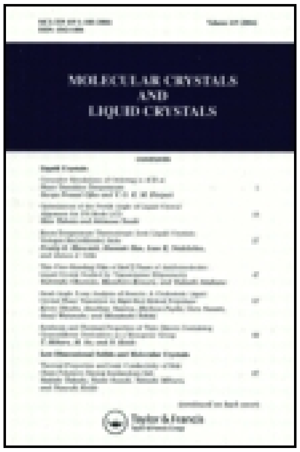

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Valeriy M.N. Yashchuk [a]

[a] Physics Department, of Kyiv Taras Shevchenko University, Academica Glushkova st., 6, 252022, Kyiv, Ukraine

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Migrating electronic excitations in π-electron-containing polymers

VALERIY M.(N.) YASHCHUK
Physics Department of Kyiv Taras Shevchenko University,
Academica Glushkova st., 6, 252022 Kyiv, Ukraine

The results of the investigations of spectral properties and excitation energy transfer in π-electron-containing polymers carried out in Kyiv University are briefly reviewed. The peculiarities of fluorescence, delayed fluorescence, singlet and triplet exciton propagation, mechanisms of elementary acts of singlet and triplet energy transfer are examined and analyzed. Some proofs of vibrational excitons in π-electron-containing polymers are presented.

Keywords: fluorescence, phosphorescence, singlet and triplet excitons energy transfer.

INTRODUCTION

There are two types of π-electron-containing polymers. In one of them π-electrons are delocalized along the macromolecule (polyacethylene, β-carotin), and in another type π-electrons are localized in the polymer cells (polystyrene, polyvinylcarbazole, DNA, etc.). The independence of energy structure of elementary cells for the second type of polymers allows us to modify the macromolecules composition without essential influence on basic unit energy sites. Such modifications gives a possibility to create the model macromolecules for unique photophysical experiments.

In the present paper the results of investigations of excitation energy transfer in intramolecular pure and doped homopolymers and specially designed copolymers that were started by Prof. Faidysh A.N. and Slobodyanik V.V. and carried out at Physics and Chemical departments of Kyiv Taras Shevchenko University were briefly reviewed and analyzed.

EXPERIMENTAL

The polymers containing π-electron systems in a side chain: polystyrene (PS), polyvinylcarbazole (PVCa), polyepoksypropilecarbazole (PEPCa), polytyiranecarbazole (PTCa), polyanthracenglycidile ether (PAGE), polyvinyl-7-benzocarbazole (PV7BCa), polyvinyl-5-benzocarbazole (PV5BCa), polyvinyl-11-benzocarbazole (PV11BCa), their low molecular model compounds and copolymers of vinylcarbazole with octhylmethacrylate (VCa-OMA), vinyl-7-benzocarbazole with octhylmethacrylate (V7BCa-OMA), vinylcarbazole with vinyl-5-benzocarbazole (VCa-V5BCa) were investigated. All these compounds were synthesized and purified on the Macromolecular chemistry department of Kyiv Taras Shevchenko University.

Measurement methods were described in our previous works [1-3].

RESULTS AND DISCUSSION

1. Absorption and Luminescence

Absorption spectra of polymers and copolymers which were investigated are near the absorption spectra of low molecular compounds. It was observed in a number of works (see for example [4,5]).

Contrary to absorption, luminescence spectra of π-electron-containing polymers are rather complicated and in a number of cases are different from luminescence spectra of their low molecular analogies. For copolymer macromolecules VCa-OMA in which the average distance between neighbour π-electron systems exceeds ~ 9 Å the spectra of fluorescence and phosphorescence are near the spectra of a low-molecular model compound. But when this distance decreases (it was realized by varying a copolymer composition) the transformation of luminescence for majority of polymers and copolymers takes place [6]. First of all the relative intensity of short-wave (0-0) maximum sharply decreased.

