

# The Nature of Trapping Centers in Amorphous Biphenyl-Containing Polymer

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**Abstract** Study of optical properties of methyl methacrylate and 4-vinylbiphenyl copolymers in a rigid amorphous polymer allowed establishing the non-excimer nature of energy traps in a polymer chain. These traps are probably related to possibility of collective states formed by macromolecule's chromophore groups. The shortening of the trap states decay time in 4-vinylbiphenyl homopolymer comparing to copolymer is observed.

**Keywords** Scintillators · Energy transfer · Excimers · Excitons 4-vinylbiphenyl

## Introduction

The problem of energy migration in organic macromolecules carrying chromophore groups interests many researches [1–3]. First of all, this interest is determined by the possibility of using the energy migration along macromolecule's chromophores for energy transfer to some reaction centers (so called, antenna effect) [4]. The main difficulty on the way of creating macromolecules which can efficiently transfer the energy along the chain is connected with existence of self-organizing energy traps in the chromophore subsystem of the macromolecule. Excimer or exciplex formations (EF) are more often considered as such traps. They occur when two chromophore, one of which is excited, are placed in a close proximity [5–9].

Such formations are observed practically in all macromolecules having aromatic chromophore groups. Some authors [3, 4] showed that alternating aromatic polymers exhibit little or no excimer fluorescence. It is to be noted that transport properties of polymer molecules were mostly studied in solutions of macromolecules. But as far as EF depend on mutual placing of chromophore groups their properties must depend on a polymer matrix state. Thus, in polystyrene solution, one can observe not only phenyl chromophore peak (279 nm) but also EF peak (330 nm) [10]. On the contrary, in polystyrene films the only single peak of EF at 330 nm is observed [9]. Therefore to implement the antenna effect in solid polymer, it is important to know the type of traps in it. And if this problem is more or less satisfactory studied for polystyrene macromolecules than for molecules with more complicated chromophore structure it practically doesn't investigated. The main purpose of the present work is to study the peculiarities of trap states in solid solutions of methyl methacrylate (MMA) and 4-vinylbiphenyl (4VBPH).

## Experimental

The starting materials for samples preparation were commercially available 4-vinylbiphenyl and methyl methacrylate (Aldrich). The materials were purified by recrystallization from benzene followed by chromatography on silica gel.  $T=153^{\circ}$ .

Steady-state spectra of absorption and emission were studied under room temperature by means of FluoroMax-4 (HORIBA Jobin 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 the 1 ns pulse width and 40 kHz repetition rate.

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## Results and Discussion

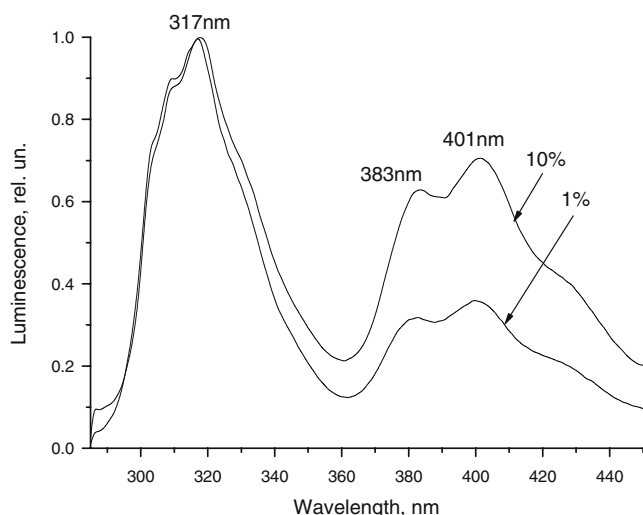
Fluorescence of chromophore moieties of 4-polyvinylbiphenyl (P4VBPH) most of all corresponds to fluorescence of isopropylbiphenyl, which thus was taken as the model compound. Its optical properties can be characterized first of all by positions of absorption spectrum maximum (279 nm), fluorescence spectrum maximum (309 and 317 nm), and life time of excited state – 13.7 ns (in hexane solution) [10].

