Functional Materials 13, No.3 (2006)

Energy transfer in scintillation composition on the base of poly(methyl methacrylate)

O.A.Khakhel, T.P.Romashko, Yu.E.Sakhno

Academy of Technological Cybernetics Sciences of Ukraine,
Poltava Division, 86/86 Marshal Biryuzov St., 36007 Poltava, Ukraine

Received January 10, 2006

Spectra of stationary fluorescence and of fluorescence synchronous scanning for a scintillation composition based on poly(methyl methacrylate) containing 1,4-bis(5-phenyloxazol-2-yl)-benzene (0.4 mass %) and naphthalene as luminescent admixtures have been studied. The naphthalene content in the samples was varied from 5 to 20 mass %. Basing on the spectral data consideration, the contribution to the polymer fluorescence characteristics due to the non-radiative energy transfer from naphthalene to 1,4-bis(5-phenyloxazol-2-yl)-benzene has been estimated.

Изучены спектры стационарной флуоресценции и синхронного сканирования флуоресценции сцинтилляционной композиции на основе полиметилметакрилата с 1,4-бис(5-фенилоксазолил-2)-бензолом (0,4 мас. %) и нафталином в качестве люминесцентных добавок. Содержание нафталина в образцах варьировалось в пределах от 5 до 20 мас. %. На основе анализа спектральных данных оценен вклад безызлучательного переноса энергии с нафталина на 1,4-бис(5-фенилоксазолил-2)-бензол в формирование флуоресцентных характеристик полимеров.

It is just a poly(methyl methacrylate) (PMMA) composition containing naphthalene and 1,4-bis(5-phenyloxazol-2-yl)-benzene (POPOP) as luminescent admixtures that is the object being studied in this work. Such systems are used as materials for production of plastic scintillators, radiation converters, etc. [1, 2].The non-radiative transfer of electron excitation energy between the chromophore centers is of great importance in performance of such devices. This work provides an approach to the efficiency estimation of that process basing on the use of fluorescence synchronous scanning spectroscopy (FSS spectroscopy) [3].

The PMMA+POPOP+naphthalene samples containing 0.4 mass % of POPOP were examined. The naphthalene content in the samples was varied to be of 5, 10, 15, and 20 mass %. The polymers were synthesized by mass polymerization in two-stage temperature regime (at 50°C for 24 h followed by additional polymerization at 115°C). Azo-isobutyronitrile was used as the polymerization initiator. The chromophores were introduced into the mixture prior to polymerization. The samples obtained were shaped as 1 mm thick sheets (glasses). The spectra were measured using a SDL-2 (LOMO, St. Petersburg) under frontal sample excitation at room temperature.

In the system under consideration, naphthalene is the electron excitation energy donor and POPOP, the acceptor. The energy transfer efficiency is a function, *inter alia*, of the donor concentration. That dependence can be determined by measuring of both stationary fluorescence spectra and the FSS ones. If the acceptor content is the same in all the samples, its component can be used to normalize the spectra from various samples.

In a specific example, Fig. 1 presents the stationary fluorescence spectrum (curve *1*) of the PMMA+POPOP+20 % naphthalene scintillation composition. The structure fluorescence in the 310–360 nm region cor-

responds to naphthalene monomer. The first vibration maximum for the naphthalene monomer emission band is at 322 nm. The POPOP fluorescence is presented by a band in the 380–500 nm region. The 0–0 transition for the POPOP introduced in PMMA is at $\lambda = 396$ nm, as can be determined from the FSS spectrum for the sample (Fig. 1, curve *2*). A component due to scattered emission of the excitation source containing a characteristic structure at wavelength exceeding 430 nm is also observable in that spectrum. However, the scattered light is responsible for an insignificant contribution only, and its component can be eliminated. Thus, the SSF and stationary fluorescence spectra for the system can be characterized by intensities I^f_D, I^f_A, I^s_D, I^s_A (Fig. 1) or by parameters $R^f = I^f_A/I^f_D$, $R^s = I^s_A/I^s_D$. The latter can be interpreted as follows:

$$R^f \sim \frac{\varepsilon_A + \alpha}{\varepsilon_D - \beta}, \qquad (1)$$

$$R^s \sim \frac{\varepsilon'_A}{\varepsilon'_D - \beta'}. \qquad (2)$$

Here, ε_D and ε_A are extinction coefficients for the energy donor and acceptor (in this case, naphthalene and POPOP, respectively) at the stationary fluorescence excitation wavelength; ε'_D and ε'_A, those at the 0–0 transition wavelengths.

