

# Plastic scintillators based on polymers with hindered excimer forming

*A.F.Adadurov, D.A.Yelyseev, V.D.Titskaya,  
V.N.Lebedev, P.N.Zhmurin*

Institute for Scintillation Materials, STC "Institute for Single Crystals",  
National Academy of Sciences of Ukraine,  
60 Lenin Ave, 61001 Kharkiv, Ukraine

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A plastic scintillator (PS) made of P(BzMA+MMA) copolymer is described. This copolymer shows the excimer forming rate by two order lower than in the known polystyrene-based matrix. The importance of migration processes comparing to excimer formation is demonstrated by studying of light yield in PS based on P(St+MMA) and P(BzMA+MMA) copolymers. It is found that to obtain PS with high scintillation efficiency, it is necessary to use the polymer base (matrix) in which excimer forming will be hindered but the migration process along the chromophores is maximally favored. The mechanism of virtual excitons exchange is proposed to explain the accelerated energy transfer between phenyl chromophores. This exchange can propagate along one-dimensional backbone of polymer molecule. Clearing the details of interaction between chromophores of a polymer molecule which is responsible for accelerated radiationless energy transfer will define in future the way to effective plastic scintillators.

Изучается пластмассовый сцинтиллятор, изготовленный из сополимера бензилметакрилата и метилметакрилата P(BzMA+MMA). В этом сополимере скорость образования эксимеров на два порядка меньше, чем в традиционной полистирольной матрице. Важность процессов миграции энергии по сравнению с формированием эксимеров демонстрируется изучением светового выхода сцинтилляторов, основанных на P(St+MMA) и P(BzMA+MMA) сополимерах. Обнаружено, что для получения пластмассового сцинтиллятора с высокой сцинтилляционной эффективностью необходимо использовать полимерную базу (матрицу), в которой образование эксимеров затруднено, а процессы миграции по хромофорам максимально усилены. Механизм обмена виртуальными экситонами предложено использовать для объяснения ускоренной передачи энергии между фенильными хромофорами. Этот обмен может осуществляться вдоль одномерного скелета полимерной молекулы. Выяснение деталей взаимодействия между хромофорами полимерной молекулы, которые ответственны за ускоренный безрадиационный перенос энергии, позволит определить будущие пути создания эффективных пластмассовых сцинтилляторов.

## 1. Introduction

A conventional plastic scintillator (PS) usually consists of luminescent molecules (activator) dissolved in a transparent luminescent polymer base (matrix). The activator (first luminescent additive —  $A_1$ , is the organic fluorophore with the absorption band overlapped with the polymer emission band. Vinyl

polymers with luminescent phenyl moieties as pendant groups (chromophores) are usually used as the polymer base (matrix).

An ionizing particle passing the polymer media excites and ionizes it. This excitation through the chain of rapid intermediate processes is transferred to chromophores which then relax to the ground state emitting the fluorescence quanta. The quantum

yield of chromophore centers of a polymer molecule is usually low (0.06 for phenyl moiety of polystyrene [1]). Therefore, the main task in plastic scintillator designing is to provide the radiationless transfer of excitation energy (RET) from chromophores (donors) to more effective fluorescent activator centers (acceptors), which have a high quantum yield.

When all other channels of energy transfer are absent, then, for an appropriate activator, it is possible to obtain the radiationless transfer efficiency approaching unity ( $\eta \sim 1.0$ ) [2].

The efficiency of radiationless energy transfer to single acceptor is:

$$\eta = \frac{w_{da}}{w_{da} + A_d + K_{im}}, \quad (1)$$

where  $w_{da}$  is the rate of radiationless energy transfer;  $A_d$ , the rate of donor spontaneous emission;  $K_{im}$ , the intramolecular conversion rate.

For dipole-dipole interaction,  $w_{da}$  is determined by the following expression [3]:

$$w_{da} = \frac{1}{\tau_d} \left( \frac{R_0}{R} \right)^6, \quad (2)$$

where  $R_0$  is Forster radius;  $R$ , distance between donor and acceptor;  $\tau_d$ , the donor life-time without acceptor presence.

It follows from (2) and (1) that when  $R < R_0$ , it is possible to provide rather effective channel of radiationless energy collection.

