2192 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (8), 2192—2194 (1979) [Vol. 52, No. 8

Singlet Excitation Energy Migration in the Glassy Organics Blended with Polymer

Yumiko SANO, Yasuhiko SHIROTA, and Hiroshi MIKAWA*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka 565

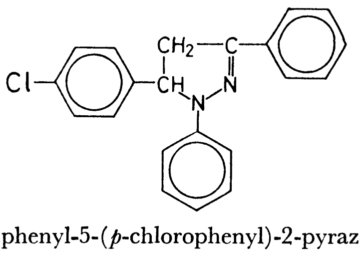
(Received December 6, 1978)

Studies have been made of the singlet excitation energy migration of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline in a glassy state blended with an ethylene–vinyl acetate copolymer by the fluorescence quenching method. The results are discussed in terms of the simple random energy migration model, showing that the efficiency of the singlet excitation energy migration does not differ between the glassy state and the polymer blend system.

Many organic photoconductors have been reported to function as photosensitive material for use in electrophotography. Among others, poly(*N*-vinylcarbazole) (PVCz) films sensitized with dyes such as benzopyrylium dyes[1–3] and the charge-transfer complex of PVCz with 2,4,7-trinitro-9-fluorenone (TNF)[4] are in commercial use. For the application of organic photoconductors to electrophotography, they are usually used as a blend system with an appropriate polymer which acts as a binder. Poly(*N*-vinylcarbazole) is also mixed with an appropriate polymer in order to improve the mechanical properties of the film. In the layered photoconductive system recently developed, organic photoconductors are dispersed in polymer materials.[5,6] Other blend systems of organic photoconductors with polymers have also been reported.[7]

From both scientific and practical aspects, it is of interest to investigate the transport phenomena in the photoconductor-polymer blend system. Studies have been carried out in detail on the carrier transport in the PVCz–TNF system.[8] The migration of the excitation energy in polymer blend systems has not been much investigated,[9–11] but it is an important precursory process for the photocarrier generation.

1,3,5-Triaryl-2-pyrazolines form a glassy state near room temperature, which is kept for quite a long period of time.[12,13] They have an intense fluorescent characteristic[14] and a photoconductive property.[15] We have made comparative studies of the singlet excitation energy migration of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline in the glassy and single crystalline states.[16] This compound is miscible with ethylene–vinyl acetate copolymer giving a transparent material over a wide blend ratio from the excess of pyrazoline to the excess of polymer. Thus the system may be appropriate for investigating the singlet excitation energy migration in the photoconductor-polymer blend system.



1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline

Experimental

Materials. 1,3-Diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline (glass transition point 16.5 °C) was prepared and purified by the zone refining technique. Dimethyl terephthalate was purified by repeated recrystallization from ethanol and then by sublimation.

Evaflex 210, a random copolymer of ethylene (*ca.* 72 wt %) and vinyl acetate (*ca.* 28 wt %) which softens at 80 °C (Mitsui Polychemicals Co., Ltd.) was reprecipitated four times from benzene with methanol. The polymer has low viscosity and is transparent after cycles of melting and cooling, the glass transition temperature being below −50 °C.

*Preparation of the Blend of 1,3-Diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline and the Polymer.* 1,3-Diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline doped with dimethyl terephthalate was prepared in a high vacuum. The doped material was diluted further with pure 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline and blended with the polymer in a pyrex glass tube (diameter 1.5 mm) by melting them together under a nitrogen atmosphere, degassed and sealed in a high vacuum (3×10^{-6} mmHg). The samples thus prepared were immediately cooled down to a liquid nitrogen temperature (77 K). This is a convenient method for keeping the samples transparent at room temperature.

Measurement. The degassed samples were subjected to measurement without being taken out from the pyrex glass tube in order to avoid exposure of the samples to oxygen. The fluorescence intensity was measured with a Hitachi fluorescence spectrophotometer MPF-3 by using a special sample holder which can hold the sample tube in a fixed position at constant temperature (10 °C).

