

Excitation energy transfer in divinylbenzene copolymers

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This article describes our attempts to produce "nonexcimer" polymer systems by means of rigid fixation of chromophore groups positioned between two vinyl bonds. Divinylbenzene and methylmethacrylate copolymers were chosen as such systems. Study of the optical properties of synthesized copolymers showed their constancy in a wide region of specific concentrations of chromophore groups. The absence of luminescent properties modification in a wide concentrations range proves the possibility of eliminating the intrasystem energy traps by means of rigid fixation of chromophores in polymer.

Описана попытка получения "безэксимерных" полимерных систем путем жесткой фиксации положения хромофорных групп через две винильные связи. В качестве систем с жесткой фиксацией положения хромофорных групп были выбраны сополимеры дивинилбензола с метилметакрилатом. Исследование оптических свойств синтезированных сополимеров показало их неизменность в широком диапазоне удельных концентраций хромофорных групп. Отсутствие модификации люминесцентных свойств в широком диапазоне концентраций подтверждает возможность подавления образования внутри системных ловушек энергии возбуждения путем жесткой фиксации хромофоров в полимере.

1. Introduction

In this paper we attempted to design a loss-free excitation delivery system [1] in polymer. Much attention has been paid to these systems in connection with "light harvesting" or the "antenna effect" (see review in [2]). They are often considered in regard to photosynthetic systems [3]. Even in the earliest papers it was mentioned that energy migration along polymer chains could be invoked to explain the ease of excited state quenching of these polymers. One contributing factor to this behavior is the possibility that some excimer states may be populated by energy migration along the polymer chain until a pair of chromophores is encountered that are in the appropriate mutual orientation and separation to form an

excimer [1, 3]. The fluorescence of polymers with aromatic chromophores has usually been observed to be dominated by excimer emission. Thus, two polystyrene chromophores separated at about 3.5 Å distance form an excimer whose quantum yield is almost an order lower than that of the initial chromophore, and luminescence band is shifted almost 50 nm to the red region. This is why an excimer is considered as an excitation energy trap [5, 6]. Optimization of harvesting is expected in polymers where energy-dissipative excimer formation and/or self-quenching are eliminated [6]. There are several ways to eliminate the excimers forming in the polymer chain. The first is the use of steric factors that make it impossible for chromophore groups to approach [6], and the second is the production of ordered

structures in which excimer formation is inhibited [7]. Alternating polymers in which the adjacent chromophore groups are in opposite positions can be considered as such a structure. Decrease of chromophore groups mobility (that is, decrease of excimer states number) can be achieved by their rigid fixation, for instance, as the result of cross-linking with different polymer back-bones. An example of such a system is polymer linked by divinylbenzene whose chromophore groups have desired luminescent properties.

The main objective of the present work was to produce polymer systems with rigid fixation of chromophore groups, and to study their optical properties. To this end, we synthesized divinylbenzene (DVB) and methylmethacrylate (MMA) copolymers (MDVB).

2. Experimental

Cross-linked structures were obtained by means of copolymerization of the base monomer and monomer containing two vinyl groups. We used methylmethacrylate (MMA) (Saratovsyntes Company, Russia) as the base monomer, and divinylbenzene (DVB), containing 75 % *para*- and *meta*-isomer mixture and 33 % of ethylstyrene (Merck, Germany).

The monomers were purified by adsorption on aluminum oxide followed by distillation with $P=-0.96$ Bar underpressure at $T = 85^{\circ}\text{C}$ and 121°C for MMA and DVB, respectively.

Cross-linked MMA-DVB copolymers containing from 0.1 wt. % to 60 wt % of DVB were obtained by free radical polymerization initiated by 0.02 wt. % of 2,2'-azobisisobutyronitrile (AIBN).

Reaction mixtures of the investigated MMA-DVB with AIBN were put in glass ampoules and filled by argon for 6 min. The ampoules were then sealed and placed in a heating cabinet. The copolymerization was run according to step temperature regime. The initial temperature was 50°C during 23 h with further rising to 60°C during 4 h and to 65°C during 20 h. As a result, the colorless transparent cross-linked MMA-DVB copolymers were obtained.