For an ensemble of fixed (during the time of excited state existence) acceptor molecules which are statistically distributed in space, the dependence of radiationless transfer efficiency on acceptor concentration in the case of dipole-dipole interaction is determined by the following equation [4]:

$$\eta = 2qe^{q^2} \int_0^{\infty} e^{-x^2} dx, \quad (3)$$

where  $q = 1.38\pi^{3/2}R_0^3c_a/\sqrt{6}$ .

According to (3), the RET efficiency in polystyrene-based plastic scintillator with 2 % p-terphenyl as LA<sub>1</sub>, achieves 95 %.

These calculations are valid only in the case when rates of excitation capture by other possible traps do not exceed the intramolecular conversion rate  $K_{im}$ . But it is known that the main RET channel in vinylaromatic polymers is excimer formation

[5–9]. Therefore, the scintillating efficiency of real PS must depend on excimer forming ability in different polymer matrices. So there is an additional summand in the denominator of (1) accounting for the channel of excitation transfer to excimer:

$$\eta = \frac{w_{da}}{w_{da} + A_d + K_{im} + A_{dd}}, \quad (4)$$

where  $A_{dd}$  is the rate of excitation trapping by excimers.

Zhang and Thomas [10] have shown that the excitation transfer time from chromophore (donor) to excimer sites in polystyrene is less than 20 ps. So, excimers formation rate  $A_{dd}$  is  $5.0 \cdot 10^{10} \text{ s}^{-1}$ , which is by a factor of  $10^2$  higher than RET to fluorescent additive. Such a high excitation trapping rate naturally decreases the probability of fluorescent additive (activator) excitation which, in turn, decreases the PS scintillator efficiency. Indeed, Harrah [5] has demonstrated that PS scintillation efficiency can be increased by decreasing the excimers formation rate. This can be achieved, for instance, by using (as a PS base) polymers with hindered excimers formation.

Inoue et al. [11] investigated fluorescent properties of random copolymers of styrene (St) and benzyl methacrylate (BzMA) with methyl methacrylate (MMA) in a  $\text{CH}_2\text{Cl}_2$  solution. They have shown that in BzMA+MMA copolymer, excimers are formed much seldom comparing to styrene homopolymer. The films of such homopolymers have been studied in [2]. It has been found that excimers concentration in polystyrene is 100 mM, while in poly(BzMA), almost by one order lower (12.5 mM). Excimer formation in bulk copolymer samples was not studied but it can be expected that the trend will be the same as in solutions and films. As far as these copolymers have the same chromophores but different ability of excimers formation, the use of those copolymers as PS matrices can answer the question about influence of excimer formation on PS scintillation efficiency. This work is devoted to this question.

## 2. Experimental

Random copolymers of styrene (St) and benzyl methacrylate (BzMA) with methyl methacrylate (MMA) were used as PS samples. The copolymers structure is shown in Fig. 1 where  $x$  represents the styrene or benzyl methacrylate concentration. Both copolymers contain phenyl rings as chromo-

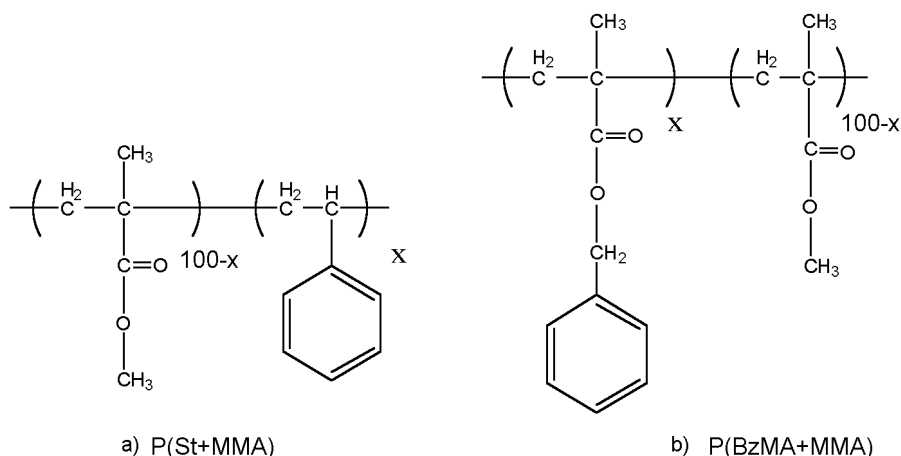


Fig. 1. Copolymers structure: a) poly(styrene methyl methacrylate) P(St+MMA); b) poly(benzyl methacrylate methyl methacrylate) P(BzMA+MMA);  $x$  — number of St or BzMA units.

