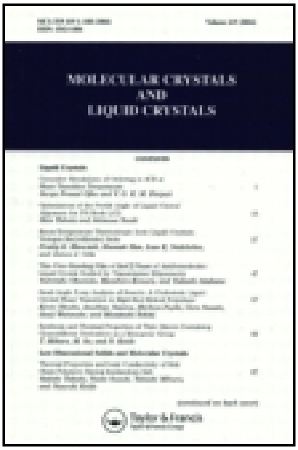

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Singlet Excitation Energy Migration in Vinyl and Methacrylate Polymers Containing the 1,3,5-Triphenyl-2-pyrazoline Chromophore as a Pendant Unit

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Singlet Excitation Energy Migration in Vinyl and Methacrylate Polymers Containing the 1,3,5-Triphenyl-2-pyrazoline Chromophore as a Pendant Unit

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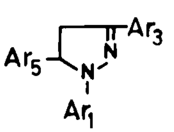
Migration of the singlet excitation energy was studied by the fluorescence quenching method for two amorphous vinyl and methacrylate polymers containing the 1,3,5-triphenyl-2-pyrazoline chromophore as a pendant unit, poly[1,3-diphenyl-5-(p-vinylphenyl)2-pyrazoline] (PVTPP) (I) and poly[1,3-diphenyl-5-(p-methacryloyloxyphenyl)-2-pyrazoline] (PMTPP) (II). The results are discussed in terms of a random migration model. It was shown that the singlet excitation energy migrates about 48 pendant groups in PVTPP and 45 in PMTPP at 0°C within the lifetime of their excited states (~5 nsec), the value being almost the same with the two polymers. These values of the excitation energy migration in the polymers, when compared with our earlier results, are about one order of magnitude smaller than that in the glassy state of a low-molecular weight analogue, 1,3-diphenyl-5-(p-chlorophenyl)-2-pyrazoline (p-ClTPP), and approximately four orders of magnitude smaller than that in the single crystal of the same material.

INTRODUCTION

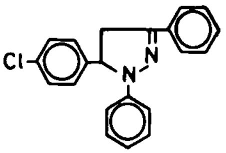
Studies of the excitation energy migration which constitutes one of fundamental photophysical properties in organic solids are of importance from both scientific and practical viewpoints. Since the excitation energy migration exists as a precursory process of the extrinsic photocarrier generation process, an understanding of the phenomena of the excitation energy migration is of fundamental importance not only for the basic understanding of the photoconduction mechanism[1,2] but also for the design and development of new photoconducting materials for use as photoreceptors in electrophotography.[3,4]

The excitation energy migration has been studied intensively in organic molecular crystals.[5-7] Recently interest has been growing in the transport phenomena in amorphous organic solids including polymers, and there have been studies of the excitation energy migration in amorphous organic solids[8-10] and polymers.[11-16] A better understanding of the nature of the transport phenomena would be gained if a direct comparison of the efficiency of the excitation energy migration is made between single crystals and amorphous solids of the same material, and polymers containing the same chromophore. We have found that 1,3,5-triaryl-2-pyrazolines, which are known to be highly fluorescent[17,18] and photoconductive,[19] are a suitable class of compounds for comparative studies of the transport phenomena between single crystals and the amorphous glassy state over the same temperature region, since these compounds give spontaneously a glassy state near room temperature through a supercooled liquid state from the melt as well as single crystals.[20,21] Using a compound of this class, e.g., 1,3-diphenyl-5-(p-chlorophenyl)-2-pyrazoline (p-ClTPP) (III), we have made comparative studies of the singlet excitation energy migration in single crystals and the amorphous glassy state.[9]

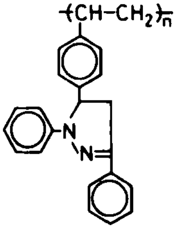
The purpose of the present investigation is to study the singlet excitation energy migration in vinyl and methacrylate polymers containing the 1,3,5-triphenyl-2-pyrazoline (TPP) chromophore as a pendant unit, poly[1,3-diphenyl-5-(p-vinylphenyl)-2-pyrazoline] (PVTPP) and poly[1,3-diphenyl-5-(p-methacryloyloxyphenyl)-2-pyrazoline] (PMTPP), and compare its efficiency with that in the amorphous glassy state and single crystals of III. Furthermore, most of the polymers studied hitherto regarding the excitation energy migration contain excimer-forming sites and exhibit excimer fluorescence besides normal fluorescence. It is, therefore, necessary in these polymers to consider the presence of excimer-forming sites as energy traps which affect the efficiency of energy migration. By the study of the excitation energy migration, the population of the excimer-forming sites in polymers have been obtained. The present two polymers, however, contain no excimer-forming sites, showing only normal fluorescence in both solutions and films.[22] It is, therefore, expected that the result in these polymers may directly provide the efficiency of the singlet excitation energy migration. The synthesis of these vinyl and methacrylate polymers, and their spectroscopic properties have been reported in our previous publications.[22,23] Triplet energy migration is also an important subject matter; however, the fact that 1,3,5-triaryl-2-pyrazolines generally show only fluorescence with no phosphorescence emission even when heavy atoms such as bromine are introduced into the molecule prevented us from studying triplet energy migration in the present polymers.[24]