The maximum of 4-vinylbiphenyl fluorescence spectrum as it known is somewhat shifted to the long-wave region relative to the maximum of isopropylbiphenyl fluorescence, and located at 321 and 334 nm [11]. In measured spectra of MMA+4VBPH fluorescence (Fig. 1) we clearly observe the peak caused by the chromophores embedded in the polymer chain (317 nm) and a double peak at 383 and 401 nm wave-lengths.

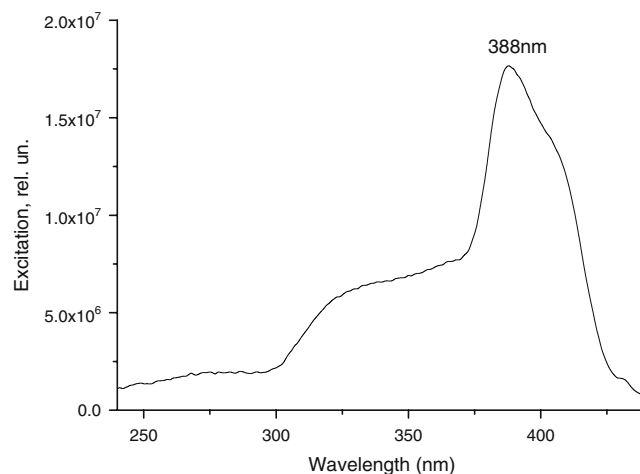
Similar peaks (but the broad ones instead of double) also have been observed in 4VBPH solutions [11, 12]. They are usually explained by the EF presence in a chain. It is to be note that the presence of such EF in our case is unexpected thing because biphenyl molecules are weakly aggregating and in biphenyl solution EF actually do not observed.

As it known, excimers have no absorption bands. So if the double peak observed in the fluorescence spectrum is caused by EF than in excitation spectrum one must observe only peaks of excimer “constituents” (single chromophore moieties) at 279 nm. But as it seen in Fig. 2 the maximum of copolymer excitation is centered at 388 nm wave-length, which is noticeably differ from the expected position.

Therefore the conclusion can be made that fluorescence centers related to the long-wave band of the spectrum



**Fig. 1** Fluorescence spectrum of methylmethacrylate copolymer with 1% and 10% 4-vinylbiphenyl



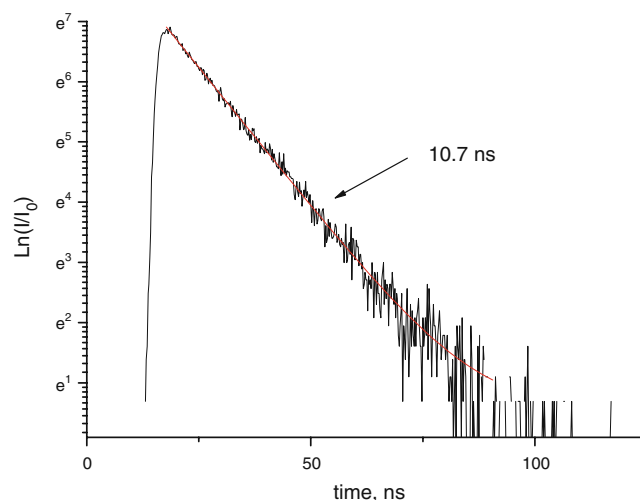
**Fig. 2** Excitation spectrum of PMMA + 1 wt.% 4-vinylbiphenyl. Observation wavelength – 450 nm

cannot be excimer formations. Energy levels of these centers also exist in the ground (non-excited) state.

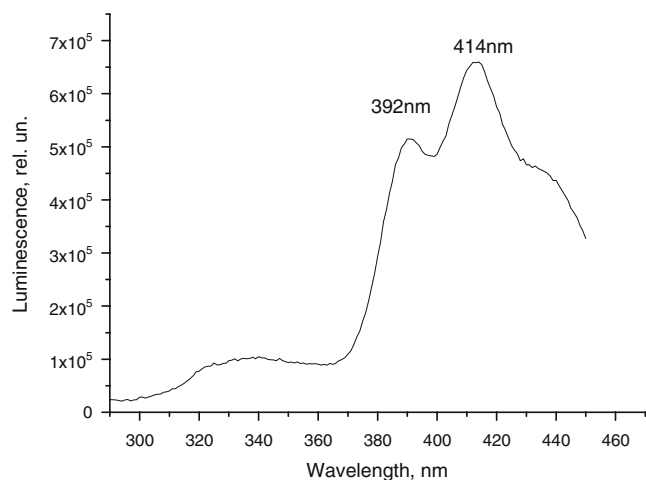
Decay times of vinylbiphenyl measured at 320 nm and 400 nm wavelengths under excitation by the pulse light source of 285 nm wave-length appeared to be the same and equal to 10.7 ns (Fig. 3).