At 77 K the main maxima (0-1) of fluorescence spectra of homopolymers (PVCa, PV5BCa, PV7BCa, PV11BCa) solutions are near the main maxima of low molecular compounds but in spectra of these polymers the first short-wave maximum which could correspond to the short-wave maximum of a low molecular model compound is absent. Besides it was demonstrated in a number of works that an increase in temperature leads to the appearance of an additional broad long-wave structureless band. So, at room temperature the spectra of a number of polymers (PS, PVN, PVCa, PV5BCa, PV7BCa, PV11BCa etc.) consist of two bands: a shortwave (with some structures) and a long-wave broad structureless bands. The first was called a monomer band, and the second was called an excimer band [22] (for tyiranecarbazole (TCa), polytyiranecarbazole (PTCa) and PEPCa only a monomer band is observed). Later, the idea of existing the second type of excimer [23] was proposed and a short-wave band was named as excimer-II band. The *alternative idea* was proposed in our laboratory. To our point of view a short-wave band is connected with the emission of polymer cells (monomer units), but the shape of its spectrum is disturbed by intramolecular reabsorption [6].

Something similar is observed for phosphorescence spectra. Below ~ 40 K short-wave structural monomer-like phosphorescence for homopolymers (solution, powders and films) is observed. Above this temperature an unstructured red shifted band appears. This band was assigned to emission of triplet excimers [24] - as analogy to singlet excimers. Later the name " deep traps" appeared [25]. In our laboratory *it was found* that long-wave structureless phosphorescence of aromatic-containing polymers is connected with products of oxidation [7]. Indeed, it was easy to prove it. We noticed that this band is practically absent for homopolymers synthesized in the atmosphere of inert gazes and appeared after keeping them in air atmosphere. Also this band was induced by irradiation of polymers in oxygen atmosphere [7].

2. Singlet Excitons

A weak interaction between separate neighbour π-electron systems in macromolecules leads to excitation delocalization and migration along polymer chains. By this way the creation of singlet (S) and triplet (T) excitons takes place. The proofs of singlet energy transfer in polymers are: *1)* Excimer fluorescence of investigated polymers is possible only due to energy supply to excimer sites. For this reason the excimer fluorescence is totally depolarized. *2)* In a number of cases small amounts of impurity (less than 1 %, which do not contribute essentially in absorption) determine the fluorescence of polymers. *3)* The initial rate of photochemical reactions in polymers is significantly higher than for equivalent solutions of model low molecular compounds. *Some evidence* of that was obtained in our laboratory [8,9].

The modification of macromolecules without essential influence on basic polymer cell energy sites allows to create the macromolecules with different concentration of exciton traps. We used photochemical (photooxidation) [5,8,9] and chemical (copolymerization) [1] modifications. The investigation of such macromolecules gives the possibility to evaluate some parameters of energy transfer without using any model of exciton propagation character. Indeed, when the concentration of traps (modified cells) reaches the value of the average range of S-excitons (l_S), it leads to saturation of fluorescence quenching of main macromolecular units and fluorescence intensity of traps. Such direct experiments give the average range of intramolecular S-excitons (the distance between points of creation and exciton deactivation) for PVCa and PVBCa type of polymers $l_S \approx 400$ Å at 77 K. At 293 K the action of excimer traps reduced this value to 80 Å [1,5,10]. It was suggested that these traps were responsible for intrinsic photogeneration [11] in polymers.

Another variant of direct evaluation of singlet exciton range was based on the investigations of dependence of fluorescence spectra of weak polymer solutions (mainly PV7BCa) on a molecular mass (different lengths of a macromolecule) [10]. It is clear that when the excitons reach the end groups of macromolecule some spectral shift in fluorescence spectra must be observed.

Really for PV7BCa we observed this effect. The experiment gives the same values of S-exciton range as were obtained in our previous quenching experiments [5,10]. Those were direct experiments which did not suggest any model of exciton propagation. The methods and results of these experiments were recognized (see, for example [12]).

Such small values of exciton range and equivalence of elementary cell's energy levels allow to suggest that the character of exciton propagation in macromolecules under study is random jumps. Really, applying the theory of random walks [1,14] (which can be comparable with the experiment through dependence of fluorescence intensity on trap concentration) gives the result close to the results obtained by direct experiments. Applying the theory of random walks is not so simple as it seems to be at first sight. For example there was the first attempt of applying this theory to describing energy transfer in polyvinyltoluene by Powell [13]. The main difficulty was to account the action of excimer traps. The matter is that excimer traps are initially presented in a pure polymer. The contribution of our laboratory *to this problem* was the consideration of the amount of excimer concentration ($C_{ex.}$) and quenching impurity (C_{imp}) as a total concentration of singlet exciton traps $q = C_{ex.} + C_{imp}$, suggesting that these traps were indistinguishable for S-excitons [1,14]. The value $C_{ex.}$ was used from direct experiments mentioned above. The question appears what intensity of fluorescence (I_0) corresponds to concentration q=0 (pure polymer and without excimer traps). We proposed to take the fluorescence intensity value of copolymer macromolecule in which excimers do not exist as the value I_0 [1,14].