Fluorescence spectra measurements were made by Fluoromax-4 (HORIBA, Joben Ivon Inc.) spectrofluorometer. Decay kinetics was measured by Combined Steady State and Lifetime Spectrometer FLS-920 (Edinburgh Instruments). The excitation source was a nanosecond flash lamp with 1 ns pulse

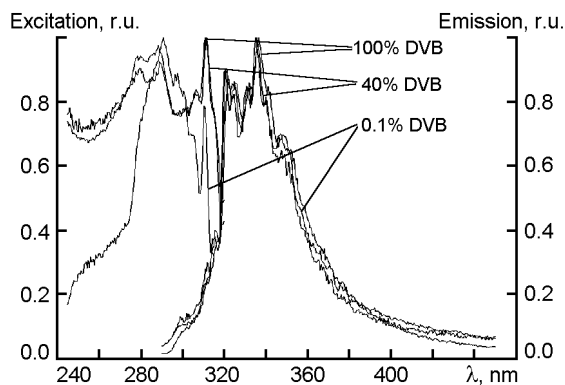


Fig. 1. Luminescence and excitation spectra of MMA and divinylbenzene copolymers.

width and 40 kHz repetition rate. Fluorescence decay was observed at the 307 nm wavelength.

3. Results and discussion

Excitation and luminescence spectra of MMA and divinylbenzene are presented in Fig. 1. A structured peak with maxima at 321 nm and 336 nm is clearly seen in luminescence spectra. This peak cannot be attributed to chromophore link (benzene ring) luminescence. Indeed, let us consider the styrene (which also has one phenyl ring) and MMA copolymer. Under small styrene concentrations, the luminescence spectrum of this copolymer has a maximum at 280 nm, while the excitation spectrum maximum is at 265 nm [6]. Life-time of this luminescence is about 26 ns. Increase of styrene concentration in copolymers leads to chromophore luminescence quenching and increase the excimer luminescence. Nothing of the kind happens in the case of divinylbenzene. As can be seen in Fig. 1, shape of the luminescence spectrum remains practically unchanged when concentration in the copolymer varies from 0.01 wt % to 100 wt %. Also, the observed luminescence spectrum cannot be attributed to excimer centers luminescence because its excitation spectrum differs from the chromophore link excitation spectrum whose maximum is distributed between 280 nm and 305 nm.

It is known that luminescent spectrum of the excimer center of polystyrene macromolecule is structureless band with a maximum at 330 nm [8]. Such a shape can be explained by the absence of rigidity of mutual arrangement of two chromophore links placed at ~ 3.5 Å distance. The different structure of the luminescent spectrum of MMA and DVB copolymer indicates a possible rigid fixation of two chromophore links

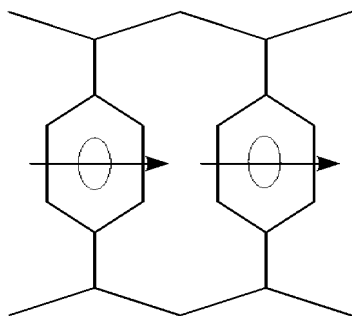


Fig. 2. Structure of the luminescence complex in the copolymer.

along both vinyl bonds. So, it seems that the structure of the copolymer considered is similar to that presented in Fig. 2.

Qualitatively, luminescent properties of such a dimer can be easily described in a framework of, so called, exciton approach, suggested by M.Kasha [9]. According to this approach new dimer states have specific splitting determined by the following equation:

$$E_{\pm} = E_{tr} + \Delta D \pm V_{dd} \quad (1)$$

where E_{tr} — energy of chromophore link transition, ΔD — energy determined by dipole-dipole interaction of excited and nonexcited molecules, and V_{dd} — energy of exciton.

Where E_{tr} — energy of chromophore link transition, Δ — energy determined

$$V_{dd} = \langle \psi_1^e \psi_1^g \left| \frac{\mathbf{d}_1 \cdot \mathbf{d}_2}{R^3} - \frac{\mathbf{d}_1 \cdot \mathbf{R} \cdot (\mathbf{d}_2 \cdot \mathbf{R})}{R^5} \right| \psi_2^e \psi_1^g \rangle. \quad (2)$$

Besides luminescence shifting to the long-wave region, the exciton model also predicts the change of dipole moments of each split level. Analysis of re-distribution of dipole moments among split levels for chromophore system with parallel transition dipole moments (this moment for diethylbenzene is directed as shown in Fig. 2) shows that transition from the ground state to the state of a lowest split level, as a rule, is dipole inhibited. It means that the life time of luminescence must be significantly increased. This was observed when the decay time of copolymer luminescence was measured.