phores but in St+MMA copolymer those are attached immediately to the macromolecule backbone while in BzMA+MMA copolymer, the chromophores and backbone are separated by carbonyl group. This increases the pendant group mobility and, therefore, decreases the probability of excimers formation even for adjacent phenyl rings of BzMA. Increasing the MMA content in the copolymers results in increasing distance between chromophores and also to hindered excimer formation.

To prepare samples of P(St+MMA)-based PS the appropriate amounts of St and MMA monomers purified by distillation under low pressure were put into a glass ampoule. The St content in copolymer was varied from 1.0 wt.% to 30 wt.%. Then luminescent additives (LA) were added. Their content was the same in all PS samples. As the acceptor (LA<sub>1</sub>), 1.5 wt.% 2.5-diphenyloxazole-1.3 (PPO) was used, and as a wavelength shifter (LA<sub>2</sub>), 0.02 wt.% 1.4-di-2-(5-phenyloxazolyl)-benzene (POPOP) was used. The copolymers were prepared by free radical polymerization using initiator (0.03 wt.% 2.2'-azodiizobutyronitrile). The initial stage was run for 22 h at  $T = 45^\circ\text{C}$ , second stage was followed during 48 h at  $60^\circ\text{C}$  and by annealing during 2 h at  $T = 115^\circ\text{C}$ .

To prepare P(BzMA+MMA)-based PS, appropriate amounts of purified monomers BzMA, MMA and LA were put into glass ampoule. BzMA content in copolymer was varied from 1.7 wt.% to 51 wt.% (to provide the chromophore content in PS with St and BzMA be the same). Then luminescent additives were added in all samples in the same amounts as in P(St+MMA)-based PS. Free radical polymerization was run in the

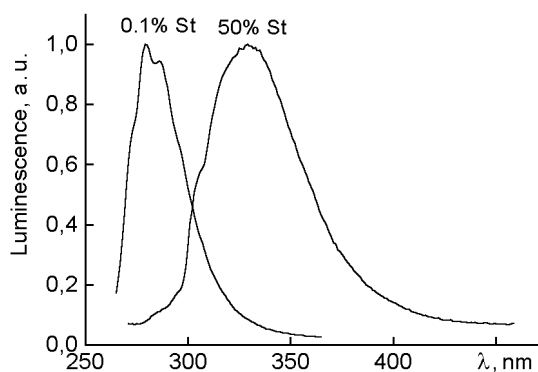


Fig. 2. Fluorescence spectra of P(St+MMA) copolymer with styrene content 0.1 and 50 %. Excitation wavelength 255 nm.

presence of initiator (0.02 wt.% 2.2'-azodiizobutyronitrile). The first stage of the process started at  $55^\circ\text{C}$  temperature and lasted 22 h. Then temperature was increased by steps:  $60^\circ\text{C}$  for 6 h,  $65^\circ\text{C}$  for 19 h,  $70^\circ\text{C}$  for 6 h, above  $75^\circ\text{C}$  for 19 h.

PS samples, cut from obtained blanks, had cylindrical shape of 16 mm in diameter and 10 mm height. All surfaces were finished up to optical surface finish class.

The influence of excimers formation on PS scintillation efficiency was observed by measuring the PS light yield under excitation with electrons of 0.975 MeV energy from a  $^{207}\text{Bi}$  source. The sample was placed on the photocathode of a Hamamatsu R1307 PMT. The PMT anode signal was transmitted to the fast charge-digit converter of Leroy 2249A type, which is a part of multichannel pulse-height analyzer. The luminescence spectra were measured by a Fluoromax-4 spectrofluorometer (HORIBA, Jobin Ivon, Inc.). The decay kinetics was measured by

