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Effect of luminophor/polymeric matrix chemical binding factor on the luminescence of PMMA-based scintillation composition

A.A.Aldongarov, N.N.Barashkov[*], *I.S.Irgibaeva, O.A.Khakhel*[**], *Yu.E.Sakhno*[**]

L.Gumilyov Eurasian National University,
5 Munaitpasov St., 010008 Astana, Kazakhstan
[*]Microtracers Co., 1370 Van Dyke Ave., San-Francisco, California, 94124, U.S.A.
[**]Poltava Division, Academy of Technological Cybernetics of Sciences of Ukraine, 86/86 M.Biryuzov St., 36007 Poltava, Ukraine

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Comparative studies have been carried out of nonradiative energy transfer efficiency in the scintillation compositions consisting of methyl methacrylate + β-naphthyl methacrylate + 1,4-bis(5-phenyl oxazolyl-2)benzene and of naphthalene and 1,4-bis(5-phenyl oxazolyl-2)benzene solid solutions in poly(methyl methacrylate). It has been established by spectral experiments that in the case of naphthalene chemical binding with the polymer the emission intensity of 1,4-bis(5-phenyl oxazolyl-2)benzene increases more than twice when the naphthalene content in the compositions rises as compared to the solid solutions.

Проведены сравнительные исследования эффективности безызлучательного переноса энергии в сцинтилляционных композициях: метилметакрилат + β-нафтилметакрилат + 1,4-бис(5-фенилоксазолил-2)-бензол и твердые растворы нафталина и 1,4-бис(5-фенилоксазолил-2)-бензола в полиметилметакрилате. Спектральными экспериментами установлено, что в случае химической связи нафталина с полимером прирост интенсивности свечения 1,4-бис(5-фенилоксазолил-2)-бензола с увеличением содержания нафталина в композициях происходит более чем в два раза быстрее по сравнению с твердыми растворами.

Among optically transparent polymers, poly(methyl methacrylate) (PMMA) is remarkable for its high optical and physico-mechanical characteristics and thus it is a material of good promise as the polymer matrix of plastic scintillators [1]. However, PMMA does not contain conjugated double bonds in the polymer chain; that is why some aromatic or heteroaromatic molecules, most often naphthalene as solid solution, are added thereto as secondary luminophors [2]. This way to introduce a chromophore into the matrix yields to the chemical modification of macromolecules with chromophore groups in such important characteristics as the "bleeding" resistance and photochemical resistance [2]. As far as we know, the polymers chemically modified with chromophores are still insufficiently studied from the viewpoint of their use as the plastic scintillator matrices.

It is to believe that the method of a luminophor additive introduction into plastic scintillators influences the efficiency of photophysical processes running therein and, as a result, the scintillation efficiency. In this work, we have studied the polymeric scintillation compositions based on PMMA

with chemically grafted chromophore. The study was aimed at the efficiency estimation of the non-radiative electron excitation energy transfer from the secondary luminophor additive to the luminophor and the effect of the secondary luminophor additive chemical binding with the polymer.

The experiments were carried out using the compositions consisting of methyl methacrylate (MMA) + β-naphthyl methacrylate (NpMA) + 1,4-bis(5-phenyl oxazolyl-2)benzene (POPOP). The compositions were obtained by mass polymerization using the two-stage temperature conditions (50°C for 24 h followed by additional polymerization at 115°C). Azo-isobutyronitrile (0.06 mole %) was used as the initiator. The MMA:NpMA molar ratio values in the compositions were 99.9:0.1; 99.5:0.5; 96.0:4.0; 92.0:8.0; 88.0:12.0 and 85.0:15.0. POPOP was added to the mixtures to be polymerized in an amount of 0.4 wt. %. The synthesized samples were shaped as 1 mm thick polymeric glasses. The absorption spectra were recorded using a Perkin-Elmer-544 spectrometer and the fluorescence ones, on a SDL-2 (LOMO) spectrophotometer under frontal sample excitation. The measurements were done at room temperature. The concentration dependence of the energy transfer in the scintillation compositions from naphthalene fragments (donor) to POPOP (acceptor) was determined as described in [3]. Within that approach, the concentration dependences were considered both in the stationary fluorescence spectra and in the synchronous scanning fluorescence spectra (SSF) of the studied systems. The latter recording method of the fluorescence spectra consists in a simultaneous scanning by monochromators of excitation and recording ($\lambda_{rec} = \lambda_{exc} + \Delta\lambda$), thus allowing to identify individual spectral centers in multicomponent mixtures [4, 5]. Each spectral center is reflected in such a spectrum as a single band.

