian function (2) describes the additional delay of the times of radioluminescence photon emission, and this delay is caused by the delay of molecular excitation in the recombination process of charge states localized on the shallow trap system. Indeed, the duration of the rest energy exchange processes such as interaction of ionizing emission with organic solids, generation of plasmons and superexcited states, nonradiative inter- and intramolecular energy exchange and nonradiative electron excitation energy transfer are too small. The duration of all these processes does not exceed 10^{-11} s, and consequently they can't cause the additional delay of 10^{-10} s. The charge carrier will have a location time τ_t if it is captured by a trap with the depth of

$$E_t = kT \ln(\tau_t \nu) \tag{4}$$

where k is Boltzmann constant, T is the temperature, ν is the attempt-to-escape frequency. Substitution[5] $kT = 0.026$ eV, $\nu \leq 10^{12}$ s^{-1} and $\tau_t = 3\sigma$ (according to Eq.(2)) into (4), at the room temperature yields $E_t \leq 0.17$ eV. So, the effect discussed is caused by the recombination of charge carriers localized on shallow traps.

The minor difference in σ- value for solids with radically different structure is caused by following. Having fallen into a trapping center a charge carrier polarized the SC molecules (or fragments of macromolecules of the PS) surrounding it. The result of the interaction of the charge with the dipoles induced on neighboring molecules can be represented as deepening of a trapping center by a value of δE_t. This value for the wide class of organic materials is about 0.1 eV.[6,7] Hence, the estimated depth of the initial structural trapping center is $E_t - \delta E_t \leq 0.07$ eV or $\sim 2kT$ at room temperature. If ΔE it is the difference between the depth of the traps, for which the times of charge location are equal τ_t and $\tau_t + \Delta\tau$, respectively, then for shallow traps

$$\Delta E = \Delta\tau \, (kT/\tau_t) \tag{5}$$

Thus, both the energies and times of charge carrier location should be described by functions of the same type. Thereby, the Gaussian function (2) assumes the Gaussion type of the trap energy distribution.[7] So, the study of the radioluminescence pulse rise shape allows to investigate the dynamical trapping centers of a polarization origin.

DELAYED RADIOLUMINESCENCE

For times $t \geq 50$ ns after excitation[1,4] the pulse-shape of the radioluminescence slow component is described by

$$I(t) \sim (1 + t/ t_D)^{-k} \qquad (6)$$

where $t_D = r_0^2 / 4D$, D is the diffusion coefficient of triplet excitation, r_0 is the mean value of a cross-section radius of high activation density regions. The symmetry of these regions defines the k - value in Eq. (6).[4] For radiations with a high ($\geq 10^1$ MeV/ cm) and a low ($\leq 10^{-1}$MeV/ cm) specific energy loss k = 1.0 (cylindrical symmetry) and k = 1.5 (spherical one), respectively. With the specific energy loss dE/ dx increase the r_0-value and the length L of the track decrease.

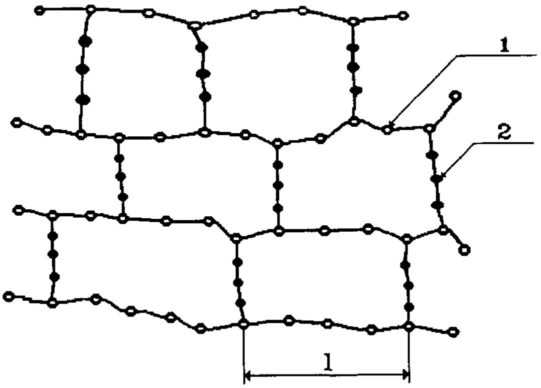

FIGURE 1 Schematic representation of a cross - linking copolimer.
1 —∘—∘— styrene chain, 2 —•—•— linking chain,
l - the mean distance between two linking chains.

Owing to the different multiplicity of T- state and the ground one S_0 the T → S_0 transition is the forbidden transition and the shape as well as intensity of the radioluminescence slow component are sensitive to the organic solids structure unperfections.[3,5] The anisotropy of the radioluminescence light yield and t_D - vales (Eq.(6)) is observed for SC. It is caused by anisotropy of the crystal lattice characteristics. The presence of deep traps of charge carriers ($E_t \sim 1.2 - 1.4$ eV) and excitons (~ 0.24 eV) effects on the light yield of the radioluminescence slow component. The study[4] of the PS based on cross-linking copolymers (Figure 1) has been shown, that by selecting the source of ionizing radiation (i.e. r_0 and L - values) it is possible to estimate the dimensions of a mean cross - linking area.

THE PROPAGATION OF THE RADIOLUMINESCENCE PULSE

It has a sense to study the radioluminescence, when ionizing radiation loses the main portion of its energy in the material. Therefore the radioluminescence study is usually performed for bulk materials. Owing to light reflection and reabsorption the radioluminescence pulse shape is distorted. Therefore, for the case, when the radioluminescence pulse shape is described by the function i(t) the shape of a detected light pulse will be described by

$$i_1(t) = i(t) * f_1(t) \tag{7}$$

where the function $f_1(t)$ describes the influence of reabsorption and light - collection processes on the shape of the radioluminescence pulse. It has been shown,[8] that

$$f_1(t) \sim \eta^{-1} \exp(-t/\eta) \tag{8}$$

where, for cylindrical or bar- shape samples with length of L, $\eta = \alpha L / V$. The $(\alpha + 1)$ - value shows the ratio between the velocity V of a single photon propagation without reflections and absorptions and the effective velocity V_e of the radioluminescence pulse propagation. The description of the function f(t) as the exponential one allows to avoid the repeated convolution integral taken during the simulation of the light propagation by the Monte-Carlo method. Having obtained η - value in the experiment it is possible to calculate the varied parameters by a comparison of results of Monte - Carlo simulations and the function f(t) (8). When the reabsorption effect is substantial

$$\eta^{-1} = \eta_c^{-1} - \eta_r^{-1} \qquad (9)$$

where $\eta^{-1} = \eta_c^{-1}$ for the case of no reabsorption. This approach allows to determine diffuse as well as mirror component of light reflection on the sample surface. Thus, having determined the constants α for the cases of "pure" diffuse and "pure" mirror reflection (α_d and α_m) in the material by using the technique described in the previous paper,[8] it is possible to determine the diffuse and mirror component of light reflection for the sample studied using the results of the direct measurements of the effective velocity V_e. Let ξ_d denote for diffuse component of reflection and ξ_m for mirror one

$$\begin{cases} \xi_d + \xi_m = 1 \\ V_e = \xi_d V_d + \xi_m V_m \end{cases} \qquad (10)$$

Since the following equation is valid[8]

$$V_i = V / \alpha_i - \eta_r^{-1} L \qquad (11)$$

where i is "d","m" or "e", it is not difficult to obtain

$$\xi_d = \frac{\alpha_d(\alpha_e - \alpha_m)}{\alpha_e(\alpha_d - \alpha_m)} \qquad (12)$$

CONCLUSIONS

The radioluminescence study of organic bulk materials allows to investigate:

- the mechanism of the processes which take place during the formation of the trapping centers of a polarization origin;
- the processes in tracks and spurs;
- the object structure perfection;

as well as to obtain the data needed for design the parameters of bulk materials with mixed light reflection on their surface.

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