Functional Materials 16, No.4 (2009) © 2009 — STC "Institute for Single Crystals"

Efficiency improvement of polystyrene-based plastic scintillators

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Received June 30, 2009

The radiationless energy transfer mechanisms between energy donor and acceptor have been studied to determine the character of their spatial distribution. The observed deviation of luminescence decay law from the root dependence indicates a inhomogeneous distribution of *p*-terphenyl in a polystyrene block. This inhomogeneity is due to *p*-terphenyl expelling from internal volume of a polystyrene macromolecule. Therefore, one way to improve the scintillation efficiency is to provide a more homogeneous distribution of activator in a scintillator block. This can be realized in a system including a plastic copolymer and the activator molecules.

Исследованы механизмы безызлучательного переноса энергии между донором и акцептором энергии с целью определения характера их пространственного распределения. Наблюдаемое отклонение кривых затухания люминесценции от корневой зависимости указывает на неравномерное распределение *п*-терфенила в блочном полистироле. Эта неравномерность обусловлена вытеснением *п*-терфенила из внутреннего объема макромолекулы полистирола. Поэтому одним из способов повышения эффективности сцинтиллятора является обеспечение более однородного распределения активатора в сцинтилляционном блоке. Это может быть достигнуто в системе, включающей пластмассовый сополимер и молекулы активатора.

Plastic scintillators (PS) are used widely in various detectors of elementary particles (counters, calorimeters, trackers, etc.). They show high action speed (0.5–3 ns), high transparency to self-luminescence, high temperature and lifetime stability, and high radiation hardness. It is to be added the manufacturing possibility of large size and different configuration PS with low cost and ease of PS coupling with light guide and spectrum-shifting fibers. However, the PS scintillation efficiency is rather low (about 50 % relative to anthracene), that is why during last decade, a great attention is given to its improvement. To understand more clearly the ways to such improvement, let us outline the effective collecting processes of the plastic matrix excitation energy. Now almost 100 % of plastic scintillators market are polystyrene based or polyvinyl toluene based scintillators. The luminescence base of these polymers is π-conjugated electron system (benzene molecule). After a high-energy particle enteres the scintillator, the excitation of polymer matrix occurs which, after a fast relaxation during about 10^{-12} s, is finally localized on luminescent moieties of macromolecules. The excited state lifetime of a luminescent moiety is about ten nanoseconds. A localized excitation may relax by radiation, migrate to a neighboring center or make a practically non-luminescent excimer with the neighboring center. It is to note that if another closely located center with appropriate properties exists in the surrounding of the excited fragment, then the excimer formation time between phenyl moieties of the polystyrene molecule is some picoseconds. The excimer concentration can reach several tens per cent, according to estimations by different authors [1]. Therefore, to eliminate ineffective excitation energy transfer paths in the polymer base, a luminescent additive (activator) is usually added thereto. The main task of that additive is to release the excitation of the polymer matrix in a radiationless manner and to prevent its migration along a polymer chain. To realize the effective radiationless energy transfer from the excited center of a polymer matrix to the activator molecule, these molecules should be spaced by a distance less than so-called Forster radius [2]. As far as Forster radius for phenyl moiety of a polystyrene molecule and molecule of a typical activator — *p*-terphenyl is not greater than 30 Å, and dimensions of polystyrene macromolecules with 10^6 conversion degree are of hundreds Angstroms, then the efficiency of radiationless transfer depends immediately on the homogeneity of activator molecules distribution in a polymer block. At present, there are no sufficiently reliable experimental methods to determine the activator distribution in a polymer matrix. In this work, we tried to answer this question by investigating the peculiarities of radiationless energy transfer from a polymer matrix to activator molecules in a plastic scintillator.