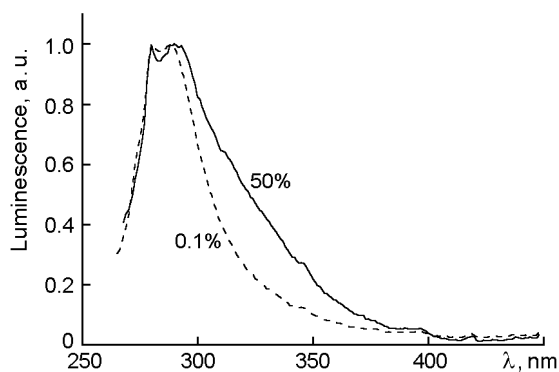


Fig. 3. Fluorescence spectra of P(BzMA+MMA) copolymer with BzMA content 0.1 and 50 %. Excitation wavelength 255 nm.

Combined Steady State and Lifetime Spectrometer FLS-920 (Edinburgh Instruments). The excitation source was a nanosecond flash lamp with 1 ns pulse width and 40 kHz repetition rate. The fluorescence decay was observed at 307 nm wavelength.

### 3. Results and discussion

The fluorescence spectra of P(St+MMA) copolymers with 0.1 and 50 % styrene concentration obtained under excitation at 255 nm wavelength are present in Fig. 2. The fluorescence intensities are scaled to unity in maxima.

It is seen in the Figure that the maxima of fluorescence spectra of all samples include two clearly visible bands with  $\lambda_1 = 285$  nm and  $\lambda_2 = 295$  nm, which is typical for styrene monomer unit fluorescence [1]. When styrene concentration in copolymer is increased, we observe a fast decrease of phenyl group fluorescence and increasing excimer fluorescence at about 330 nm wavelength. At 50 % styrene concentration, chromophores emission almost disappears. This is specific not only for copolymer solutions but also for solid copolymer samples [11].

The P(BzMA+MMA) fluorescence dependence on BzMA content is somewhat different (Fig. 3). Even for high BzMA concentration (50 %), P(BzMA+MMA) copolymer fluorescence is defined by phenyl chromophore emission. Only a weak broadening of long-wavelength wing of 330 nm emission is observed when BzMA concentration is higher than 30 % which can be caused by excimer emission.

Fig. 4 presents decay curves of bulk BzMA+MMA copolymer fluorescence. It is seen that even at 1 % BzMA, the fluorescence decay can be adequately described by single exponent with 26 ns lifetime, which

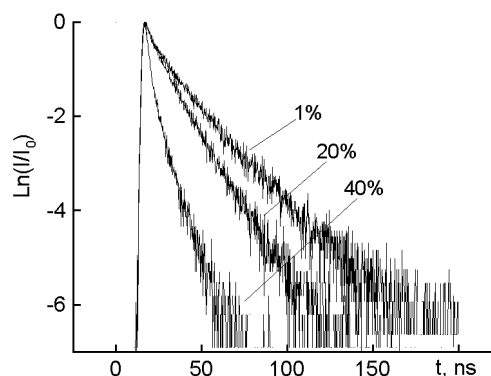


Fig. 4. P(BzMA+MMA) copolymer fluorescence decay curves.

is specific for phenyl chromophore fluorescence. Only at 20 % BzMA concentration, some deviation from the single exponent is noticeable. If the main mechanism of excitation quenching is dipole-dipole mechanism of energy transfer on the uniformly distributed traps which can be excimers, then the donor emission intensity should be written as [4]:

$$I_d = I_0 \exp\left(-\frac{t}{\tau_d} - \frac{1.38}{\sqrt{6}} \pi^{3/2} R_0^3 c_a \sqrt{\frac{t}{\tau_d}}\right). \quad (5)$$

The concentration of excimer centers  $c_a$  is usually unknown a priori, but from (5) we can calculate  $R_0^3 c_a / \tau_d^{1/2}$ , which ultimately allows to estimate the decay rate according to [4]:

$$w = \frac{4\pi}{3} \frac{R_0^6}{\tau_d R_{min}^3} c_a, \quad (6)$$

where  $R_{min}$  is the possible minimum distance between donor and acceptor. Thus, for 20 % BzMA in MMA,  $R_0^3 c_a / \tau_d^{1/2}$  is  $0.26 \text{ ns}^{-1/2}$ .

A close (in the order of magnitude) value, namely,  $0.16 \text{ ns}^{-1/2}$ , was obtained for St-MMA copolymer with 0.1 % styrene concentration, that is, with a two order of magnitude lower than BzMA concentration in the above case.