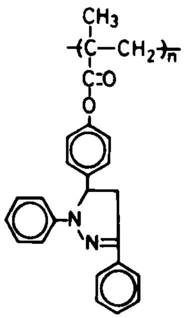
1,3,5-triaryl-2-pyrazoline



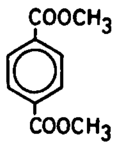
p-ClTPP



PVTPP



PMTPP



dimethylterephthalate
(DMTP)

EXPERIMENTAL

Materials

Two polymers, PVTPP and PMTPP, were prepared by the radical polymerization of the corresponding monomers at 60°C,[23] and purified by repeated reprecipitations from THF-methanol, and dried. The molecular-weight of the polymers used for the present study was $\overline{Mn} = 2.40 \times 10^4$, $\overline{Mw}/\overline{Mn} = 1.72$ for PVTPP, and $\overline{Mn} = 2.50 \times 10^4$, $\overline{Mw}/\overline{Mn} = 1.72$ for PMTPP, as determined with a Water Associates ALC/GPC 244 high performance liquid chromatographs with tetrahydrofuran as an eluent. Commercially available extra pure grade dimethylterephthalate was purified by repeated recrystallizations from ethanol, followed by repeated sublimations.

Film preparation

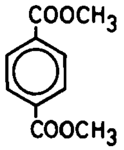
The polymer film (20–25 μm thick) was cast from a polymer solution in tetrahydrofuran (3.2×10^{-2} mol/l in monomer unit) onto the surface of a Pyrex glass plate.

Measurement of fluorescence

The film sample in a cryostat which was evacuated at 1×10^{-2} torr to avoid oxygen effects was placed in the cell chamber of a Hitachi MPF-3 emission spectrophotometer equipped with a 150 W Xe excitation lamp and a HTVR 446F photomultiplier. The intensity of the 460 nm fluorescence of the film by the excitation at 350 nm was measured at various temperatures. The fluorescence lifetimes of PVTPP and PMTPP in thin film states were measured by means of a pulsed N_2 laser (half-width of the pulse: 2.8 nsec).

RESULTS AND DISCUSSION

The method employed for the present study of the singlet excitation energy migration is to measure the extent of fluorescence quenching of the host molecule by the guest molecule as a function of the guest molecule concentration. A weak electron acceptor, dimethylterephthalate (DTMP), was selected as a guest molecule in the present study.



DMTP

The absorption and fluorescence spectra of PMTPP in the film state are shown in Figure 1. The spectra of PVTPP are virtually the same with those of PMTPP. The fluorescence spectra of the two polymers reveal only normal fluorescence with no excimer fluorescence. When the polymers were mixed with a small amount of DMTP, the fluorescence of the polymers was partly quenched as shown in Figure 1. Neither new absorption due to the formation of a ground-state charge-transfer complex nor new emission due to exciplex formation was observed when the polymers were doped with DMTP.

In the present host-guest system, energy transfer from the excited host to the ground state guest by either long-range resonance-excitation or short-range electron exchange mechanism is improbable since, as shown in Figure 1, the lowest excited singlet energy level of the guest molecule is much higher than that of the host molecule. Instead, the trapping of the excitation energy of the host molecule by the guest molecule will occur by the charge-transfer mechanism which requires a close approach of the excited state host and ground state guest molecules, the excited state host molecule, i.e., a pendant TPP chromophore, functioning as an electron donor and the guest molecule DMTP as an electron acceptor. Consequently, the fluoroscence quenching of the host TPP chromophore by the guest molecule will take place through excitation energy migration over the host TPP chromophores attached to the polymer chain both intramolecularly and intermolecularly, followed by the trapping of the excitation energy by the nearby guest molecule as shown in Figure 2.