To study the spatial distribution of the activator (*p*-terphenyl) molecules, polystyrene samples were synthesized with different *p*-terphenyl concentrations (from 0.01 % to 4 % mass). The samples were synthesized by the standard technique described elsewhere (see, for example [1]). The residual monomer concentration did not exceed 0.1 %. The steady-state absorption and emission spectra were studied at room temperature using a FluoroMax-4 (HORIBA Jobin Ivon Inc.) spectrofluorimeter. The decay kinetics was measured by Combined Steady State and Lifetime Spectrometer FLS-920 (Edinburgh Instruments). The excitation source was a nanosecond flash lamp with the pulse width 1 ns and repetition rate 40 kHz. The fluorescence decay was observed at 307 nm wavelength.

It is generally admitted [3] that the luminescence of a pure (non-activated) polystyrene is presented by the luminescence of excimers which are formed between two neighboring (~ 3.2 Å) phenyl moieties of macromolecules. The luminescence maximum is at 307 nm wavelength, which is clearly seen in Fig. 1. It is very important for the further analysis that these excimers are homogeneously distributed within a polystyrene molecule. It is seen in Fig. 1 that with increasing *p*-terphenyl concentration, the quenching of the polymer base is occurred and for *p*-terphenyl concentration 1 mass. %, polymer luminescence is totally absent. The radiationless luminescence quenching of the polymer base is confirmed by observed character of its decay.

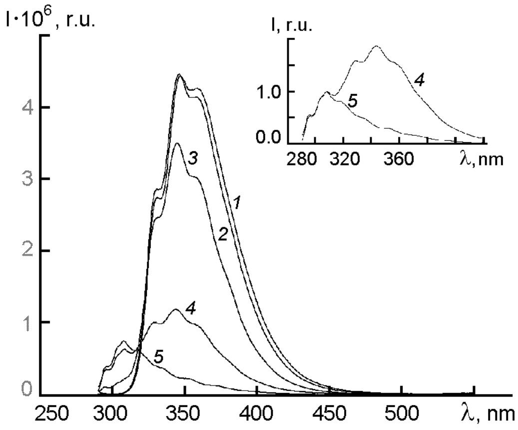

Fig. 1. Luminescence Spectra of a block polystyrene activated with *p*-terphenyl molecules: *1* – 2% p-TP; *2* –1%; *3* – 0,1%; *4* – 0,01%; *5* – pure polystyrene.

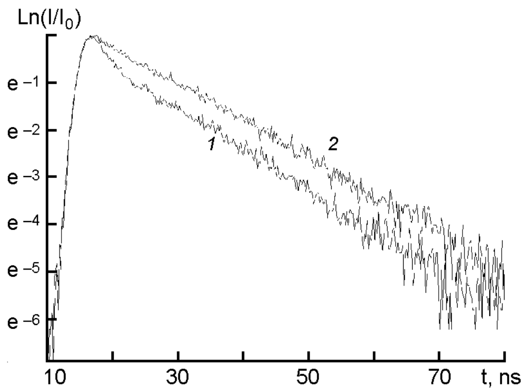

Fig. 2. Decay of excimer luminescence (307 nm) of a block polystyrene activated with *p*-terphenyl: *1* – 0,1% p-TP; *2* – 0,01% p-TP.

Fig. 2 shows time-resolved curves of excimer luminescence obtained after pulse excitation at 265 nm wavelength. It is seen in the Figure that at small activator concentrations (0.1 % and below), the decay curves of a block polystyrene luminescence are single-exponential with lifetimes about 13 ns. The lifetime of non-activated polystyrene is constant in the whole observed luminescence spectrum from 300 nm to 350 nm, which indicates the presence of only single luminescence center.

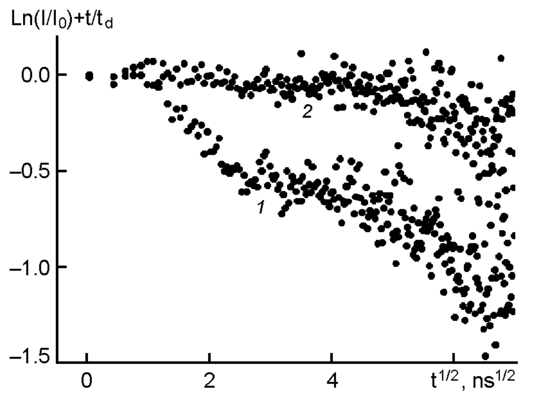

Fig. 3. Decay curves of the donor (styrene) luminescence in $\ln f(t) + 1/\tau_0$ vs. $\sqrt{t}$ coordinates: *1* – 0,1% p-TP; *2* – 0,01% p-TP.