Let the excimer concentration be related to concentration of chromophores in copolymers. Remember also that the lifetime of chromophore groups in our copolymers is approximately the same and are defined by the phenyl group lifetime. Then it follows from obtained results that the P(St+MMA) chromophore luminescence quenching rate is almost two order of magnitude higher than that of P(BzMA+MMA). This means that in accordance to (4), the efficiency of energy

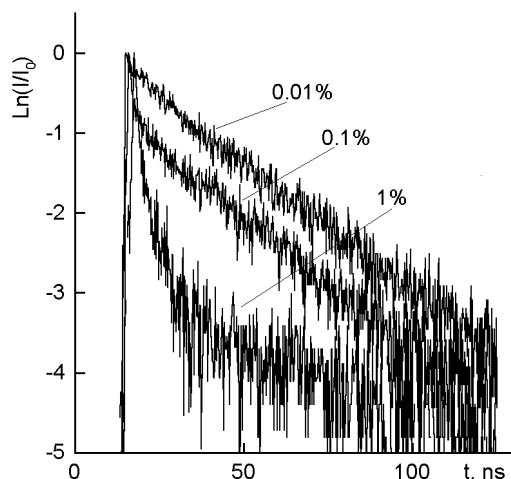


Fig. 5. Decay curves of the bulk copolymer P(St+MMA).

transfer between donor and acceptors in P(BzMA+MMA) matrix must be much higher than in P(St+MMA) polymer matrix. Therefore, P(BzMA+MMA)-based scintillator will have higher efficiency than P(St+MMA)-based one.

To verify this assumption, we have prepared several scintillators based on copolymers described above with equal concentrations of chromophore parts. 2,5-diphenyloxazole in 1.5 wt.% concentration was used in these scintillators as the activator, while *p*-bis[2-(5-phenyloxazolyl)] benzene in 0.02 wt.% concentration was used as the wavelength shifter. The resulting light yield values presented in Fig. 6 were obtained for different concentrations of benzyl methacrylate and styrene in corresponding copolymers.

The Figure shows clearly that the result is completely opposed to the expected one. First, the scintillation light yield for the P(BzMA+MMA)-based scintillator is lower than that for P(St+MMA)-based one. Second, it does not depend substantially on concentration of phenyl chromophores in the sample. This means that either the energy relaxation process in polystyrene differs essentially from that in methyl methacrylate or the radiationless energy transfer process from chromophore parts is presumably defined not by direct radiationless transfer from matrix to activator but by excitation migration along identical chromophores.

Indeed, as it shown, for example, by J.B.Birks [12], the process of radiationless energy transfer from donor to acceptor follows the migration of excitation along iden-

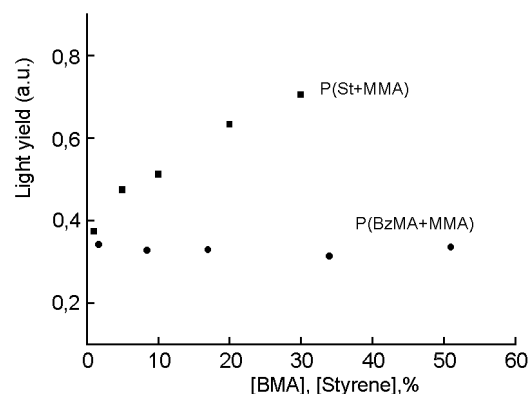


Fig. 6. Light yield of scintillators based on P(St+MMA) and P(BzMA+MMA) copolymers. Light yield is given relative to that of PS based on styrene homo polymer with 1.5 wt.% PPO and 0.02 wt.% POPOP.

tical chromophores. Mechanism of this migration is supposed to be Forster dipole-dipole interaction. But Zhang and Thomas (1995) have shown in experiment that the migration rate along the chromophores is higher than that of trapping by excimers and amounts  $5 \cdot 10^{10} \text{ s}^{-1}$ . It is impossible to provide such a rate in the dipole-dipole approximation. If we remember the diffusion character of such a migration and estimate the diffusion coefficient as

$$D = \frac{1}{3} \frac{R_0^6}{\tau_d R^4}, \quad (7)$$

where  $\bar{R}$  is the average distance between chromophores, than it follows that the maximal possible diffusion coefficient will be only  $3.5 \cdot 10^{-7} \text{ cm} \cdot \text{s}^{-1}$ , and migration rate will be only  $3.4 \cdot 10^8 \text{ s}^{-1}$ . This migration rate is much lower than experimentally measured rate of excitation trapping by excimers in polystyrene. Zhang and Thomas [10] explained the observed migration rate by, so called, exchange mechanism.