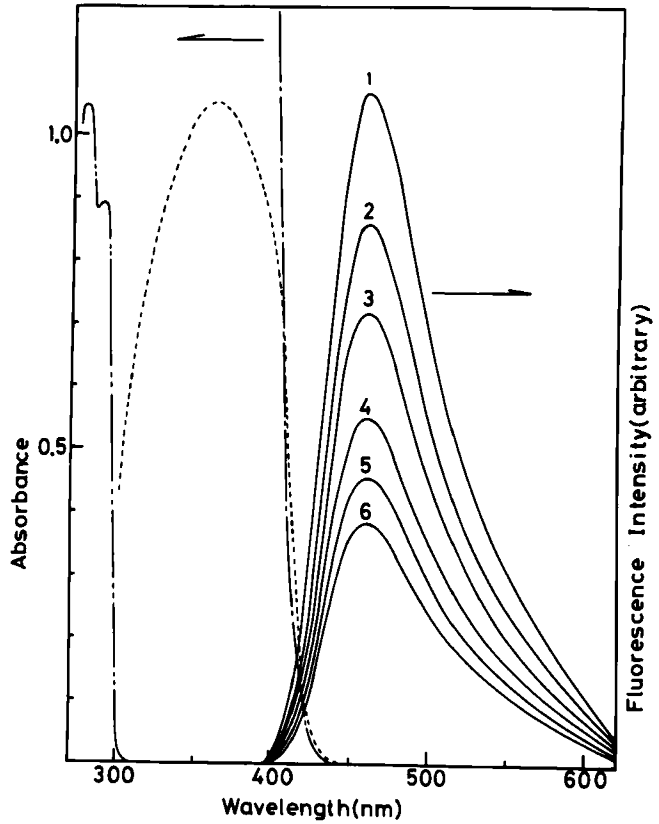


FIGURE 1 Absorption (transmission and reflection methods) spectra of PMTPP and DMTP, and fluorescence spectra of PMTPP in the absence and presence of DMTP. Absorption spectrum of DMTP (—-—) in a THF solution; absorption spectra of PMTPP film (----- reflection), (—-— transmission); fluorescence spectra of PMTPP film in the absence (1) and presence (2 ~ 6) of DMTP at 0°C (——). N_g/N_h (mol/mol, basic unit): 0.006 for 2, 0.01 for 3, 0.02 for 4, 0.03 for 5, 0.04 for 6. N_h and N_g are the concentrations of host chromophore and guest molecule, respectively.

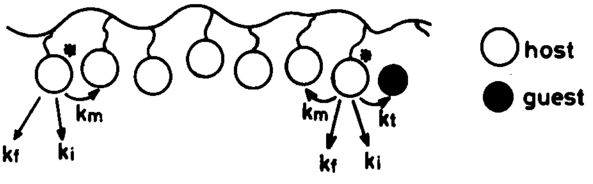


FIGURE 2 Random migration model for singlet excitation energy migration in the polymer.

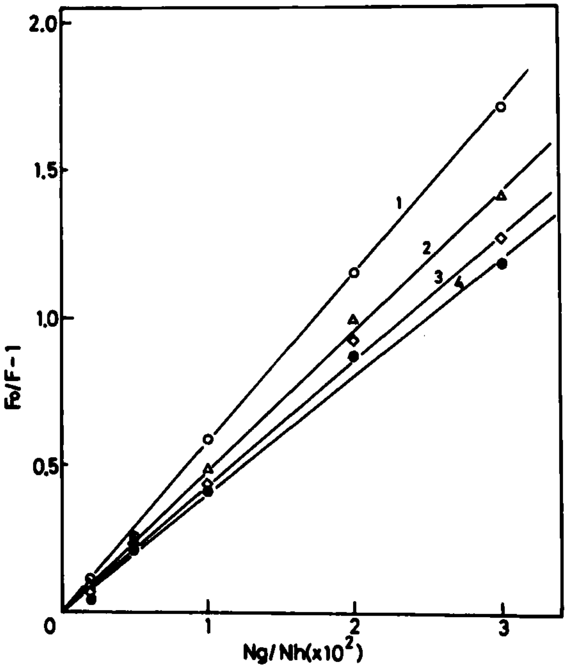


FIGURE 3 Quenching of the fluorescence of PVTPP (host) as a function of the concentration of DMTP (guest) in films at different temperatures. Temp.: 1, 40°C; 2, 0°C; 3, −40°C; 4, −80°C. F and F_0 are the host fluorescence intensities with and without the guest molecule. N_h and N_g are the concentrations of the host chromophore and guest molecule.