When the activator concentration is higher than 0.1 %, the decay curve obtains a distinct trend to non-exponential character, as is seen in Fig. 2. The observed non-exponential law evidences the existence of a radiationless energy transfer channel from the polymer matrix to activator molecules. In this case, the decay curves are described rather well by Forster theory where the main parameter is the critical radius of energy transfer R_0 determined by overlapping of the donor luminescence spectrum and the acceptor absorption spectrum [2]:

$$R_0 = \left(\frac{9\chi^2 c^4}{8\pi N_a}\int F_d(\omega)\cdot\mu_a(\omega)\frac{d\omega}{\omega^4}\right)^{1/6}, \quad (1)$$

where $F_d(\omega)$ is the normalized spectrum of the donor luminescence; $\mu_a(\omega)$, molar extinction of the acceptor; c, light speed; N_a, the activator molecular concentration.

Using the donor luminescence spectra in Fig. 1 and known absorption spectrum of *p*-terphenyl, we can, according to Eq.(1), calculate the critical radius of energy transfer in our system. This value is found to be of 16 Å.

The time dependence of the donor luminescence decay depends immediately on spatial distribution of acceptors with respect to a donor [3]:

$$f(t) = \quad (2)$$

$$= \exp\left(-\frac{t}{\tau_d} - \int_0^\infty dr\cdot\rho_{d\text{-}a}(r)(1 - \exp(-t\cdot W(r))\right),$$

where $\rho_{d\text{-}a}(r)$ is the function of acceptor distribution relative to donor; $W(r)$, radiationless energy transfer rate between donor and acceptor placed at distance r and defined by the following equation:

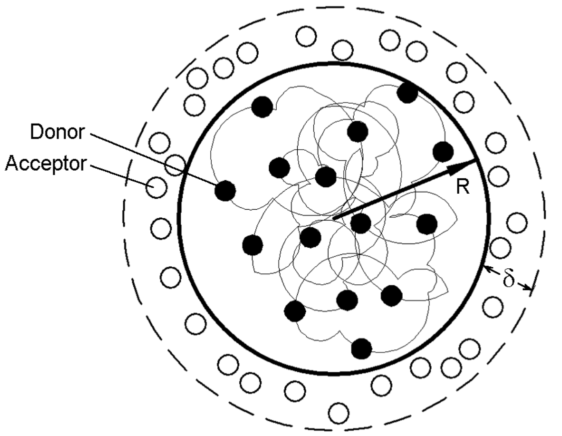

Fig. 4. Arrangement model of donors (phenyl moieties of a polystyrene molecule) and acceptors (*p*-terphenyl) in a plastic scintillator.

$$W = \frac{1}{\tau_d}\left(\frac{R_0}{r}\right)^6, \quad (3)$$

where τ_d is the donor lifetime in the absence of acceptor.

If the donors are homogeneously distributed relative to acceptor, then their spatial function of mutual distribution is:

$$\rho_{d\text{-}a}(r) = 4\pi c_a r^2, \quad (4)$$

where c_a is the acceptor concentration.

Substituting (4) into (2), we get the donor decay law as:

$$f(T) = \exp\left(-t/\tau_d - 2\frac{1.38}{\sqrt{6}}\pi^{3/2}R_0^3 c_a\sqrt{t/\tau_d}\right). \quad (5)$$

It is seen from Eq.(5) that the donor decay curve in $\ln f(t) + 1/\tau_d$ vs. $\sqrt{t}$ coordinates can be fitted by linear function. The decay curves of Fig. 2 re-drawn in the new coordinates are presented in Fig. 3. The obtained experimental points do not lie on a straight line. This may indicate the inhomogeneity of *p*-terphenyl distribution in a block of polystyrene.