Results and Discussion

The absorption and fluorescence spectra of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline in the glassy state are shown in Figs. 1(a) and (b), respectively. Even when the pure 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline glass is mixed with an equal amount of ethylene–vinyl acetate copolymer, the shape of the fluorescence spectrum remains unchanged (curve c). When pure 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline is mixed with a small amount of dimethyl terephthalate, the fluorescence of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline is partially quenched. Figure 1(d) shows the reduced fluorescence of pure 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline when $\approx10^{-3}$ mol/mol of dimethyl terephthalate is doped. The copolymer does not work as a trapping center of the pyrazoline excitation energy.

In the present study, the quenching of the fluorescence of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline in the polymer matrix was investigated by doping dimethyl terephthalate as a quencher. When the polymer

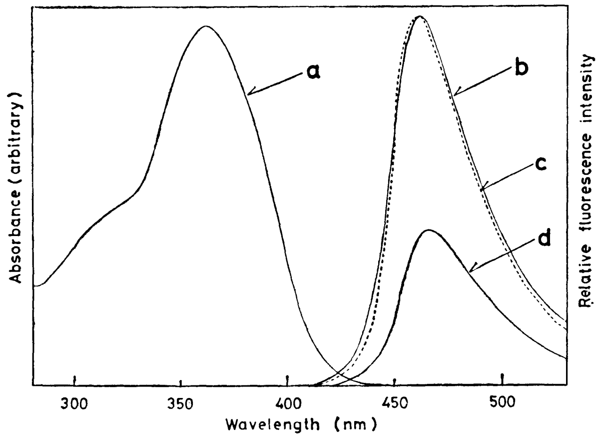


Fig. 1. Absorption and fluorescence spectra of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline in the glassy state. (a) Absorption spectrum; (b) fluorescence spectrum; (c) fluorescence spectrum when mixed with an equal amount of ethylene–vinyl acetate copolymer, the spectrum being normalized at the fluorescence peak of curve (b); (d) fluorescence quenching by 10^{-3} mol/mol dimethylterephthalate.

content is less than 20%, *viz.*, the content of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline exceeds 80%, no perfectly homogeneous transparent samples can be prepared, apparently due to the phase separation in the micro scale. Examination was therefore made with polymer content of more than 20%.

For such a homogeneous system, the Stern-Volmer type equation is expected to hold for the fluorescence quenching:

$$\frac{F_0(p)}{F(p)} = 1 + K_{sv}(p)\frac{(1-p)N_g}{N_h} \tag{1}$$

where $F_0(p)$ and $F(p)$ are the fluorescence intensity of the pyrazoline in the absence and presence, respectively, of the quencher, in a system containing the polymer of the fraction p of the total. $K_{sv}(p)$ is the quenching constant, and N_h and N_g are the number of host and guest molecules, respectively. Since p stands for the volume fraction of the polymer, the quencher concentration is $N_g/[(N_h+N_g)/(1-p)] \fallingdotseq (1-p)N_g/N_h$. Figure 2 shows the Stern-Volmer plot for a system containing 80% polymer. As expected, the plot shows approximate linearity.

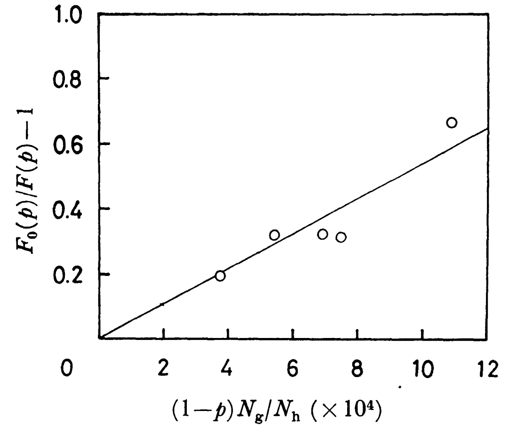


Fig. 2. Fluorescence quenching of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline in the ethylene–vinyl acetate copolymer matrix with dimethylterephthalate as a quencher. The polymer content is 80% by weight, which is almost equal to the volume %, if the specific volume of the polymer is assumed to be approximately equal to that of the pyrazoline. Based on this approximation, p represents the volume fraction of the polymer, $p=0.8$.