The exchange interaction rate is defined by the following equation [11]:

$$w_{da}^{ex} = \frac{1}{\tau_{d0}} \exp(\gamma(1 - R/R_0)), \quad (8)$$

where  $\gamma = 2R_0/L$ ,  $L$  is the spatial index of exchange interaction attenuation. It is seen from (8) that this mechanism can provide considerable increase of energy transfer rate only for very small distances between chromophores (much smaller than the critical radius of radiationless transport). But

actually the chromophores in polymer are placed on distances which are of order of the critical radius. Therefore, exchange mechanism cannot provide any significant increasing of excitation transfer rate.

Moreover, the model of excitation energy transport by means of exchange interaction does not answer the question: why exchange interaction increases the migration rate between P(St+MMA) chromophores and does not do so in P(BzMA+MMA) copolymer, where the average distance between chromophores is the same (at the same concentration of chromophores).

In [13, 14], the mechanism of accelerated migration has been proposed due to exchange of virtual excitons which can propagate along the backbone of polystyrene macromolecule. It should be noted that in this model, the transfer efficiency is higher when energy levels of chromophores and excitons are close. This mechanism can explain the results obtained in this work. Indeed, the P(St+MMA) and P(BzMA+MMA) molecules differ significantly. In contrast to styrene, in a monomer unit of BzMA the chromophore group is separated from the polymer backbone by a carbonyl group which is a good UV energy quencher, and therefore, effectively blocks the excitation energy migration between chromophores along  $\sigma$ -bonds of main backbone of P(BzMA+MMA) macromolecule.

#### 4. Conclusions

Basing on P(BzMA+MMA) copolymer, PS have been made in which the excimer formation rate is two orders lower than in polystyrene-based polymer matrix. Light yield studies of PS based on P(St+MMA) and P(BzMA+MMA) copolymers are demonstrated the importance of migration processes comparing to excimer formation. It is

found that to obtain PS with high scintillation efficiency, it is necessary to use the polymer base (matrix) in which excimer formation is hindered but the migration process along the chromophores is maximally favored. To explain the accelerated energy transfer between phenyl chromophores, it is proposed to use the mechanism of virtual exchange by excitons which can propagate along one-dimensional backbone of polymer molecule. Clearing the details of mechanism of interaction between chromophores of polymer molecules which is responsible for accelerated radiationless energy transfer will define in future the way to effective plastic scintillators-designing.

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## **Пластмасові сцинтилятори на полімерах з утрудненим утворенням ексимерів**

***А.Ф.Ададуров, Д.А.Єлисеєв, В.Д.Тицька,  
В.Н.Лебедев, П.Н.Жмурін***

Описано пластмасовий сцинтилятор, виготовлений зі співполімеру бензилметакрилату і метилметакрилату P(BzMA+MMA). У цьому співполімері швидкість утворення ексимерів на два порядки менша, ніж у традиційній полістирольній матриці. Важливість процесів міграції енергії у порівнянні з формуванням ексимерів демонструється вивченням світлового виходу сцинтиляторів на основі співполімерів P(St+MMA) та P(BzMA+MMA). Виявлено, що для отримання пластмасового сцинтилятора з високою сцинтиляційною ефективністю необхідно використовувати полімерну основу (матрицю), в якій утворення ексимерів утруднене, а процеси міграції по хромофорам максимально підсилені. Механізм обміну віртуальними екситонами запропоновано використовувати для пояснення прискореної передачі енергії між фенільними хромофорами. Цей обмін може відбуватися уздовж одномірного скелету полімерної молекули. Прояснення деталей взаємодії між хромофорами молекули, що відповідальні за прискорений безрадіаційний перенос енергії, дозволить визначити майбутні шляхи створення ефективних пластмасових сцинтиляторів.