The observed coincidence of fluorescence times at different wave-lengths shows the close relation of long-wave fluorescence centers with copolymer’s chromophore groups rather than a presence of some impurity fluorescent molecules.

Let us note that the decay time does not changed with vinylbiphenyl concentration up to 10 wt.%. When the content of vinylbiphenyl in MMA+4VBPH copolymer is increased, there is a gradual decreasing of the short-wave part of the spectrum. Homopolymer P4VBPH fluorescence is actually presented by the long-wave part only (Fig. 4).



**Fig. 3** Fluorescence decay of methylmethacrylate and 4-vinylbiphenyl copolymer at 320 nm wavelength

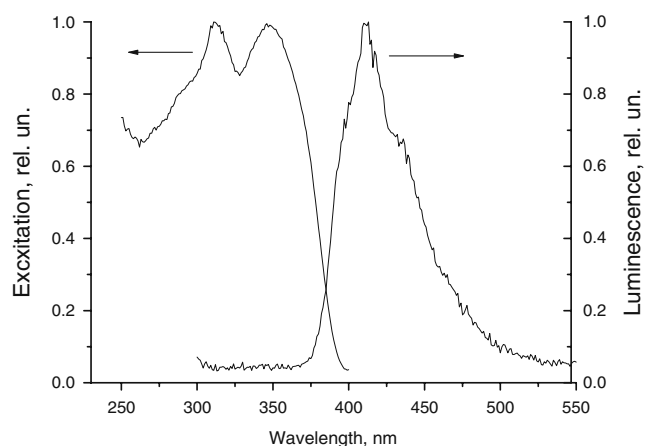


**Fig. 4** Fluorescence spectrum of P4VBPH homopolymer film

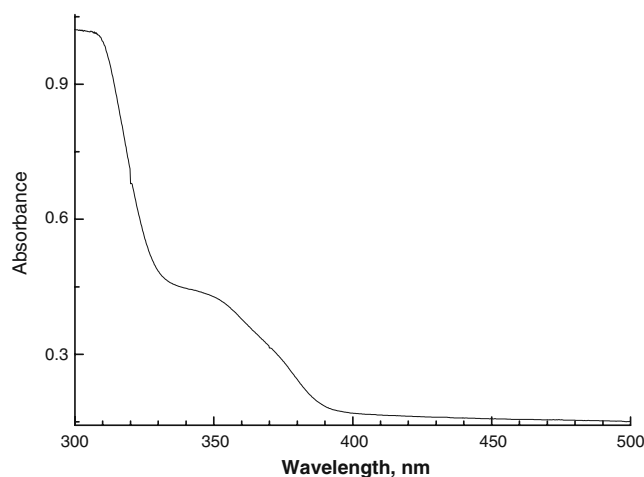
As it seen in the figure, in the fluorescence spectrum of both the P4VBPH homopolymer and the copolymer one can select the weak short-wave peak related to chromophore moiety fluorescence. Compared to copolymer, the peak of long-wave fluorescence is shifted into the red region nearly on 10 nm.

To eliminate the fluorescence of non polymerized aggregates of vinylbiphenyl molecules, the polymer was dissolved in toluene and than was precipitated in tetrahydrofuran. After successive dissolving and precipitation, the obtained polymer was precipitated onto a quartz substrate. It was found that in the fluorescence spectrum of such samples the peak of chromophore fluorescence at 317 nm wave-length is totally absent (Fig. 5).