We have applied such approach (considering excimer traps in total concentration of exciton traps and so on) in describing the energy transfer in macromolecules with the help of theory of one-dimensional diffusion of excitons [30]. The passage from solutions (isolated macromolecules) to a solid polymer state leads to increasing S-exciton capturing efficiency (according to our measurements, quenching factor I_0/I for S-excitons increases to value

5÷6). To our thinking, this effect is connected with capturing excitons that are spreading along different macromolecules by the same trap.

3. Triplet Excitons

The proofs of T-exciton existing in polymers are nearly the same that for S-excitons: dominant in number of cases phosphorescence of impurities, modified cells and exciplexes; depolarization of phosphorescence [2] due to energy migration. But it is worth to emphasis that there is one more important proof - the existence of delayed fluorescence as a result of T-exciton annihilation.

It is known that for T-excitons in pure π-electron-containing polymers: shallow and deep traps manifest the monomer-like short-wave structure phosphorescence and, to our opinion, these traps - are the polymer cells in suitable positions. There are many of such traps more than 10 % according to our evaluation. We can observe the phosphorescence of these traps at 4,2 K. Increasing the temperature above 40 K leads to delocalization of excitons from these traps, their migration along macromolecules and then their capturing by deep traps [15,16,17]. Namely these traps determined the long-wave phosphorescence of polymers above 40 K. It was shown in our laboratory [5] that deep traps were created by products of polymer's chromophore oxidation in polymers. Phosphorescence of these traps was observed for PVCa, PV7BCa, PEPCa and PS.

We showed that in isolated PV7BCa macromolecules already at low exciton intensity ($L \leq 10^{12}$ photon/cm^2·s) a nonlinear dependence of delayed fluorescence and phosphorescence intensities (I_{df}, I_{ph}) on exciting light intensity (L) (resulting from triple-triplet exciton annihilation) took place. Two extreme variants were observed [15,16]: 1) $I_{df} \sim L$ at 4,2 K; 2) $I_{df} \sim L^2$ at 77 K. The first fact is connected with the process of annihilation of trapped and free T-excitons; the second – T-T-annihilation of free T-excitons. The processes of T-T-annihilation are also manifested by the dependencies of phosphorescence and delayed fluorescence on molecular weight of polymers (the intensity of delayed fluorescence increases with increasing the macromolecular length while the intensity of phosphorescence decreases) [10].

According to our evaluation the range of T-excitons at 77 K under conditions ($L \leq 10^{12}$ photon/cm^2·s when processes of T-T- annihilation are negligible) equals 600-800 Å (an average distance between deep traps).

It is worth to add that molecular oxygen is a very effective trap for T-excitons too. We showed that presence of this molecule was the reason of polymer phosphorescence absence at 293 K. To our minds namely oxygen molecules are main traps for triplet excitons in macromolecules under these conditions [15,17]. The range of T-T-exciton under these conditions in PVCa $l_s \leq 500$ Å according to our evaluation [17].