Equation 1 can be derived also in terms of a simple model of random energy migration. In the present system, energy migration from pyrazoline molecules to the polymer is energetically impossible. Thus the excitation energy migration should take place only from pyrazoline to pyrazoline. The probability of some site being the guest molecule should be $N_g/(N_h+N_g)/(1-p)$. Since the probability of an excited state at some site to migrate to the next site during the course of energy dissipation is $k_m(p)/(k_f(p)+k_i(p)+k_m(p))$, the probability $P_m(p)$ of the excited state reaching the guest molecule is

$$P_m(p) = \sum_{n=1}^{\infty}\left(\frac{k_m(p)}{k_f(p)+k_i(p)+k_m(p)}\right)^{n-1}\left(1-\frac{\dfrac{N_g}{N_h+N_g}}{1-p}\right)^{n-1}$$
$$\times\frac{k_t(p)}{k_f(p)+k_i(p)+k_m(p)+k_t(p)}\,\frac{\dfrac{N_g}{N_h+N_g}}{1-p}$$

where $k_f(p)$, $k_i(p)$, and $k_m(p)$ are the rate parameters for radiative decay, non-radiative decay and migration, respectively, of the excitation energy in the pyrazoline-polymer blend system. $k_t(p)$ is the rate parameter for energy trapping by the guest molecule. In the case $k_t(p) \gg k_m(p)$, the above equation is written as

$$P_m(p) = \sum_{n=1}^{\infty}\left(\frac{k_m(p)}{k_f(p)+k_i(p)+k_m(p)}\right)^{n-1}\left(\frac{N_h+pN_g}{N_h+N_g}\right)^{n-1}$$
$$\times\frac{(1-p)N_g}{N_h+N_g}.$$

The probability $P_f(p)$ with which the excited state releases the energy as fluorescence would be $P_f(p)=(1-P_m(p))k_f(p)/(k_f(p)+k_i(p))$. Since $F_0(p)/F(p)$ is the ratio of the fluorescence intensities for $N_g=0$ and $N_g=N_g$, which should be proportional to the probability $P_f(p)$, we can get Eq. 2 which is the same as Eq. 1 with $K_{sv}(p)=k_m(p)/(k_f(p)+k_i(p))$.

$$\frac{F_0(p)}{F(p)} = 1 + \frac{k_m(p)}{k_f(p)+k_i(p)}\,\frac{(1-p)N_g}{N_h} \tag{2}$$

Since $1/(k_f(p)+k_i(p))$ is lifetime (τ_0) of the excited state of the pyrazoline in the absence of the quencher molecule, $k_m(p)/(k_f(p)+k_i(p))=n(p)$ is the number of hops of the singlet excitation energy over the pyrazoline molecules within its lifetime. The experimental results shown in Fig. 2 give the value $n(0.8)=538\pm32$. This does not differ within experimental errors from the value obtained for the pure glassy state of the pyrazoline $n(0)=523\pm9$.[16] This indicates that the number of hops $n(p)$ of the singlet excitation energy within its lifetime does not differ between the pure glassy state and the polymer blend system ($p=0.8$). In order to confirm this for a wider range of the polymer content, it is necessary to carry out a series of similar fluorescence quenching experiments over various polymer contents; however, the following simple method was employed instead.

$F_0(p)/F(p)$ is plotted against the varying $(1-p)$ for Eq. 2 by keeping N_g/N_h constant and varying only the amount of the polymer (p). The amount of quencher molecule in the system is thus continuously varied by a factor $(1-p)$. Consequently, if $n(p)$ is independent of the polymer content as actually found to be the case for $p=0.8$, the plot of $F_0(p)/F(p)$ *vs.* varying $(1-p)$ (more strictly *vs.* $(1-p)N_g/N_h$ with constant N_g/N_h) for Eq. 2 would give a straight line; if $n(p)$ varies with polymer content the plot would not be linear.