To analyze the obtained curves, we can suppose that *p*-terphenyl molecules are distributed inhomogeneously in the polystyrene volume and tend to preferable collecting between balls of macromolecules. Therefore, the process of the excitation energy quenching in a block polystyrene can be considered as radiationless transfer of excitation energy from excimers (energy donors) randomly distributed in a ball, to *p*-terphenyl molecules (energy acceptors) randomly distributed on the ball surface (Fig. 4).

As is seen from (2), to provide numerical assess of the quenching process, it is necessary to know the function of mutual distribution between donor and acceptor. To define it, we can use the characteristic function method known from the probability theory. Thus, if we know the centrally symmetric distribution functions of donor $\rho_d(r)$ and acceptor $\rho_a(r)$, then we always can calculate their characteristic functions which have the general form $\varphi_{d(a)}(\mathbf{k}) = <\exp(i\mathbf{k}\cdot\mathbf{r})>$[5]. Integrating this equation with angular parameters as integration variables, we can write the characteristic functions of donor and acceptor for the centrally symmetric case in the form:

$$\varphi_{d(a)}(k) = \int_0^\infty \rho_{d(a)}(r)\frac{\sin(k\cdot r)}{k\cdot r}dr. \tag{6}$$

To find the function of donor against acceptor mutual distribution defined in $\mathbf{r}_d - \mathbf{r}_a$ variables, it is sufficient to use the fact that a characteristic function of a sum of independent random variables is the product of their characteristic functions. So the donor-acceptor distribution function can be written in the form:

$$\rho_{d(a)}(r) = \frac{2}{\pi}\int_0^\infty \varphi_d(k)\varphi_d(k)k\cdot r\sin(k\cdot r)dk. \tag{7}$$

Let us suppose the donor molecules to be distributed homogeneously in a sphere of radius R. Then the function of the donor spatial distribution is:

$$\rho_d(r) = \theta(R-r)\cdot 3r^2/R. \tag{8}$$

If the acceptor distribution is a simple function $c\cdot\delta(r-R)$, then, according to [4], the unknown spatial function of donor-acceptor distribution has the form:

$$\rho_{d-a}(r) = c\frac{3r^2}{R^3}(2R-r)\cdot\theta(r-R). \tag{9}$$

We have used (9) to fit the experimental decay curve (Fig. 5). The acceptor density and the sphere radius were chosen as adjustable parameters. The best approximation is obtained for R = 162 Å and c = 1.06 (Fig. 5).

It is known that in the model of free link connecting with no self-crossing, the average ball dimension can be expressed as [6]:

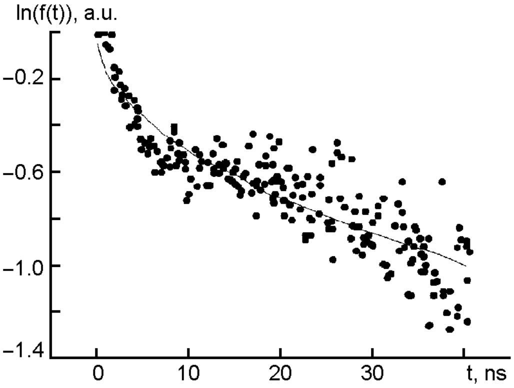

Fig. 5. Fitting of experimental decay curve (Fig. 3) for 0.1 mass. % p-terphenyl.

$$<h^2> = N^{6/5}l^2, \tag{10}$$

where N is the total molecular chain length; l, elementary unit length of the chain.

The total length N of a polymer macromolecule depends on the polymerization temperature. In our case, the experimental samples were polymerized at 140°C. For this temperature, $N \sim 3.44\cdot10^4$. In this case, the average ball radius is 194.48 Å, agreeing rather well with experimental value.