As an example, Figs. 1a, 1b illustrate the stationary fluorescence and SSF spectra for the MMA (85 %) + NpMA (15 %) + POPOP (0.4 %) composition. The spectra are seen to be characterized by quantities $R^f = I_A{}^f/I_D{}^f$ and $R_s = I_A{}^s/I_D{}^s$, where $I_A{}^f$ and $I_A{}^s$ are intensities characterizing the energy acceptor emission bands in the stationary fluorescence and SSF spectra, respectively, $I_D{}^f$ and $I_D{}^s$ denote the respective intensities for the energy donor. When the acceptor concentration is constant, as is the case for the samples studied here, the concentration dependence of $1/R^s$ is in proportion with

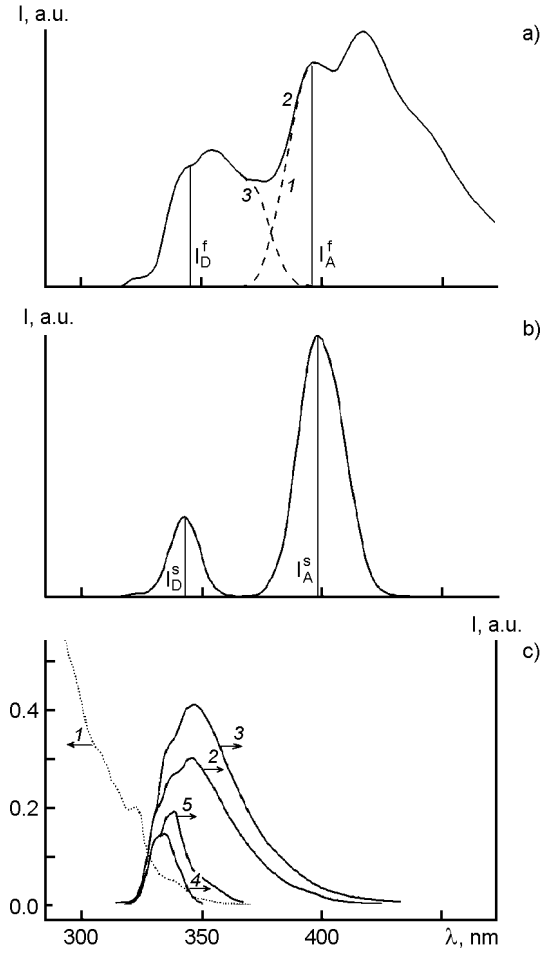

Fig. 1. (a) Fluorescence spectra of POPOP (0.4 wt %) solid solution in PMMA (*1*) and 85 % MMA + 15 % NpMA+0.4 % POPOP polymer (*2*). λ_{exc} = 280 nm. Curve *3* is the difference between spectra *2* and *1*. (b) SSF spectrum of 85 % MMA + 15 % NpMA + 0.4 % POPOP polymer obtained in the scanning mode $\lambda_{rec} = \lambda_{exc}$ + 10 nm. The wavelengths are indicated according to the record scale. (c) Absorption spectrum of 99.9 % MMA + 0.1 % NpMA copolymer (*1*); fluorescence (*2*, *3*) and SSF (*4*, *5*) spectra of 99.9 % MMA + 0.1 % NpMA (*2*, *4*) и 99.5 % MMA + 0.5 % NpMA (*3*, *5*). The SSF spectra are obtained in the scanning mode $\lambda_{rec} = \lambda_{exc}$ + 10 nm. The wavelengths are indicated according to the record scale.

the concentration dependence of the donor emission intensity, while the R^f/R^s ratio value characterizes the concentration dependence of the acceptor emission intensity [3]. Thus, when measuring the R^f/R^s ratio values for a series of samples, the gain in the acceptor emission intensity is caused by the energy transfer thereto from the donor.