1,3-Diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline containing 2.70×10^{-3} mol/mol of dimethyl terephthalate was prepared first and the doped pyrazoline was mixed with various amounts of the ethylene–vinyl acetate copolymer. The intensity of the fluorescence of the samples, $F(p)$, and that of each corresponding mixture of the undoped pyrazoline with the polymer, $F_0(p)$, were measured, the values of $F_0(p)/F(p)-1$ being plotted against $(1-p)$. As shown in Fig. 3, the results (open circles) lie on a straight line over the polymer content range from 90% $(1-p=0.1)$ to pure pyrazoline $(1-p=1.0)$. The black circle represents the value for the pure pyrazoline glass. The linearity indicates that $n(p)=k_m(p)/(k_f(p)+k_i(p))$ remains unchanged irrespective of the difference in polymer content. The results indicate that $k_m(p)$ is independent of polymer content, since the lifetime of the excited state, $\tau_0=1/(k_f(p)+k_i(p))$, is practically independent of polymer content.

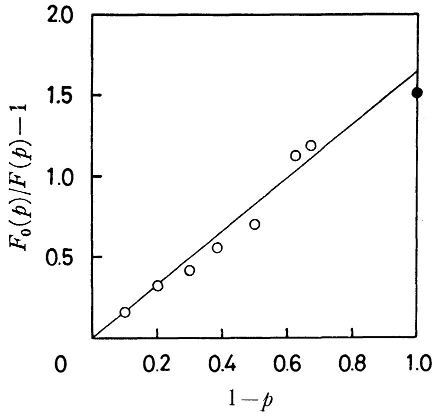


Fig. 3. Plot of $F_0(p)/F(p)-1$ as a function of $1-p$. $F_0(p)$ and $F(p)$ are the fluorescence intensities of the undoped and the doped materials, respectively, when the ethylene–vinyl acetate copolymer is blended with the fraction of p.

The efficiency of the singlet energy migration of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline was found to be invariable between the pure glassy state and the polymer blend system over a wide range of polymer content when suitable polymers inert to excited molecules are chosen.

References

1) Y. Murakami and K. Morimoto, U. S. Patent 3 526 502 (1970).

2) Y. Murakami and K. Morimoto, U. S. Patent 3 712 811 (1972).

3) Y. Murakami and K. Morimoto, Brit. Patent 1 353 264 (1974).

4) R. M. Schaffert, *IBM J. Res. Develop.*, **75**, Jan (1971).

5) Y. Hayashi, M. Hasegawa, and E. Ando, *SPSE 25 Ann. Conf.*, April, 1972.

6) P. J. Melz, R. B. Champ, L. S. Chang, C. Chiou, G. S. Keller, L. C. Liclican, R. R. Neiman, M. D. Shattuck, and W. J. Weiche, *Photogr. Sci. Eng.*, **21**, 73 (1977).

7) P. Borsenberger, A. Chowdry, W. Dulmage, D. Hoesterey, W. Light, S. Marino, W. Mey, C. Salzberg, D. Smith, and W. Staudenmayer, Third International Conference on Electrophotography, November 15—18, 1977, Washington D. C., preprint p. 31.

8) W. D. Gill, *J. Appl. Phys.*, **43**, 5033 (1972).

9) R. Katraro, A. Ron, and S. Speiser, *Chem. Phys. Lett.*, **52**, 16 (1977).

10) R. D. Burkhart and E. R. Lonson, *Chem. Phys. Lett.*, **54**, 85 (1978).

11) N. J. Turro, I. E. Kochevar, Y. Noguchi, and M. Chow, *J. Am. Chem. Soc.*, **100**, 3170 (1978).

12) K. Kato, M. Yokoyama, Y. Shirota, H. Mikawa, M. Sorai, H. Suga, and S. Seki, "Energy and Charge Transfer in Organic Semiconductors," ed by K. Masuda and M. Silver, Plenum Publishing Corp. (1972), p. 77.

13) Y. Sano, K. Kato, M. Yokoyama, Y. Shirota, and H. Mikawa, *Mol. Cryst. Liq. Cryst.*, **36**, 137 (1976).

14) I. H. Leaver, *Mol. Photochem.*, **5**, 411 (1973) and references cited therein.

15) Japanese Patent Application Disclosure No. 5466 of 1959, Kalle and Company, A. G.

16) Y. Sano, M. Yokoyama, Y. Shirota, and H. Mikawa, *Mol. Cryst. Liq. Cryst.*, in press (1979).