As it is seen in Fig. 3 when divinylbenzene concentration is small, the decay curve can be rather well fitted by a single exponential with 90 ns life time. This time is considerably greater than that of diethyl-

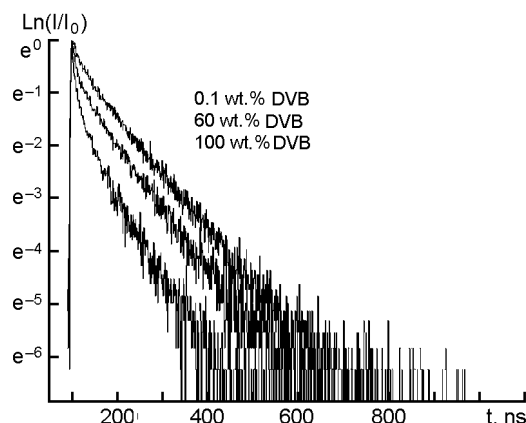


Fig. 3. Luminescence decay curves of MMA-DVB copolymers with various DVB concentration.

benzene (26 ns). Therefore, the possibility of energy exchange inside the dimer complex indeed leads to noticeable increasing of a split state life time. When DVB concentration increases, a small (and under 100 % concentration — significant) deviation from the exponential is observed. This is typical for systems with radiationless energy capture. If our system has additional centers of energy capture then excitation (absorption) spectra must change in luminescence region. But in our spectra these changes are not observed. It means that luminescent centers themselves serve as traps of excitation energy. This often happens in systems with excitation energy migration followed by localization of excitation energy on a single center producing a high excited state. This state depopulation via the radiationless transition leads to an additional channel of the energy loss.

High overlapping of the copolymer's excitation and luminescence curves indicates the possibility of radiationless energy transfer. Note that the rate of this process is proportional not only to this overlapping integral but is also inversely proportional to the distance between centers. So, when DVB concentration in the copolymer increases, energy migration along identical centers became possible. This can lead to an additional channel of excitation energy loss when two excitations are localized in a single center. It is to be noted that the mere excitation energy migration along identical centers cannot change the life time of the excited state.

The decay mechanism presented can be described by the following equation:

$$\dot{n} = -\alpha n - \gamma n^2, \quad (3)$$

where n — population density of the excited state, α — luminescence decay rate, γ — the rate of the optical center radiationless transition from a high excited state to the ground state.

The solution of (3) can be written as follows:

$$\frac{1}{n(t)} = \left(\frac{1}{n(0)} + \frac{\gamma}{\alpha} \right) \exp(\alpha t) - \frac{\gamma}{\alpha}, \quad (4)$$

where $n(0)$ — initial population density.

It is seen from (4) that if described decay mechanism really works then decay curves from Fig. 3 in $1/n(t)$, $\exp(\alpha t)$ coordinates must be linear functions. Indeed, this dependence is observed, for example, for pure polyvinylbenzene (Fig. 4).

The obtained dependence clearly indicates that annihilation of two excitations on a single optical center is the main mechanism of quenching in divinylbenzene and methylmethacrylate copolymers.

4. Conclusions

In this paper we demonstrated that in MMA-DVB copolymers the excimers are inhibited. But the chromophores' specific orientation leads to formation of a new channel of excitation energy loss, namely, annihilation of two excitations on a single optical center. This results in appearance of luminescent spectrum which is differ from that of single phenyl ring. Further studies will show to what extent the radiation of such a system can be used in practice.

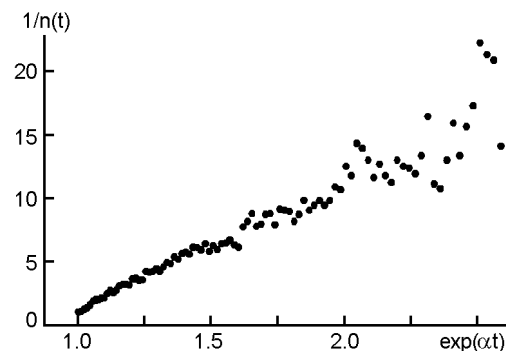


Fig. 4. Polyvinylbenzene decay curves (Fig. 3) in $1/n(t)$, coordinates.

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Передача енергії збудження у співполімерах дивінілбензолу

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Описано спроби отримання "безексимерних" полімерних систем шляхом жорсткої фіксації положення хромофорних груп через два вінільних зв'язки. У якості систем з жорсткою фіксацією положення хромофорних груп вибрано співполімери дивінілбензолу з метилметакрилатом. Дослідження оптичних властивостей співполімерів, що були синтезовані, показало їх незмінність у широкому діапазоні питомих концентрацій хромофорних груп. Відсутність модифікації люмінесцентних властивостей у широкому діапазоні концентрацій підтверджує можливість пригнічення утворення внутрисистемних пасток енергії збудження шляхом жорсткої фіксації хромофорів у полімері.