The experimental results were analyzed by using Eq. (1) which can be derived based on the random excitation energy migration as schematically shown in Figure 2,[9] where k_m, k_f, k_i and k_t are the rate parameters of the excitation energy migration, fluorescence emission, radiationless deactivation and excitation energy trapping, respectively. The efficient quenching of the host fluorescence by the guest molecule will occur when the singlet excitation energy is efficiently trapped by the guest molecule, namely, k_t is much larger than k_m, and k_m is much larger than k_f and k_i. In this case, the fluorescence quenching process becomes migration-controlled. Under these conditions and since N_h is much larger than N_g, Eq. (1) can be obtained which correlates the host fluorescence quenching with the concentration of the guest molecule,

$$\frac{F_0}{F} = 1 + \frac{k_m}{k_f + k_i}\frac{N_g}{N_h} \tag{1}$$

$$n = \frac{k_m}{k_f + k_i} = k_m\tau_0 \tag{2}$$

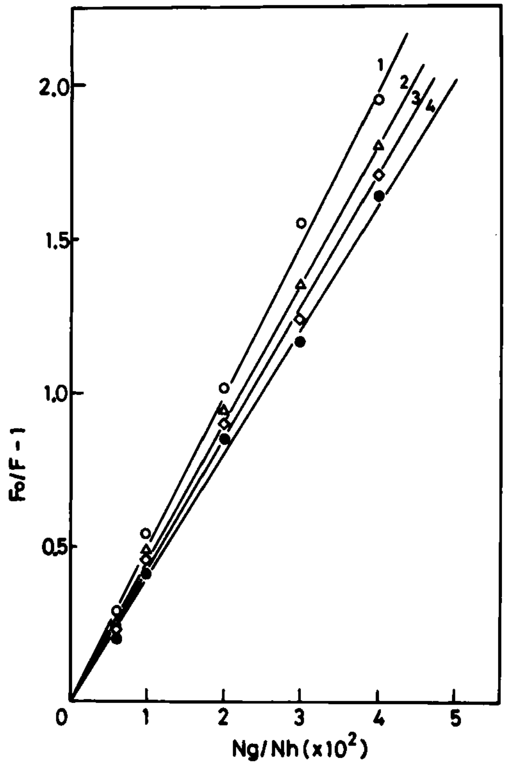


FIGURE 4 Quenching of the fluorescence of PMTPP (host) as a function of the concentration of DMTP (guest) in films at different temperatures. Temp.: 1, 40°C; 2, 0°C; 3, −40°C; 4, −80°C. F and F_0 are the host fluorescence intensities with and without the guest molecule. N_h and N_g are the concentrations of the host chromophore and guest molecule.

where F_0 and F are the fluorescence intensity of the host chromophore in the absence and presence of the guest molecule, respectively, and N_h and N_g are the concentrations of the host chromophore and the guest molecule, respectively. In Eq. (2), n represents the number of hops of the singlet excitation energy over the host chromophores within its lifetime τ_0 (~5 nsec).

The results of the quenching of the fluorescences of PVTPP and PMTPP films as a function of the concentration of DMTP at various temperatures are shown in Figures 3 and 4. A good linear relationship was observed as expected from Eq. (1), and the value of n was obtained from the slope of these linear plots. Table I summarizes the values of n and the rate parameter k_m for the excitation energy migration in PVTPP and PMTPP. It was found that the number of hops of the singlet excitation energy over the TPP chromophores within its lifetime at near room temperature is approximately 50, the rate parameter k_m being approximately 1×10^{10} sec^{-1} for both polymers. As seen in

TABLE I

Number of hops (n) of the singlet excitation energy within its lifetime and the rate parameter of its migration (k_m) in (a) PVTPP and (b) PMTPP

	(a) PVTPP		(b) PMTPP	
T(°C)	n	$k_m \times 10^{-9}$ (sec^{-1})	n	$k_m \times 10^{-9}$ (sec^{-1})
60	68	13.6	53	10.6
40	58	11.6	50	10.0
20	52	10.4	48	9.6
0	48	9.6	45	9.0
−20	45	9.0	44	8.8
−40	43	8.6	42	8.4
−60	42	8.4	41	8.2
−80	40	8.0	41	8.2

* Observed value of the lifetime of PVTPP excited singlet state: $\tau_0 = 5.4$ nsec (at room temp.); $\tau_0 = 5.6$ nsec (at 77 K).

** Observed value of the lifetime of PMTPP excited singlet state: $\tau_0 = 5.0$ nsec (at room temp.); $\tau_0 = 5.3$ nsec (at 77 K).