The quantity α in (1) characterizes the increase in the acceptor emission intensity due to the energy transfer. This evaluation method of the energy transfer efficiency makes it possible to use directly the spectral data [4, 5]. The α quantity has the dimensionality of extinction coefficient. In other words, the increase in the acceptor emission intensity can be considered as a fictitious increase of extinction at its excitation wavelength. The β and β' quantities in (1) and (2) characterize the fluorescence intensity reduction of the electron excitation energy donor due to the energy transfer to the acceptor. These quantities have the dimensionality of extinction coefficient, too. The β and β' quantities characterize the fictitious reduction of the donor extinction at the excitation wavelength of the stationary spectrum and at that of the 0–0 transition, respectively. Of course, α, β, and β' are functions of all the factors defining the energy transfer efficiency, *inter alia*, of the energy donor concentration. The quantities

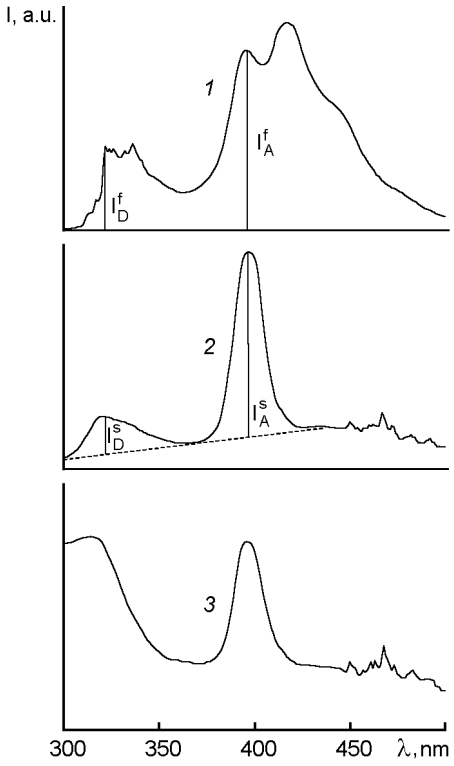

Fig. 1. Stationary fluorescence (*1*) and FSS (*2*, *3*) spectra for a PMMA + POPOP + 20 % naphthalene sample. The fluorescence spectrum is recorded under excitation at $\lambda = 280$ nm; the FSS ones, in the $\lambda_{ex} = \lambda_{em}$ scanning mode with (*2*) and without (*3*) polarizers.

β and β' differ from one another as a rule, but the ratios β/ε_D and β'/ε'_D could be assumed to be equal. Therefore, we obtain from (1) and (2) that

$$(\alpha/\varepsilon_A - 1) \sim R^f/R^s. \qquad (3)$$

Thus, determining the concentration dependence of R^f/R^s ratio, we can determine the concentration dependence of the acceptor emission intensity. Note that the $1/R^s$ quantity defines the concentration dependence of the donor emission intensity.

However, it is rather difficult to realize the above in experimental practice. First, this concerns the registration of the FSS spectra in the $\lambda_{ex} = \lambda_{em}$ scanning mode. Such a mode is selected mainly to record the FSS spectra for liquid solutions forming homogeneous media [3]. For polymer samples, the surface quality is of importance along with the homogeneity. In principle, it is possible to obtain polymers providing the FSS spectra recording without the monochromator disadjustment [5, 6]. If this is a

problem, the FSS spectra are recorded in the $\lambda_{ex} = \lambda_{em} + \Delta\lambda$ scanning mode, but the latter method complicates additionally the quantitative analysis of the spectra.

Nevertheless, we have managed to prepare the polymer samples suitable for registration of the FSS spectra in the $\lambda_{ex} = \lambda_{em}$ scanning mode. This was possible, however, only using perpendicularly oriented polarizers to suppress the scattered emission at the exciting and recording monochromators. This technique results in a considerably reduced scattered light background [6]. This statement is illustrated by comparison of the curve *2* in Fig. 1 that is recorded with polarizers with the curve *3* of the same sample recorded without polarizers.