The spectral investigations of systems with high chromophore concentrations are

always difficult due to the reabsorption and other spectrum distortions. Moreover, the chromophore aggregation in the ground and/or excited state is possible in such systems, thus, the photophysical process image becomes complicated. The spectral observations evidence that POPOP in the polymers under study is in the molecular form. However, naphthalene in the scintillation compositions exhibits aggregation features in its ground state. So, the fluorescence component belonging to the secondary luminophor additive can be discriminated by subtracting the POPOP fluorescence component from the total polymer emission spectrum. In Fig. 1a, curve *1* shows the fluorescence spectrum of the POPOP solid solution in PMMA not modified by naphthalene fragments. The subtraction result of that spectrum from the spectrum *2* presenting the total polymer emission is shown as the dependence *3* in Fig. 1a.

In the SSF spectrum of the polymer (Fig. 1c) the components of two spectral centers are seen clearly, namely, the longer-wavelength one belonging to POPOP. The second component can be associated to the energy donor having the fluorescence spectrum shown as curve *3* in Fig. 1a. Obviously this band is not the naphthalene monomer fluorescence but most likely that of naphthalene dimers. The monomer naphthalene emission is present in the spectra considered as weak bands at their short-wavelength edge (λ = 220 to 230 nm).

Qualitatively, the spectra of Fig. 1a are similar to each other for all the MMA + NpMA + POPOP samples starting from the minimum studied NpMA concentration (4.0 mole %). The emission bands of POPOP and aggregated naphthalene are predominant therein. The naphthalene monomer components are seen in those spectra only as weak bands in short-wavelength region. The naphthalene fragments begin aggregate in the copolymers starting from low NpMA concentrations. Fig. 1c illustrates the spectra for 99.9 % MMA + 0.1 % NpMA and 99.5 % MMA + 0.5 % NpMA demonstrating that fact. Although the aggregate band is noticeable in the absorption spectrum of the 99.9 % MMA + 0.1 % NpMA copolymer (curve *1*) as a "tail" in the bathochromic region from the first vibrational maximum (λ = 332 nm) in the S_1 absorption band of naphthalene monomer, the fluorescence spectrum of that copolymer (curve *2*) contains mainly the naphthalene monomer component, what is confirmed also by the single component in its SSF spectrum (curve *4*). The fluorescence spectra of

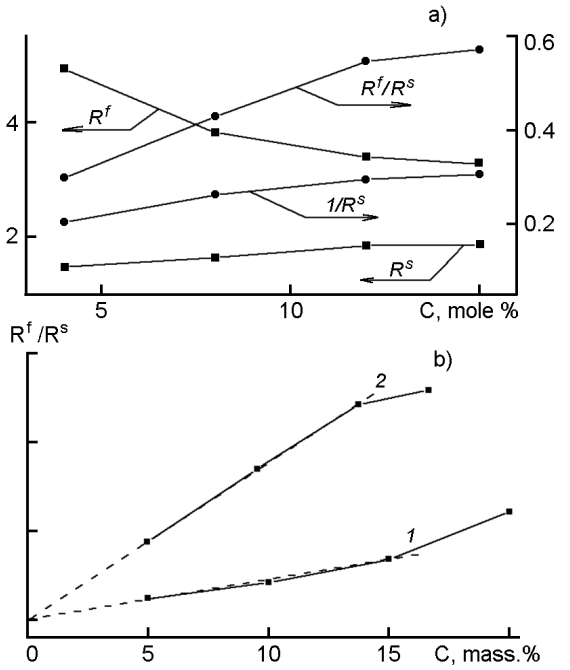

Fig. 2. (a) Dependences of R^f, R^s, $1/R^s$ and R^f/R^s for MMA + NpMA + 0.4 % POPOP compositions as functions of NpMA unit concentration. (b) Concentration dependences of R^f/R^s for solid solution of naphthalene and POPOP in PMMA [3] (*1*) and for MMA + NpMA + 0.4 % POPOP copolymers (*2*).

99.9 % MMA + 0.1 % NpMA и 99.5 % MMA + 0.5 % NpMA copolymers in Fig. 1c are normalized in the short-wavelength region, and comparison thereof evidences the arising emission components of naphthalene aggregates as the NpMA concentration increases (cf. spectra *2*, *3* and *4*, *5* in Fig. 1c).