If observed fluorescence is connected with mutual packing of P4VBPH chromophore groups then the absence of the specific peak at 317 nm wave-length can be caused by more tight ordering of chromophores in precipitated films. In this case the excitation spectrum (Fig. 5) and



**Fig. 5** Fluorescence and excitation spectra of P4VBPH homopolymer film



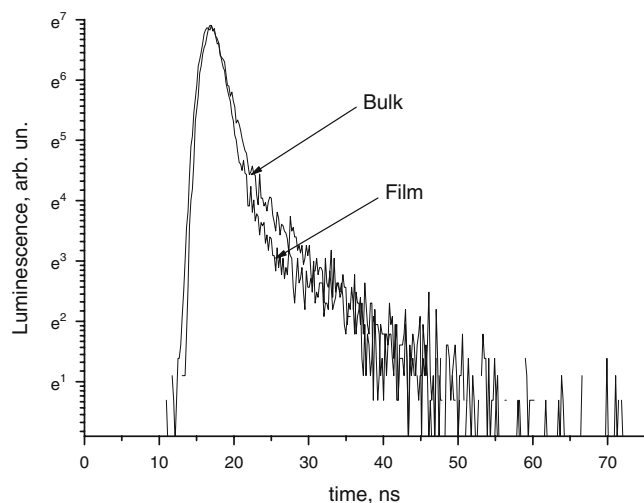
**Fig. 6** Absorption spectrum of P4VBPH homopolymer film

absorption spectrum (Fig. 6) of have the specific maximum at 350 nm.

Note that the intensity of absorption peak at 350 nm is much lower than that of chromophore groups.

Another peculiarity of homopolymer P4VBPH is its decay kinetics. It is presented in Fig. 7. As it seen comparing Figs. 3 and 7, the life time is decreased from 10 ns for copolymer to 1 ns for homopolymer. The life time of precipitated sample is somewhat lesser comparing to bulk sample of P4VBPH (again due to more tight ordering of chromophores).

This gradual life time shortening as well as peak at 317 nm disappearing in copolymers MMA+4VBPH can be satisfactory described by the model of collective states generation (like exciton states which are observed in molecular crystals). These properties most brightly manifest themselves in *J*-aggregates [13]. The rigidity of the chromophores spatial arrangement in MMA+4VBPH and P4VBPH macromolecules can lead to their flattening.



**Fig. 7** Fluorescence decay curves of P4VBPH homopolymer

Remember also that the angle between the phenyl planes in a biphenyl molecule is  $35^\circ$ , which in turn must increase the intermolecular chromophore interaction. This interaction can cause the lowering of the ground energy state which is actually observed in MMA+4VBPH copolymers. But in a copolymer there is only small probability of having the same chromophores in the close proximity. Therefore in the copolymer fluorescence spectrum, besides the peak of bonded inter-chromophore group we clearly observe peaks of single biphenyl moieties at 317 nm (the maximum of vinylbiphenyl fluorescence is placed at 335 nm). When concentration of chromophore groups is increased, the forming of collective states with many chromophores became possible. The energy of these states is lowered which is observed in fluorescence spectra. Indeed, the observed spectrum of homopolymer fluorescence is shifted to the red region nearly on 10 nm.

The second manifestation of excited states grouping is their life time decreasing. It is known that the fluorescence lifetime of collective states must be decreased proportionally to the number of coherently bonded molecules. The main factors affecting this value in polymer systems is the topological and dynamical order factors [14]. The factors lead to dephasing of collective states which affects their life-times. Therefore it can be said that in the limit, lifetimes of collective formations are changed between  $\tau_0/N_c$  (where  $N_c$  is the number of coherently bonded molecules) in MMA+4VBPH and  $\tau_0$  in P4VBPH homopolymer.

## Conclusion

Study of optical properties of solid solutions of MMA+4VBPH copolymer and P4VBPH homopolymer allows establishing the influence of phase content of macromolecules on their fluorescence properties. Collective states in a polyvinylbiphenyl which unites chromophore links of the macromolecule, can effectively collect the excitation energy of chromophore groups and re-emit it in 410 nm region which is traditionally used for optical radiation

registration by PMT. Possible ordering of macromolecule's chromophore groups can significantly decrease the life time of excited states without significant loss of energy. The search of systems with ordering chromophores is the way to obtaining the fast luminescent systems which are so required for high-energy particles registration.

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