*** k_m was calculated by using the value of $\tau_0 = 5$ nsec.

Table I, the values of n and k_m at various temperatures are virtually the same for the two polymers: this indicates that the efficiency of the excitation energy migration is not significantly affected by the presence of the ester group in PMTPP and by the difference in the distance of the pendant TPP chromophore from the polymer main chain. As shown in Figure 5, the singlet excitation energy migration in the present polymers was found to be a slightly activated process probably due to the presence of shallow traps in the host chromophores. Although the k_m value did not significantly depend on temperature from −80°C up to room temperature, a slightly larger temperature dependence was observed in a higher temperature region. It is conceivable that the segment movement of TPP chromophores as well as intramolecular rotation motion of the phenyl group at the 5-position of the pyrazoline ring becomes easier in the higher temperature region; however, the origin for the different temperature dependence is not clear at present.

The primary concern in a study of the excitaton energy migration is how fast and how far the excitation energy migrates. The n values of the singlet excitation energy migration for PVTPP and PMTPP, when compared with our earlier results on the amorphous glassy state and single crystals of p-ClTPP,[9] are about one order of magnitude smaller than those for the glassy state of p-ClTPP and approximately four orders of magnitude smaller than those for the single crystals of the same material. However, since the lifetime of the excited singlet state of the TPP chromophore in the polymers is shortened compared to p-ClTPP in single crystals and the glassy state, the k_m values for the polymers are about one-fifth of those for the glassy state and ca. 3.5×10^3

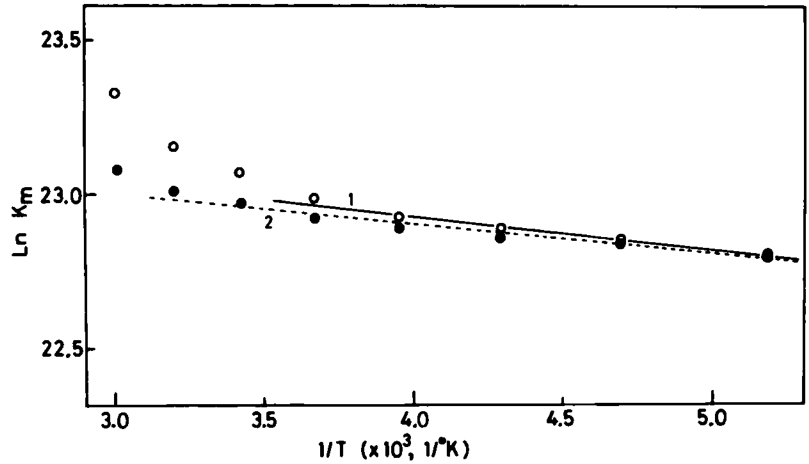


FIGURE 5 Temperature dependence of the rate parameter (k_m) for the singlet excitation energy migration in PVTPP (1, O) and PMTPP (2, ●).

times smaller than those for single crystals of p-ClTPP in the same temperature region. Table II summarizes the data for comparison of the efficiency of the singlet excitation energy migration between single crystals and the amorphous glassy state of p-ClTPP, and the present polymers containing the TPP chromophore as pendant groups. It is suggested that the difference in the values of n and k_m between the polymers and the amorphous glassy state of the low-molecular-weight analogue, p-ClTPP, is due to a different packing of the TPP chromophore, viz., a certain short-range order exists in the packing of chromophores in the glassy low-molecular-weight solids, whereas such an order does not exist in the polymers. Hence, the orientation of the TPP chromophores in the polymers may not be as favorable for energy migration as in the glassy

TABLE II

Comparison of the number of hops (n) of the singlet excitation energy and the rate parameter (k_m) of its migration between the single crystalline and amorphous glassy state of p-ClTPP, and polymers, PVTPP and PMTPP

compound	n	τ_0 (nsec)	k_m (sec^{-1})
p-ClTPP			
single crystalline state[a]	3.71×10^5	9.9	3.73×10^{13}
amorphous glassy state[b]	493	9.4	5.24×10^{10}
PVTPP[b]	48	ca. 5.0	9.6×10^9
PMTPP[b]	45	ca. 5.0	9.0×10^9

[a] measured at 10°C.
[b] measured at 0°C.

state of p-ClTPP, or the number of shallow traps might be larger in the polymers. It should be mentioned that the hole carrier mobility in p-ClTPP has recently been measured for single crystals and the glassy state.[25] The measurement of the charge carrier mobility in PVTPP and PMTPP is now under investigation.

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