4. Mechanisms of Elementary Triplet and Singlet Exciton Jumps

The possibility of creating the macromolecules with different average distances between chromophore groups allow us to observe the evolution of photophysical processes in macromolecules upon variating the distance between neighbor π-electron systems. For copolymers of N-vinyl-7-benzocarbazole ("active units") with octhylmethacrylate ("neutral units") the value of critical jump distance for S- and T-excitons was determined [2]. As it was shown copolymer fluorescence quenching by intramolecular impurity of some concentration (photooxides, C=2%) practically didn't vary upon decreasing concentration of "active" unit from 100% PVCa (average distance between "active" units $R \approx 3{,}5$ Å) to value 20% $R \approx 18$ Å and then dramatically decreased (the ratio of fluorescence intensity I/I_0 arose). The dependence of fluorescence polarization degree on concentration of "active" units is of the same character (a low value and independence of an average distance from $R \approx 3{,}5$ Å to $R \approx 18$ Å) and then sharp increase with increasing R. It shows that the efficiency of singlet energy migration in macromolecules sharply decreases when the distance $\langle R \rangle$ between chromophores reaches the value ~18Å. This value can be interpreted as critical length (h_s) of an elementary jump for S-excitons. It was not expected but results of polarization phosphorescence measurements, dependencies of delayed fluorescence and phosphorescence intensities on average distance between chromophore cells in macromolecule (sharp decrease in delayed fluorescence intensity and increasing the phosphorescence intensity above $<R>\approx 18$ Å) give practically the same value for critical length of T-excitons elementary jump (h_T) $h_T \approx h_S$. From these data it seems to us that S and T energy transfer elementary acts occur due to the same mechanism. What kind of mechanism is it? There is a strong forbidance for energy transfer between triplet sites with the help of dipole-dipole or another multipole mechanism. Only the exchange mechanism can be responsible for this type of energy transfer. But there is not any forbidance for singlet-singlet energy transfer with the help of exchange mechanism. That's why from the above data it follows (contrary to traditional point of view, see, for example [26,27]) that the mechanism of elementary S-exciton jumps in macromolecules of investigated type are mainly exchange at least on the distances $R \leq 18$ Å between neighbor π-electron systems in macromolecule. Such conclusion is proved by experimentally obtained dependence [2] of the probability of the elementary singlet energy transfer act on average distances between chromophores. The tail of this dependence is described by Dexter exponent [2].

5. Data which Manifest the Existence of VIbrational Excitons in Polymers

The investigations of copolymers with different average distances between carbazole chromophores lead to the conclusion on existence of migration along macromolecule vibrational excitations [3]. Indeed, phosphorescence spectra of vinylcarbazol-methylmethacrylate copolymers (VCa-MMa) under study show an interesting effect appearing as redistribution of the vibrational band intensities when passing from low excitation intensities ($L_1=10^{19}$ photon/cm$^2\cdot$s) to higher ones ($L_2=10^{23}$ photon/cm$^2\cdot$s). It was shown that the effect of increasing long wave bands intensities was connected with increasing in population of carbazole group vibrational levels for copolymers

VCa-MMa. At L_1 the distribution of vibron band intensities is independent of the distance between chromophores (R) up to $R \approx 3{,}5$ Å (pure PVCa). Increasing illumination intensity to $L_2=10^{23}$photon/cm^2·s leads to considerable redistribution to the vibrational bands. Essential increasing is observed in intensities of long wave bands [3]. This effect is observed for all compositions of copolymers excluding macromolecules of pure PVCa. In PVCa macromolecules with much shorter distances between the carbazole groups (compared with VCa-MMa copolymers) intrachain relaxation reduces the effect to zero. This indicates the spreading of vibration excitations along the PVCa macromolecules. The data obtained give us the critical distance for the elementary jump of vibration excitons $\langle h_V \rangle \approx 3{,}5 \div 7$ Å in macromolecules.

CONCLUSIONS

Finally, we note that the main results given in this work are as follows:

1. The energy sites of π-electron-containing polymers (localized in elementary cells) are mainly determined by their individual properties. The electronic excitation energy transfer in such polymers is realized by singlet and triplet excitons, the propagation of which can be described by the theory of random walks which considers the probability of spontaneous exciton deactivation and indistinguishably of excimer and impurity traps for intramolecular excitons.
2. The direct experiments and the application of the theory give the average range of S-excitons (l_s) in macromolecules of PVCa and PVBCa type 80 Å at 293 K and 400 Å at 77 K. For T-excitons $l_T \approx 600$ Å-800 Å at 77 K and $l_T \leq 500$ Å at 293 K.
3. The critical jump distance (h_S, h_T) for S- and T-excitons $h_S \approx h_T \approx 18$ Å. It was suggested that the exchange mechanism is mainly responsible for singlet-singlet elementary act of energy transfer at least at the distances $R \leq 18$ Å as well as for elementary triplet-triplet act.

4. The investigations of polymer delayed emission show the number of nonlinear phenomena which are connected with triplet excitons propagation.
5. The transition from solutions (isolated macromolecules) to solid polymer state leads to increasing exciton capturing efficiency (quenching factor I_0/I for S-excitons increases to the value of 5÷6). To our minds this effect is connected with capturing excitons that are spreading along different macromolecules by the same trap (impurity).
6. In PVCa-type macromolecules the vibrational excitons exist which spread along macromolecules when the distance between π-electron groups does not exceed 7 Å.

We have made attempts to apply these results to same branch of high intelligent technology such as: information recording [19], molecular electronics [18,19,20,21,28], applied photochemistry [29].

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