To validate the described approach to determination of the spatial distribution of activator molecules in the plastic scintillator block, it is to consider a system where donors are randomly distributed relative to acceptors. A styrene/methyl methacrylate copolymer may be such a system. Here, phenyl moiety of styrene molecule acts as a donor and acceptors are excimers, the formation probability of the latter increases with specific fraction of styrene molecules.

To consider the quenching processes in such a system, we have synthesized some methyl methacrylate/styrene (MMASt) copolymers with different styrene concentrations. As was expected, when styrene concentration is increased, the quenching of their chromophore fragments is observed which is clearly seen in Fig. 6. The luminescence of the p-MMASt copolymer is due to luminescence of styrene phenyl moieties with the maximum at 290 nm, while methacrylate moiety is not luminescent in this spectral region.

When the specific fraction of styrene molecules is increased, the luminescence quenching is observed. The reason for such a quenching is described in detail in literature [7] and is connected with the mutual arrangement of styrene and methyl methacrylate molecules in the copolymer.

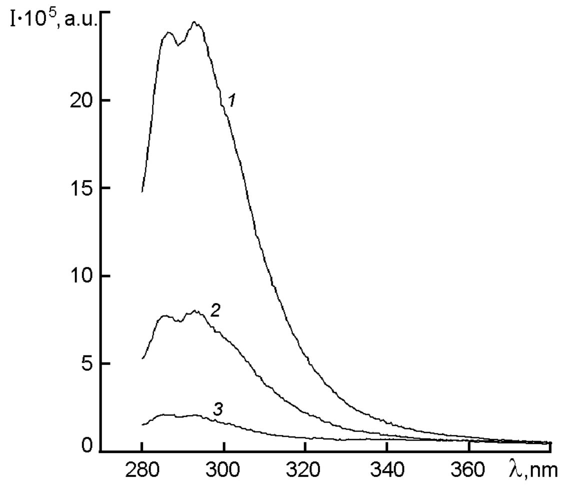

Fig. 6. Luminescence spectra of copolymer (*p*-MMASt) for excitation at 255 nm wavelength: *1* – styrene concentration 0,01%; *2* – 0,1%; *3* – 1%.

The copolymerization constants do not favor the direct alternation of styrene molecules in a copolymer chain; nevertheless, such an alternation is possible and may result in formation of excimers which are the excitation energy traps localized at the phenyl moieties of styrene molecules. With increasing concentration, the probability of styrene pair coupling in the *p*-MMASt copolymer rises, thus increasing the excimer formation probability which, in turn, causes a decrease of the copolymer luminescence intensity (Fig. 6).

The luminescence quenching connection with the radiationless energy transfer processes is confirmed by observed luminescence decay curves which are presented in Fig. 7. It is seen in the Figure that as concentration increases, ever more deviation of the decay law from single exponential is observed. This indicates the presence of a radiationless channel of energy transfer. Even for 0.1 % of styrene molecules in copolymer, the luminescence quenching is observed. When considering the process in more detail and drawing dependences $\ln(I/I_0) + t/\tau_0$ vs. $\sqrt{t}$, then, as it seen from (5), for the homogeneous distribution of acceptor relative to donor, the linear dependence must be observed. Rebuilding the decay curves in Fig. 3 and taking 26 ns as the donor lifetime when there is no quenching, we can see that obtained dependences are well fitted by a straight line (Fig. 8). This is in accordance with our analysis of excimers formation in the studied copolymer chain.

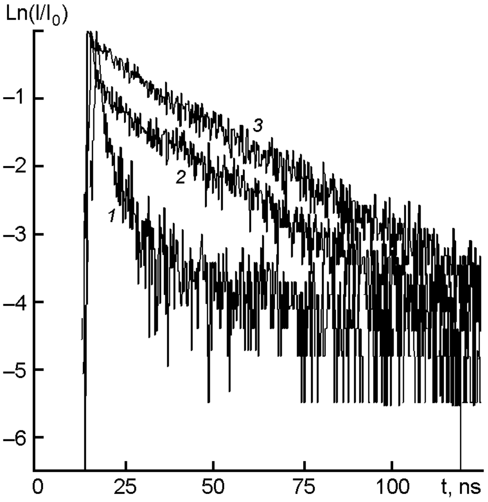

Fig. 7. Decay curves of *p*-MMASt copolymer luminescence with different content of styrene: *1* – 1%; *2* – 0,1%: *3* –0,01%.