The high naphthalene concentration in the polymer composition is another unfavorable circumstance that may result in appearance of reabsorption and internal filter effects in the stationary fluorescence and FSS spectra. At the other hand, a high naphthalene concentration gives rise to its aggregation in ground state that influences the photophysical processes in the system. So, as is seen in Fig. 1, curve *2*, the naphthalene band is asymmetric being extended towards the longer-wavelength side. This is typical of the aromatic hydrocarbon aggregation in the ground state [6]. The aggregation influences the photophysical processes because it reduces the real concentration of the monomer chromophore as well as gives rise to a possible energy transfer from the naphthalene monomer not only to POPOP but also to the aggregates. The aggregated naphthalene may be excited directly, too. Since the 0–0 transitions for naphthalene aggregates have a higher energy than that for POPOP, the energy transfer from the aggregates to POPOP is possible. In our opinion, however, the naphthalene aggregation influences the energy transfer estimation results only insignificantly. The quantity α in (1) takes into account the energy transfer to POPOP independently of the donor nature. Since R^f and R^s are determined for the same sample, the donor and acceptor concentrations are not included into (3). As to other circumstances, it is known [8] that the fluorescence recording method in the reflection mode is optimal from the viewpoint of elimination of the emission reabsorption influence on the spectra of various concentrated samples and even of the crystalline chromophore. In fact, the band of so-called "hot" naphthalene fluorescence having a weak maximum

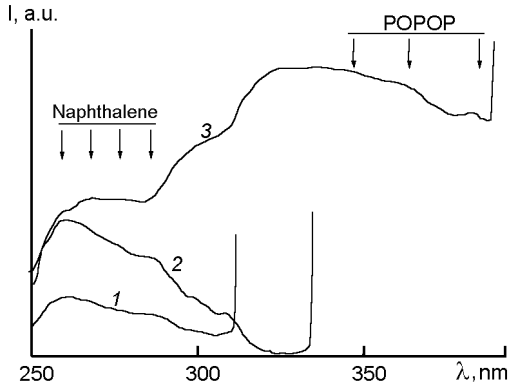

Fig. 2. Fluorescence excitation spectra for a PMMA + POPOP + 10 % naphthalene sample at recording wavelengths (nm): 317 (*1*), 340 (*2*), and 396 (*3*).

at $\lambda = 317$ nm appears in the short-wavelength region of the (Fig. 1, curve *1*), thus, the spectrum distortion due to reabsorbtion is insignificant.

The internal filter effect takes place in all the samples used in this work. Fig. 2 presents the fluorescence excitation spectra for naphthalene and POPOP in the PMMA + POPOP + 10 % naphthalene sample at some wavelengths. The arrows mark the maxima positions in the absorption spectra of those chromophores that are seen to be absent in the presented excitation spectra.

The data on concentration dependences of R^f and R^s obtained for the system under study under excitation at $\lambda = 280$ nm are shown in Fig. 3. The Figure presents also the dependences for R^f/R^s and for $1/R^s$. The latter can be extrapolated to zero naphthalene concentration. The quantity $1/R^s$ is in proportion to the donor chromophore emission intensity, so it is zero if naphthalene is absent in the system. In the concentration range of 5 to 20 mass %, emission increase is seen to be insignificant. It seems that such a behavior of the $1/R^s$ dependence is due to such factors as the concentration quenching and the chromophore aggregation rather than the energy transfer. But the latter also takes place, as is evidenced by the concentration dependence of R^f/R^s. As it follows from (3), it is in proportion to $(\alpha/\varepsilon_A - 1)$. The proportionality factor is defined by absorption and emission characteristics of the energy donor and acceptor as well as by the instrument parameters, such as spectral sensitivity of the photoreceiver and the spectral intensity distribution of the excitation source. The extrapolation of R^f/R^s dependence to zero naphtha-