In general, the chromophore aggregation in polymers may take numerous forms [6, 7]. It should be noted, however, that only one type of naphthalene dimers arises in the MMA-NpMA copolymers. Here, it is valid to consider the dimers, since a chromophore chemically grafted to a macromolecular chain is hardly able to form the contacting sites consisting of three units or more. The dimers seem to be formed between neighboring chromophores in the blockcopolymerized NpMA regions.

Thus, it is not only monomer naphthalene that acts as the electron excitation energy donor for POPOP in the MMA + NpMA + POPOP scintillation compositions but also its dimers that may be excited both directly and due to the energy transfer from the monomer. As the naphthalene concentration increases, its monomer component in the emission spectra of the copolymers weakens sharply and is almost absent

already in the samples with 5 % NpMA content. That is why we have taken the intensity values in the maxima of dimer components in stationary spectra (λ = 354 nm) and in SSF ones (λ = 343 nm) as the $I_D{}^f$ and $I_D{}^s$ values. The $I_A{}^f$ and $I_A{}^s$ intensities were measured also in the band maxima of stationary POPOP fluorescence (λ = 417 nm) and its component in the SSF ones (λ = 398 nm). The results of those measurements are presented in Fig. 2a as the concentration dependences of R^f, R^s, $1/R^s$ and R^f/R^s.

As noted above, the R^f/R^s dependence characterizes the concentration dependence of the energy acceptor (POPOP) emission intensity. It is seen in Fig. 2a that, as the NpMA fragment content in the copolymers increases, the POPOP emission intensity rises almost linearly up to NpMA concentration of 12.0 %. These data can be compared to the similar results from [3] for PMMA + naphthalene + POPOP compositions where naphthalene was introduced into PMMA as a solid solution. In Fig. 2b, the concentration dependences of R^f/R^s for such compositions are shown by curve *1*. In the same Figure, the R^f/R^s values for the MMA + NpMA + POPOP are plotted (curve 2) where the naphthalene content is reduced to its mass concentrations in the polymer mixture. The linear extrapolation of the dependences *1* and *2* to zero naphthalene concentration is shown by dashed lines in Fig. 2a. Both dependences are normalized so that the extrapolation results in $R^f/R^s = 1$ at zero naphthalene content. In other words, Fig. 2b shows the POPOP emission intensity (assumed to be 1 in naphthalene-free samples) for naphthalene solid solutions in PMMA and for the MMA-NpMA copolymer as a function of the naphthalene content. In both cases, the dependences characterize the POPOP emission under excitation at λ_{exc} = 280 nm.

The dependences *1* and *2* in Fig. 2b evidence that the electron excitation energy transfer to POPOP is more intense in the systems where naphthalene is chemically grafted to the polymer. The gain in the POPOP emission intensity in this case increases more than twice dynamically than in naphthalene solid solutions in PMMA. This fact may be due to a more homogeneous and ordered chromophore distribution over the copolymer matrix volume. Moreover, the naphthalene introduction into PMMA as a solid solution favors formation of its aggregates and microcrystals that fluoresce weakly but narrow considerably the PMMA transparency window in the region of up to 500 nm [8].

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Вплив фактора хімічного зв'язку люмінофора з полімерною матрицею на інтенсивність світіння сцинтиляційної композиції на основі поліметилметакрилату

А.А.Алдонгаров, М.М.Барашков, І.С.Іргібаєва, О.А.Хахель, Ю.Е.Сахно

Виконано порівняльні дослідження ефективності безвипромінювального переносу енергії у сцинтиляційних композиціях: метилметакрилат + β-нафтилметакрилат + 1,4-біс(5-фенілоксазоліл-2)-бензол та тверді розчини нафталіну та 1,4-біс(5-фенілоксазоліл-2)-бензолу у поліметилметакрилаті. Спектральними експериментами встановлено, що у випадку хімічного зв'язку нафталіну з полімером приріст інтенсивності світіння 1,4-біс(5-фенілоксазоліл-2)-бензолу при збільшенні вмісту нафталіну у композиціях відбувається більш ніж удвічі швидше у порівнянні з твердими розчинами.