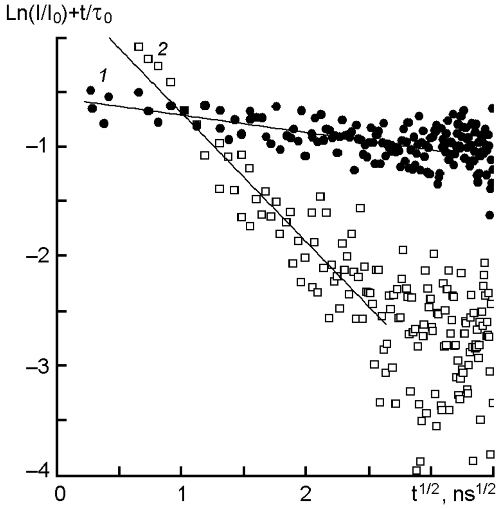

Fig. 8. Decay curves of *p*-MMASt copolymer luminescence in $\ln(I/I_0) + t/\tau_0$ vs. $\sqrt{t}$ coordinates: *1* – 0,1%, tanα = -0,158; *2* – 1%, tanα = -1,178.

Thus, the consideration of decay curves allows us to answer the question about the spatial distribution homogeneity of activator molecules in a plastic scintillator block. Moreover, in Fig. 8, it is seen that the rate of radiationless quenching is essentially proportional to the fraction of styrene molecules in a copolymer chaim. The line slope in $\ln(I/I_0) + t/\tau_0$ vs. $\sqrt{t}$ coordinates must be determined by Eq.(5), while knowing the Forster radius of energy transfer allows to determine the ratio of absorption centers (excimers) in the phenyl subsystem of a polymer. The calculation made in such a way let suggest that within the limits of error this fraction is essentially equal to the total concentration of styrene molecules in the copolymer. That is, all styrene molecules act as energy donors and acceptors simultaneously. The presented analysis of the excimer state fraction is of course not fully correct, because it must take into account the possibility of excitation energy migration over identical centers, its rate being dependent on the square of concentration. But this dependence is not observed in Fig. 8. This indicates that the migration influence on the quenching processes is considerably lesser than influence of caption by traps which appear because of excimers forming.

Thus, a detailed study of radiationless energy transfer mechanisms between energy donor and acceptor makes it possible to determine the character of their spatial distribution. The observed deviation of luminescence decay law from the root dependence indicates a inhomogeneous distribution of *p*-terphenyl in a polystyrene block. This inhomogeneity is due to *p*-terphenyl expelling from internal volume of a polystyrene macromolecule. The simplest model of such an expelling allowed to estimate the average size of a macromolecule ball to be of 32 nm. Therefore, one way to improve the scintillation efficiency is to provide a more homogeneous distribution of activator in a scintillator block. This can be realized in a system including a plastic copolymer and the activator molecules.

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Підвищення ефективності пластмасових сцинтиляторів на основі полістиролу

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Досліджено механізми безвипромінювального переносу енергії між донором та акцептором енергії з метою визначення характеру їхнього просторового розподілу. Відхилення кривих затухання люмінесценції від кореневої залежності вказує на нерівномірний розподіл *п*-терфенілу у блоковому полістиролі. Ця нерівномірність обумовлена витисненням *п*-терфенілу з внутрішнього об'єму макромолекули полістиролу. Тому одним зі способів підвищення ефективності сцинтилятора є забезпечення більш однорідного розподілу активатора у сцинтиляційному блоці. Це може бути досягнуто у системі, яка включає пластмасовий співполімер та молекули активатора.