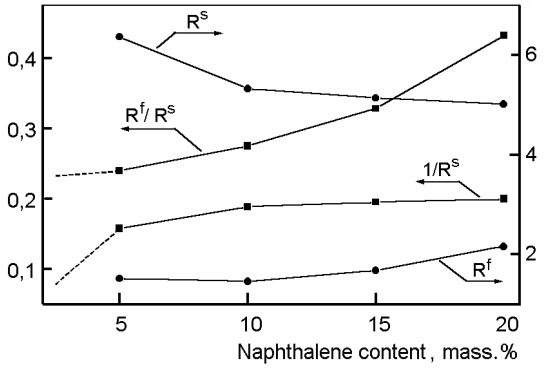

Fig. 3. Concentration dependences of R^f, R^s, R^f/R^s and $1/R^s$ for PMMA + POPOP + naphthalene composition.

lene concentration (i.e., to $\alpha = 0$) gives the factor value of about 0.225 (see Fig. 3), that corresponds to the POPOP emission intensity due to its direct excitation. The same dependence shows that in the sample where naphthalene concentration is 20 %, the energy transfer is responsible for about a half of the POPOP emission intensity. Thus, $\alpha/\varepsilon_A \approx 1$ for that sample.

Moreover, the R^f/R^s depends non-linearly on the naphthalene concentration. In the region of its values exceeding 15 %, the R^f/R^s increases in a more dynamic manner (Fig. 3). This fact might be assumed to be due to the appearance of an additional energy transfer mechanism. Perhaps the excitation transfer to POPOP at low naphthalene concentrations proceeds in one stage in the nearest environment only. As the naphthalene concentration rises, the energy transfer between the donor molecules becomes possible, thus enlarging the radius of a sphere where POPOP acts as the naphthalene fluorescence quencher.

The composition PMMA + 0.4 % POPOP+naphthalene has been selected for this work due to its practical importance. This composition with 15 % naphthalene content has been proposed [1] as an efficient scintillation material and is produced now on industrial scale. The scintillators are tested using special equipment [9] that, however, provides determination of the total light yield only. Here, in contrast, we are able to estimate the contribution of the energy transfer to the polymer fluorescence characteristics.

Thus, this work illustrates the possibility to use the FSS spectroscopy to determine the efficiency of non-radiative energy transfer between luminescent admixtures in materials being used in the plastic scintillator production. Within the frame of that approach, determined are the concentration dependences of emission for primary and secondary luminescent admixtures in the PMMA + 0.4 % POPOP + naphthalene scintillation composition in the naphthalene concentration range of 5 to 20 mass %. The results obtained have shown a non-linear concentration dependence of the elctron excitation energy transfer from naphthalene to POPOP.

References

1. N.N.Barashkov, O.A.Gunder, Fluorescent Polymers, Ellis Horwood, New York, London (1994).
2. V.Salimgareeva, S.Kolesov, *Instrum. and Exp. Techn.*, **48**, 273 (2005).
3. J.B.F.Lloyd, I.W.Evett, *Annal.Chem.*, **49**, 1710 (1977).
4. T.V.Sakhno, E.Ya.Elizarov, N.N.Barashkov et al., *Vysokomol. Soed. Ser.A*, **36**, 1486 (1994).
5. O.A.Khakhel', V.E.Krykunova, *J. Lumin.*, **81**, 79 (1999).
6. N.N.Barashkov, T.V.Sakhno, R.N.Nurmukhametov, O.A.Khakhel, *Polymer*, **37**, 1109 (1996).
7. E.L.Inmann Jr., J.D.Winefordner, *Anal.Chem.*, **54**, 2018 (1982).
8. C.A.Parker, Photoluminescence of Solutions, Elsevier, Amsterdam, (1968)
9. C.Aurouet, H.Blumenfeld, G.Bosc et al., *Nucl. Inst. Meth. in Phys. Res.*, **169**, 57 (1980).

Переніс енергії у сцинтиляційній композиції на основі поліметилметакрилату

О.А.Хахель, Т.П.Ромашко, Ю.Е.Сахно

Досліджено спектри стаціонарної флуоресценції та синхронного сканування флуоресценції сцинтиляційної композиції на основі поліметилметакрилату з 1,4-біс(5-фенілоксазоліл-2)-бензолом (0,4 мас. %) та нафталіном як люмінесцентними домішками. Вміст нафталіну у зразках варіювався в межах від 5 до 20 мас. %. На основі аналізу спектральних даних оцінено внесок безвипромінювального переносу енергії з нафталіну на 1,4-біс(5-фенілоксазоліл-2)-бензол у формування флуоресцентних характеристик полімерів.